

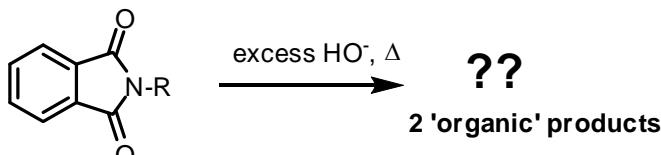
UNIVERSITY OF WINDSOR
Chemistry and Biochemistry

Chemistry 59-235
Final Exam

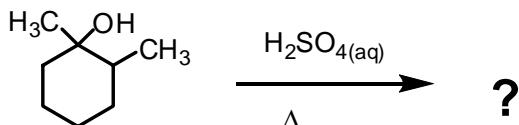
Apr. 9, 2011
Time: 3 hours

Answer all questions in the exam booklet(s). Use the following values for molecular weights: C, 12.011; H, 1.008; Br, 79.904; Cl, 35.453; O, 15.999; N, 14.007

1. The hydrolysis of phthalimides is commonly done with hydrazine, but is more easily shown with hydroxide ion as the reagent. Give the full mechanism of the following transformation, including products (10 marks)

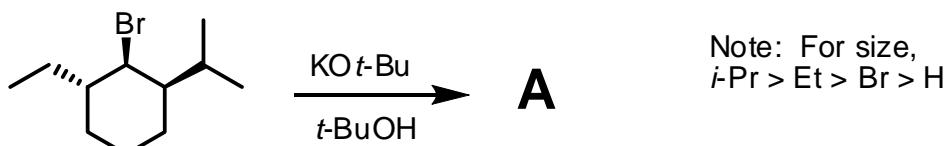


2. Give the complete mechanism for the indicated reaction below. Include all steps, any small molecules given off, and show the major product structure. Indicate the rate determining step. What is the name for the mechanism involved? (10 marks).

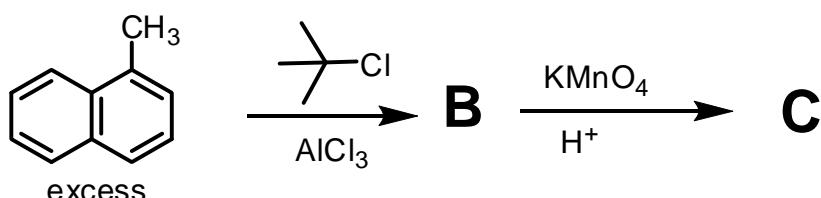


3. Predict the major products of the following transformations. Mechanisms are not necessary, but showing your work may be useful (5 marks each, 50 total).

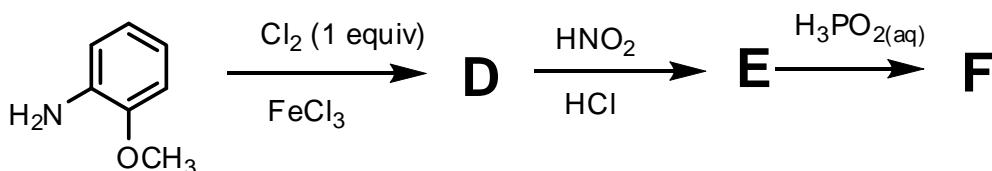
a)



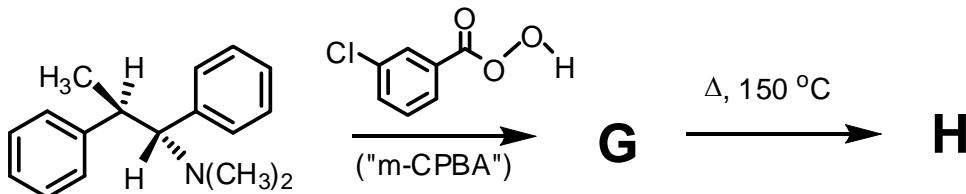
b)



