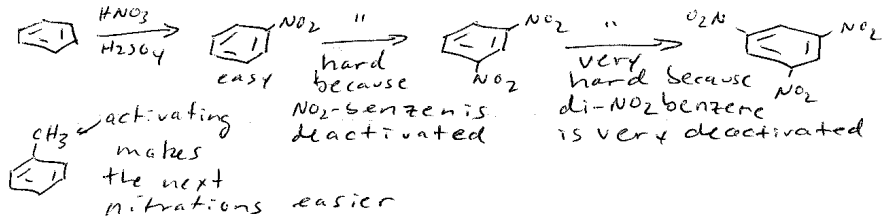
Chemistry 336 Winter 2001 Sample Exam 2

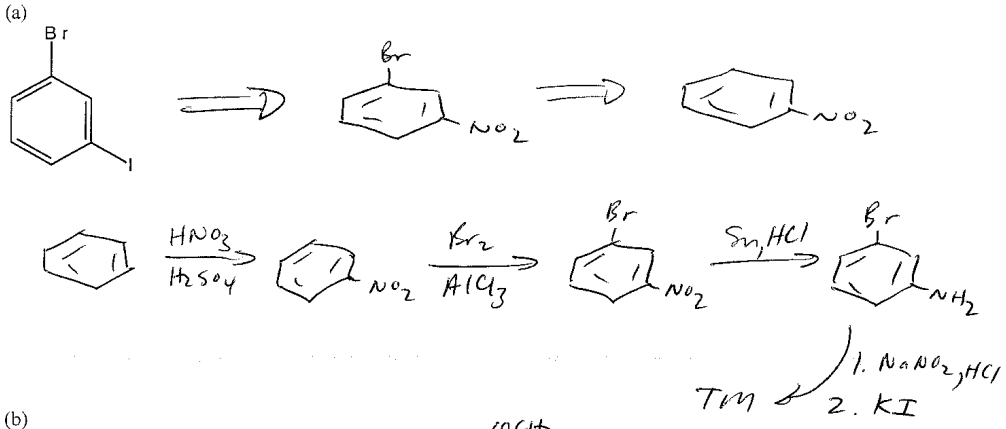
Note: The last page of the exam is a list of organic starting materials, inorganic reagents and spectral tables to be used for the exam.

1. 1,3,5-Trinitrobenzene (TNB) is a superior explosive when compared to 2,4,6-trinitrotoluene (TNT). Although TNB is no more dangerous to handle than TNT, the latter more commonly used. The reason for the preferred use of TNT is simply that it is easier to manufacture. Offer an explanation as to why TNT might be easier to manufacture. You may use a drawing of the structures of TNB and TNT as part of your explanation.

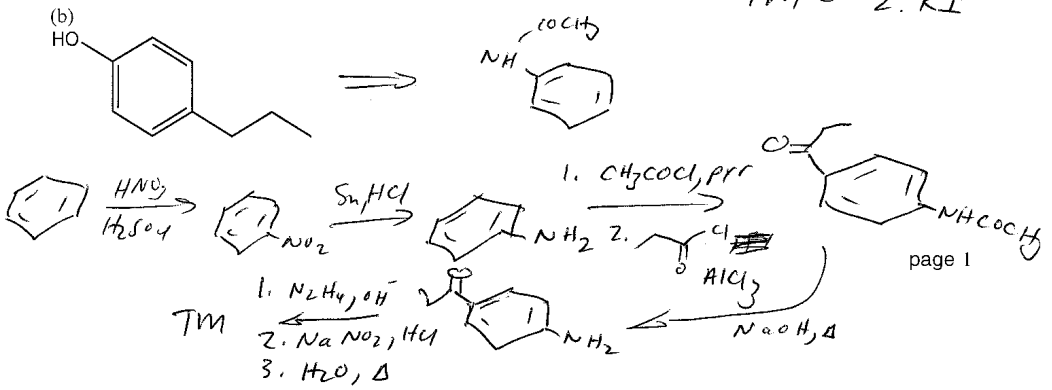


2. Given below are two disubstituted benzenes. Provide a scheme to illustrate a possible synthesis for each. The synthesis should be of reasonable yield and selectivity.

