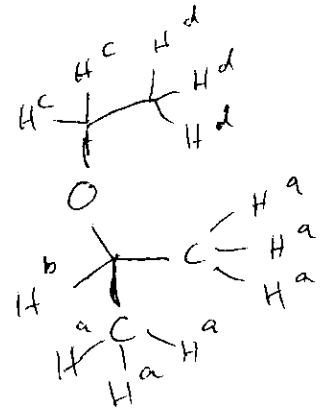
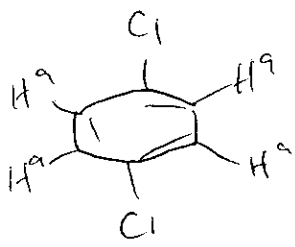
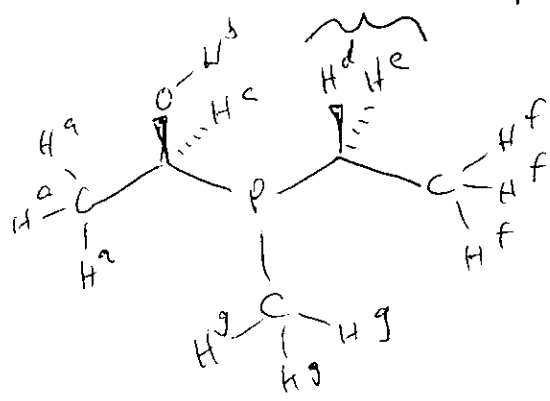
Practice Exam 1 Answers

1.

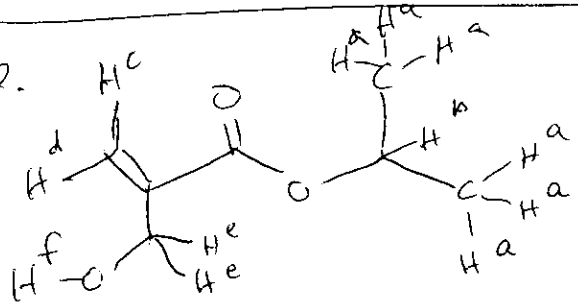




diastereotopic

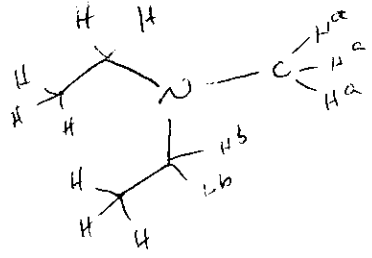


2.



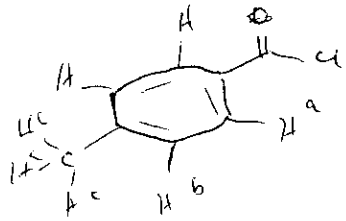
H_a	6H	doublet	1 ppm
H_b	1 H	septet	3-4 ppm
H_c	1H	doublet	5 ppm
H_d	1H	doublet	5 ppm
H_e	2 H	singlet (or doublet)	4 ppm
disappears on addn of D_2O → H_f	1 H	broad	dependent on solvent + concentration

3.



H_a	3H's	singlet	2.2 ppm
H_b	4H's	quartet	2.4 ppm
H_c	6H's	triplet	1.2 ppm

4.



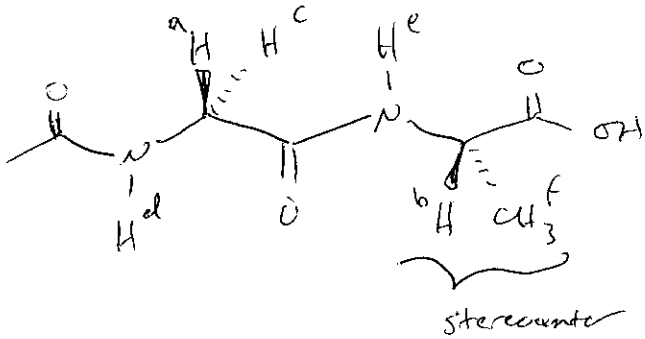
only cmpd to fit ^1H and ^{13}C data

H_a	8.0 ppm	doublet	# of aromatic H's + coupling pattern indicates para substitution
H_b	7.3 ppm	doublet	
H_c	2.5 ppm	singlet	

6 ^{13}C signals only fits molecule drawn, ~~190~~ 170 ppm indicates $\overset{O}{\overset{\|}{C}}$

(expect 5 ^{13}C signals)

5.

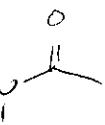


Due to the stereocenter in the molecule, H^a + H^c are diastereotopic $\Rightarrow$ different δ

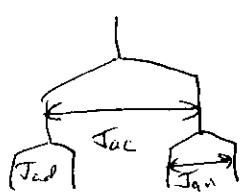
H^a couples w/ H^c $\Rightarrow$ ^2J (2-bond coupling)

" " w/ H^d $\Rightarrow$ ^3J (3-bond coupling)

doublet / doublet } doublet of doublets

(note H^d is an amide () proton, not an amine proton. Observations of amide proton couplings w/ other protons is very important to protein NMR (such as is done in determining 3-D structures of proteins by NMR).)