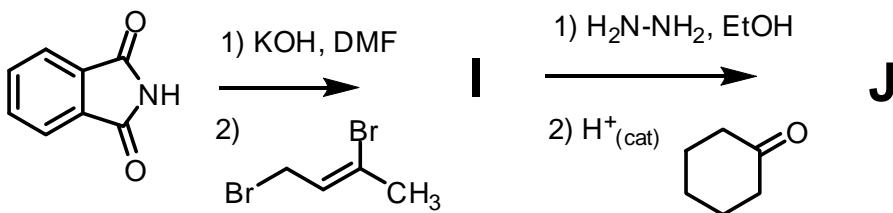
c)



d)

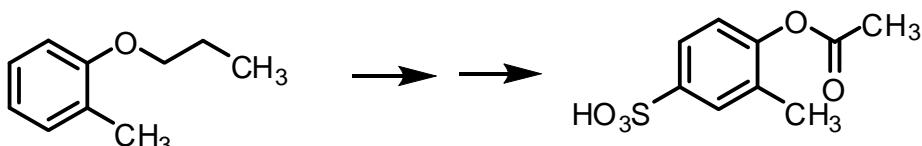


e)

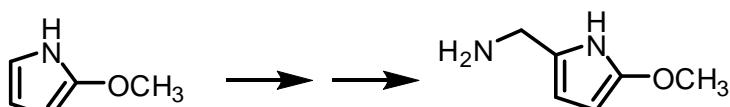


4. Show by equation (in one or several steps) how you could prepare the products illustrated below from the given starting materials. You may use any other reagents you deem fit. Show all reagents, conditions, and isolable intermediates. Mechanisms are not necessary, but showing your work may be a help. **Do any four (40 marks)**.

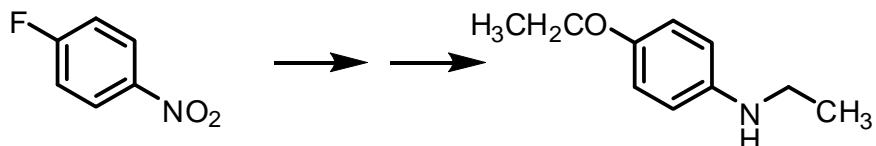
a)



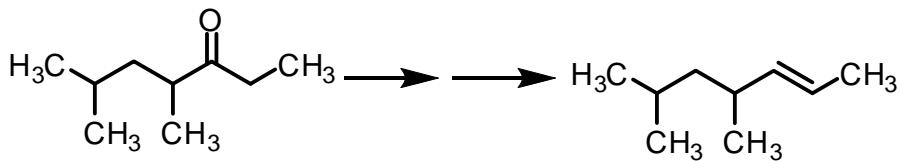
b)



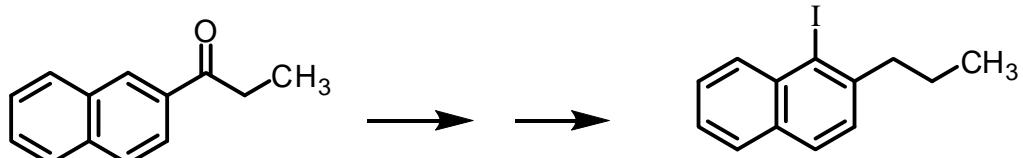
c)