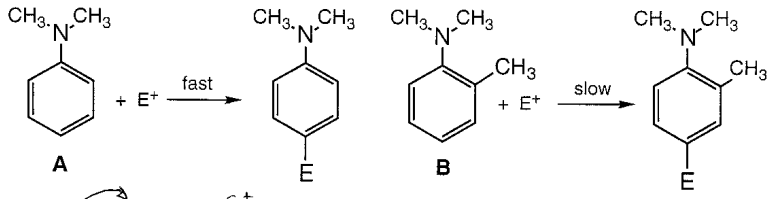
(a)

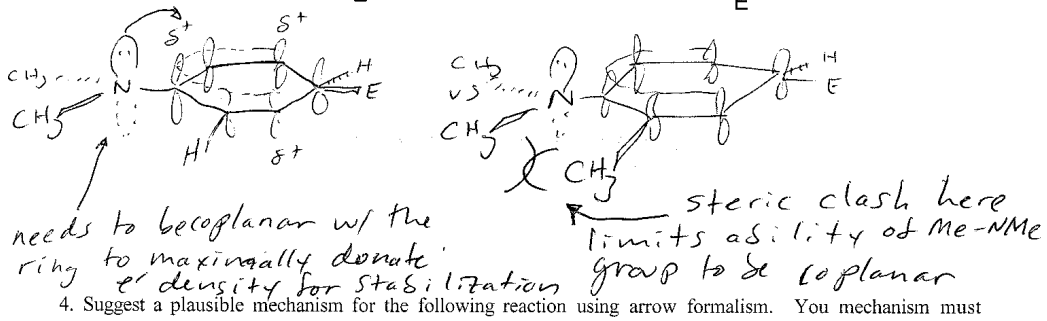


(b)

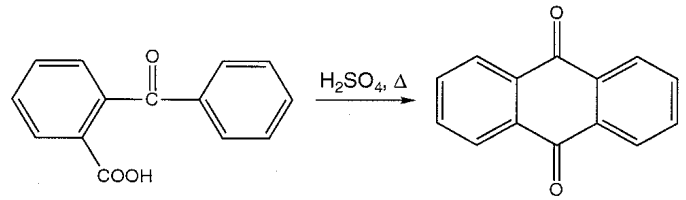


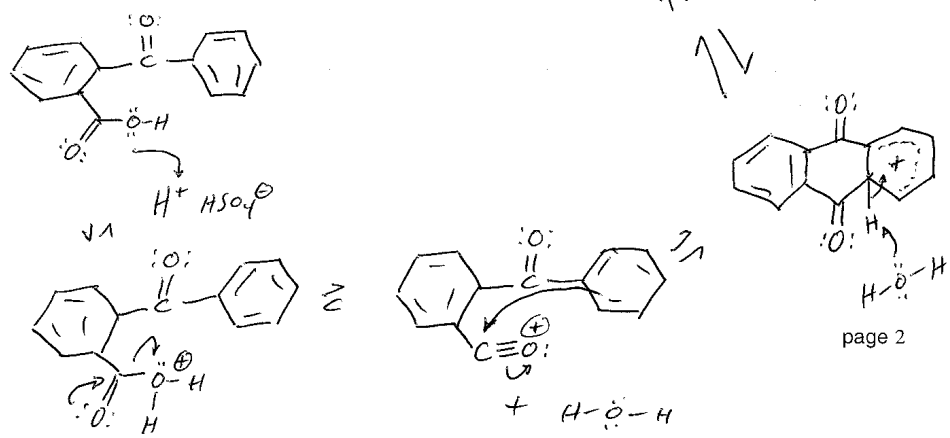
3. The reaction of N,N-dimethylaniline (**A**) with an electrophile is fast while the same reaction for N,N-dimethylaniline with an *ortho*-methyl substituent (**B**) is slow. Explain this observation. You will probably want to use a chemical structure as part of your explanation.





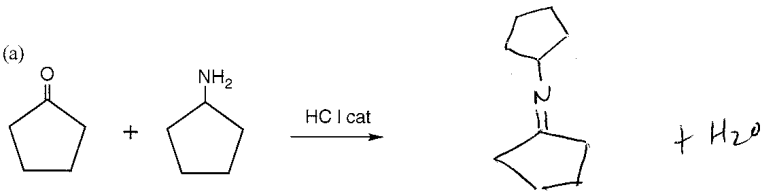
4. Suggest a plausible mechanism for the following reaction using arrow formalism. You mechanism must include each step and illustrate explicitly where electrons and atoms are participating in the reaction.



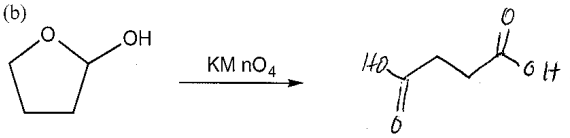


5. Draw the chemical structure(s) of the product(s) expected for the following reactions. Indicate stereochemistry when relevant. For any reactions in which more than one product is expected, indicate which is expected to be the major product if the reaction is kinetically controlled.