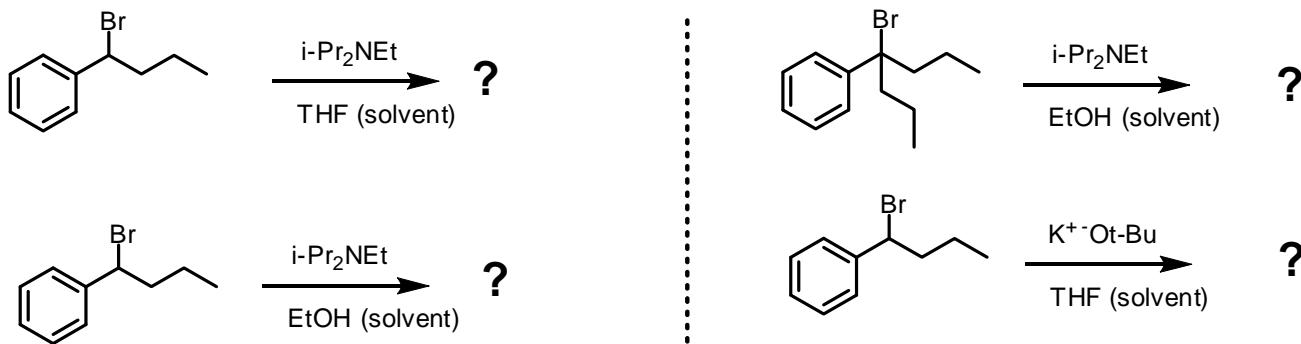
d)



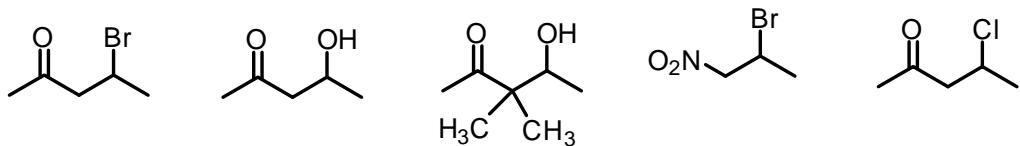
e)



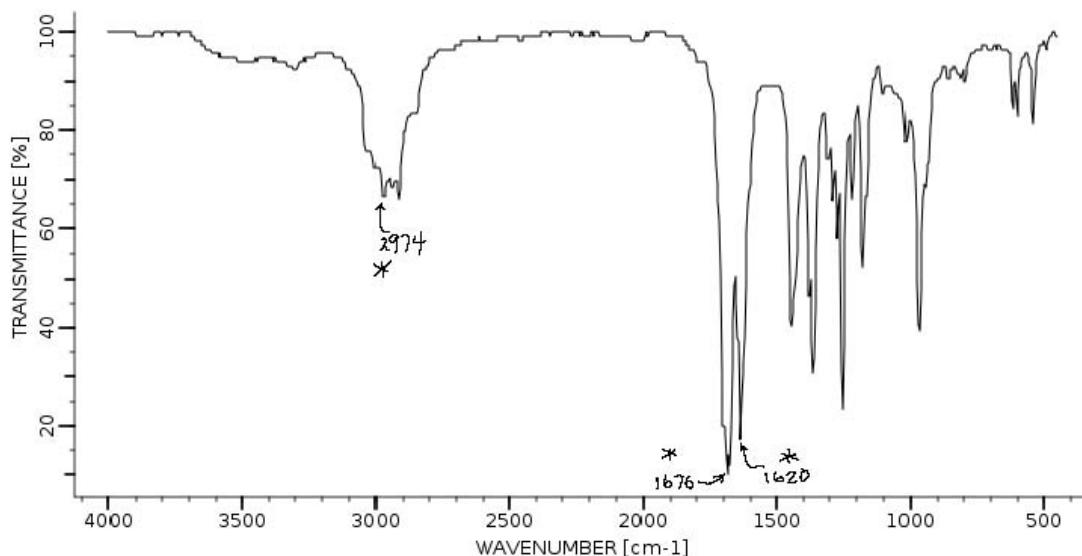
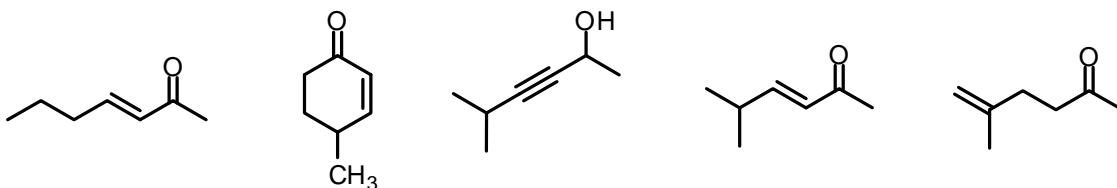
5. Rank *all four* of the following reactions in their relative ability to undergo E2 elimination as opposed to an E1. Include the reasons for your ordering and the product structures. It is possible that there might be small amounts of substitution products in some cases; *you may ignore the substitution products*. Note: $^1\text{Pr}_2\text{NEt}$ is 'just like' Et_3N , except it gives less $\text{S}_\text{N}2$ side products. Note: solvent dielectric constants EtOH 25; THF 7.6 (10 marks).

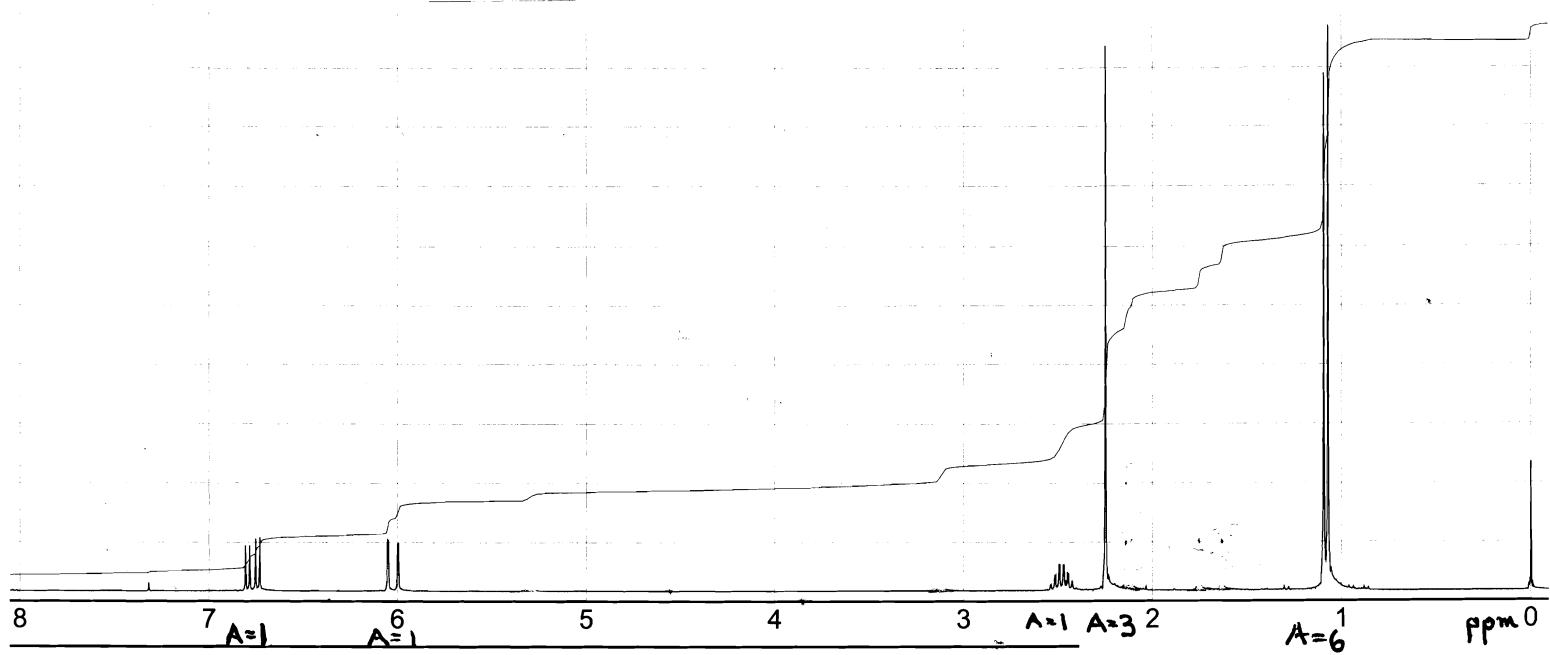


6. Rank the following in terms of the rate under which they do an E1cb elimination (**5 marks**)

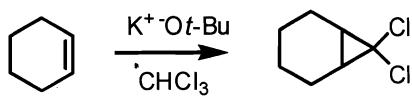


7. The following compound has been analyzed, revealing a composition of C, 74.95%; H, 10.78%; O, 14.26%. The mass spectrum gives a highest m/e of 112. The IR (infrared) and ^1H NMR spectra are also included below. Which of the following structures is the most reasonable candidate for the compound in question, and why? Assign the NMR spectrum, showing the comparison of your calculated chemical shifts with the observed ones. Your answer should include the assignment of the most important features (i.e., the starred ones) of the IR spectrum. (**15 marks**)





Bonus: 95% of all eliminations are β -eliminations, but there are some important exceptions. The following is one of the most important ways of making cyclopropanes. Propose a reasonable mechanism for the following reaction, most importantly the reactive intermediate involved.