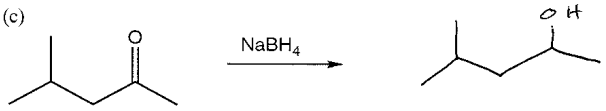
(a)



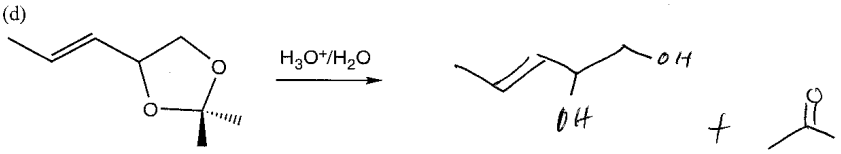
(b)



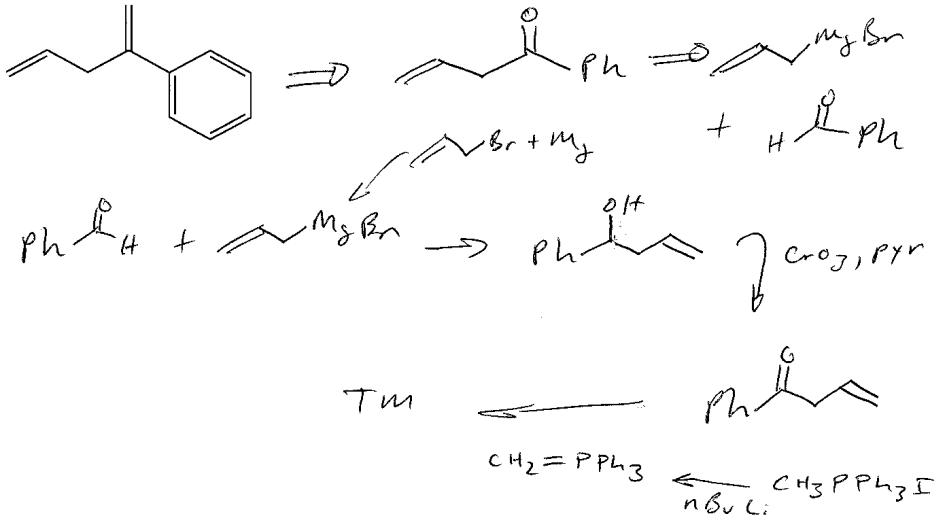
(c)



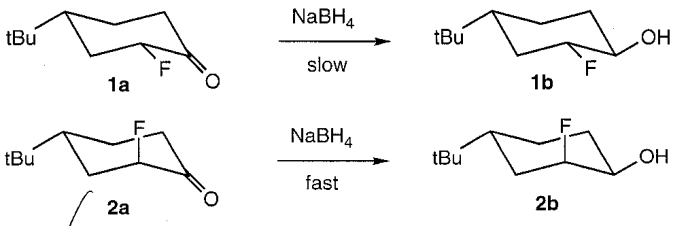
(d)

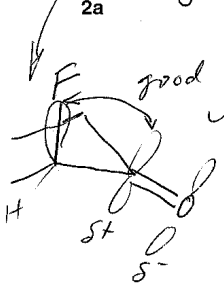


6. Propose a plausible synthesis for the molecule below. For starting materials you are to use only those organic molecules in the Toobox (last page of exam) and any inorganic reagents.

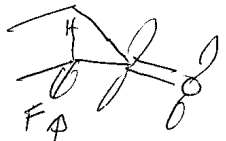


7. The sodium borohydride reduction of *cis*-2-fluoro-4-*t*-butylcycloxexanone **1a** at -20 ßC to give the equatorial **1b** alcohol is slow relative to the reduction of the *trans* isomer **2a**. Briefly explain why the axial fluorine substituent accelerates the borohydride reduction.



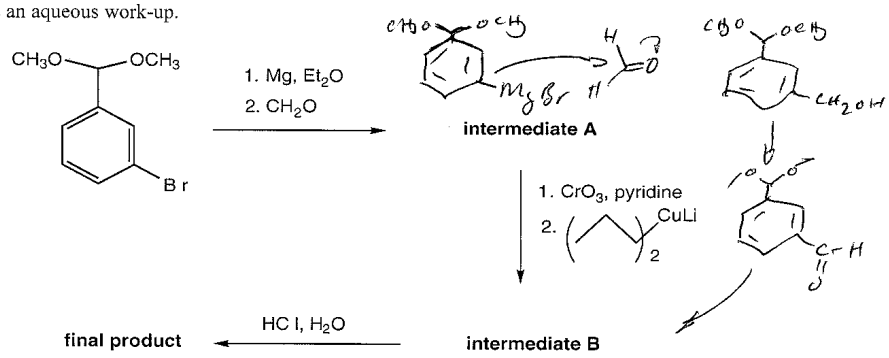


good orbital overlap of π system with strongly electron withdrawing Fluoro group - makes the carbonyl syst+ carbon especially e⁻ deficient relative to

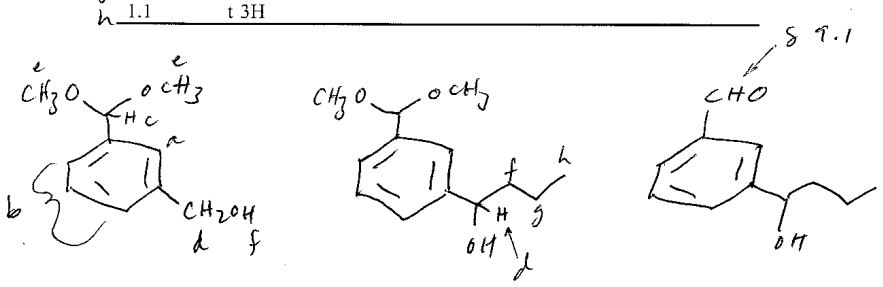


now the F-C orbital is ⊥ to the carbonyl π system, No overlap

8. Consider the synthetic scheme given below. The researcher who did this synthesis took NMR spectra for the two intermediate products **A** and **B** and the final product. However, the spectra were unmarked and thus, they were mixed up. Please help the researcher. Draw the chemical structure for the final product and the two intermediate products **A** and **B**. Also, indicate which of the spectra corresponds to each of the structures. Each step includes an aqueous work-up.



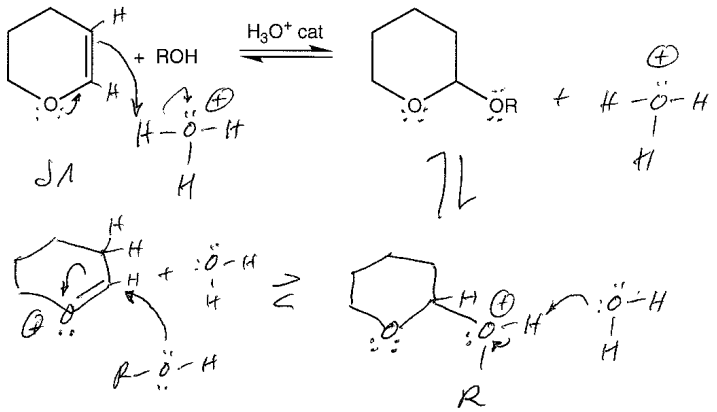
	spectrum 1		spectrum 2			spectrum 3	
	_ (ppm)		_ (ppm)			_ (ppm)	
a	7.8	m 1H	9.1	s 1H	a	7.8	m 1H
b	7.4	m 3H	7.8	m 1H	b	7.4	m 3H
c	5.2	s 1H	7.4	m 3H	c	5.2	s 1H
d	4.2	t 1H	6.2	d 1H	d	4.2	s 2H
e	3.6	s 6H	5.5	m 1H	e	3.6	s 6H
f	1.6	m 2H	2.5	m 4H	f	3.2	Broad 1H
g	1.3	m 2H	1.2	t 3H			
h	1.1	t 3H					



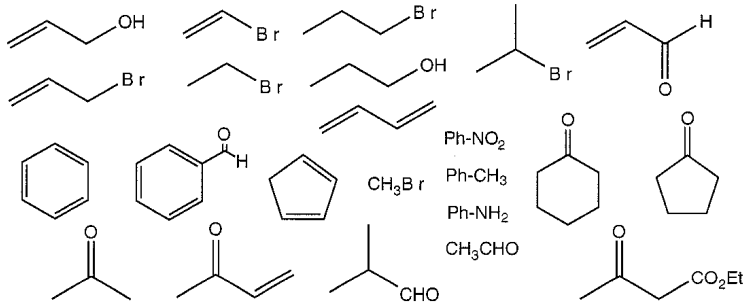
intermediate A **intermediate B** **final product**

spectrum # 3 **spectrum #** 1 **spectrum #** 2

9. Suggest a plausible mechanism for the following reaction using arrow formalism. Your mechanism must include each step and illustrate explicitly where electrons and atoms are participating in the reaction.



Organic Starting Materials



Inorganic and Organometallic Reagents

$NaBH_4$	$BF_3{:}OEt_2$	CH_3MgBr	Mg
$LiAlH_4$	$AlCl_3$	$(CH_3)_2CuLi$	H_2, Pd/C
NaH	$AlBr_3$	PhMgBr	$SOCl_2$
$LiHBEt_3$	HNO_3	CH_3Li	CH_3NH_2
BH_3	HCl	Ph_3P	$(CH_3)_4NBr$
$Na_2Cr_2O_7$	H_2SO_4	Et_3B	B_2H_6
CrO_3/pyridine	NaOH	Ph_3PCH_3	H_2O_2
$KMnO_4$	nBuLi	$Ph_3PCH_2CH_3$	HBr
			PBr_3