¹H Nuclear Magnetic Resonance Chemical Shifts

Chemical Shifts in ppm downfield from tetramethylsilane (defined as $\delta = 0.000$ ppm). Values are approx. ± 0.2 ppm).

Protons on a Carbon Adjacent to a Functional Group

Functional Group	<u>CH₃</u>	<u>CH₂</u>	<u>CH</u>			
	δ	$(\Delta\delta)$	δ	$(\Delta\delta)$	δ	$(\Delta\delta)$
saturated system	0.8		1.2		1.6	
M-C=C	1.6	(0.8)	2.0	(0.8)	2.4	(0.8)
M-C≡C	1.7	(0.9)	2.2	(1.0)	2.8	(1.2)
M-Phenyl	2.2	(1.4)	2.6	(1.4)	2.8	(1.2)
M-Cl	3.0	(2.2)	3.4	(2.2)	4.0	(2.4)
M-Br	2.7	(1.9)	3.4	(2.2)	4.1	(2.5)
M-I	2.2	(1.4)	3.1	(1.9)	4.2	(2.6)
M-OH	3.2	(2.4)	3.4	(2.2)	3.8	(2.2)
M-OR	3.2	(2.4)	3.4	(2.2)	3.6	(2.0)
M-O-Phenyl	3.9	(3.1)	4.1	(2.9)	4.5	(2.9)
M-OC(=O)R	3.6	(2.8)	4.1	(2.9)	4.5	(2.9)
M-OC(=O)Ph	3.8	(3.0)	4.2	(3.0)	5.0	(3.4)
M-CH=O (aldehyde)	2.2	(1.4)	2.4	(1.2)	2.5	(0.9)
M-C(R)=O (ketone)	2.1	(1.3)	2.3	(1.1)	2.6	(1.0)
M-COOH (acid)	2.1	(1.3)	2.3	(1.1)	2.5	(0.9)
M-COOR (ester)	2.0	(1.2)	2.2	(1.0)	2.5	(0.9)
M-NR ₂	2.4	(1.6)	2.6	(1.4)	2.9	(1.3)
M-NHC(=O)R	2.9	(2.1)	3.3	(2.1)	3.9	(2.3)

Protons on a Carbon Once Removed from a Functional Group

Functional Group	<u>CH₃</u>	<u>CH₂</u>	<u>CH</u>			
	δ	$(\Delta\delta)$	δ	$(\Delta\delta)$	δ	$(\Delta\delta)$
M-C-CH ₂	0.8		1.2		1.6	
M-C-C=C	1.0	(0.2)	1.55	(0.35)	1.8	(0.2)
M-C-C≡C	1.2	(0.4)	1.5	(0.3)	1.8	(0.2)
M-C-Ph	1.2	(0.4)	1.6	(0.4)	1.8	(0.2)
M-C-Cl	1.5	(0.7)	1.8	(0.6)	2.0	(0.4)
M-C-Br	1.8	(1.0)	1.9	(0.7)	1.9	(0.3)
M-C-I	1.8	(1.0)	1.8	(0.6)	2.1	(0.5)
M-C-OH (or OR)	1.2	(0.4)	1.5	(0.3)	1.8	(0.2)
M-C-OPh	1.3	(0.5)	1.6	(0.4)	2.0	(0.4)
M-C-OC(=O)R	1.3	(0.5)	1.6	(0.4)	1.8	(0.2)
M-C-CH=O	1.1	(0.3)	1.6	(0.4)	2.0	(0.4)
M-C-C(R)=O	1.1	(0.3)	1.6	(0.4)	2.0	(0.4)
M-C-CO ₂ R	1.1	(0.3)	1.7	(0.5)	1.9	(0.3)
M-C-NR ₂	1.0	(0.2)	1.5	(0.3)	1.7	(0.1)

M-C-NH-C(=O)R	1.1 (0.3)	1.5 (0.3)	1.9 (0.3)
<u>Protons on sp^2 and sp Hybridized Carbons</u>			
$R_2C=CH_2$	4.7-5.3	$C=CH-C=O$	6.0
$R_2C=CHR$	5.1	$C=CH-Cl$	6.5
$RCH=CHR$	5.3	$C=CHBr$	6.5
cyclohexene	5.6	$CH=CH-C=O$	6.9
$ArCH=C-C=O$	7.7	$RCH=O$	9.1
$R-C\equiv C-H$	2.3-3.3	$R-OH$ (alcohol)	0.5-5.5
Aromatic hydrogens	6.0-9.0 (mostly 6.7-8.2)	$R-NHR$ (amine)	0.5-5.0
$R-C(=O)OH$	12-14	$R-NH-C(=O)R$ (amide)	5-8

Nuclear Magnetic Resonance Chemical Shifts

Chemical Shifts in ppm downfield from tetramethylsilane (TMS) (defined as $\delta = 0.000$ ppm).

General Regions:

0 - 1 δ	cylopropyl hydrogen s and methyl groups not shifted by electronegative atoms
1 - 2 δ	methyl groups β - to O or N atoms, attached to C=C or attached to aromatic rings; methylene groups
2 - 3 δ	methyl and methylene groups next to carbonyls or attached directly to nitrogen of amines
3 - 4 δ	methyl and methylene groups attached to oxygen or halogens (Br, Cl). $C=CH_2$ groups
4.5 - 6.5 δ	hydrogens on sp^2 hybridized carbons of alkenes (not aromatics)
6.8 - 8.5 δ	aromatic protons
9 - 10 δ	<u>aldehyde protons</u>

IMPORTANT AND DIAGNOSTIC INFRARED BANDS
(a very condensed table)

<u>ν (cm⁻¹)</u>	<u>Comments</u>
3000-3400	O-H stretching alcohols- unassociated OH's - 2 bands around 3600 (sharp) H-bonded - broad absorption at 3400 acids- very broad, centred at ca. 3000
3400-3200	N-H stretching amines- unassociated NH's - 2 bands around 3400 (sharp) H-bonded - broad absorption at 3200, weaker than OH
3300	C-H stretching of an acetylene
3100-2850	C-H stretching sp^2 - hybridized > 3000; sp^3 - hybridized < 3000
2900-2700	C-H stretching of ALDEHYDE
2250-2100	C≡C stretching of ALKYNE usually weak (weaker than C≡N), unless conjugated to C=O
2250-2225	C≡N stretching of NITRILE 2250 if not conjugated, 2225 conjugated Band <u>may</u> be weak
1800	C=O stretching of ACID CHLORIDE >>> >>> >>>
1735-1740	C=O stretching of ESTER >>> >>> >>>
1730	C=O stretching of ALDEHYDE >>> >>> >>>
1710	C=O stretching of KETONE >>> >>> >>>
1700	C=O stretching of ACID >>> >>> >>>
1660	C=O stretching of AMIDE >>> >>>
1650-1600	C=C stretch may be weak. Intensity increases with conjugation, especially to C=O