$^2J > {}^3J$ (in general) $\therefore J_{ac} > J_{ad}$

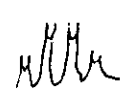


← doublet of doublets
4 peaks same height

H^b split by H^e (doublet)
split by H^f (quartet) } both ^3J, unknown which is larger

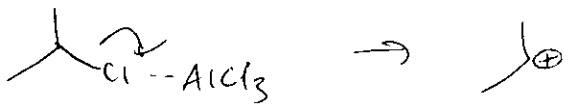
doublet of quarters

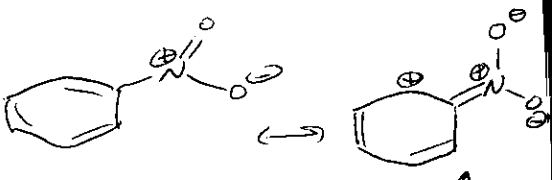
If $J_{be} > J_{bf}$ will see 

If $J_{bf} > J_{be}$ will see 

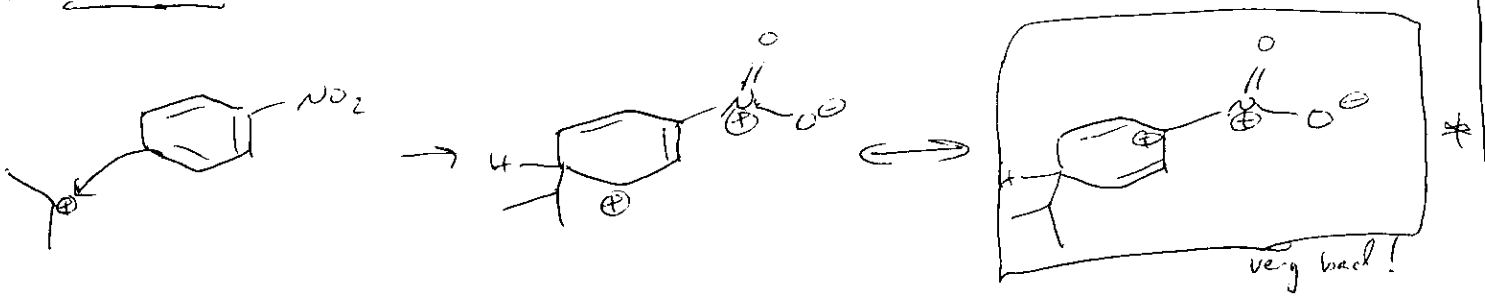
If $J_{bf} \sim J_{be}$ will see  (multiplet)

6.

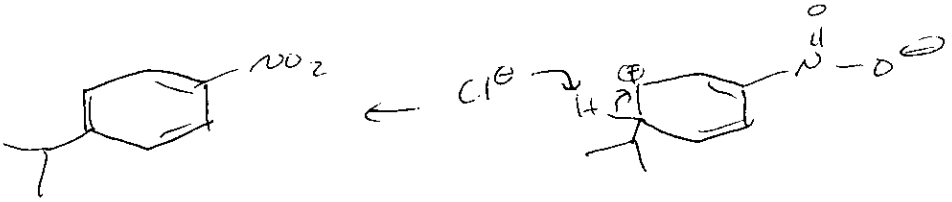




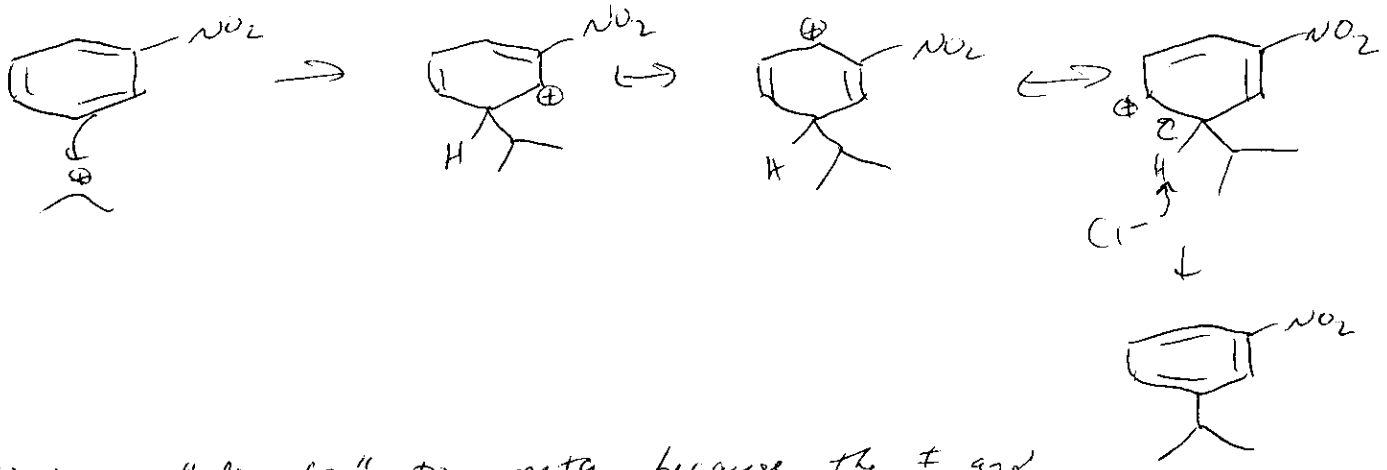
(a) ~~Ortho~~ Para



very bad!

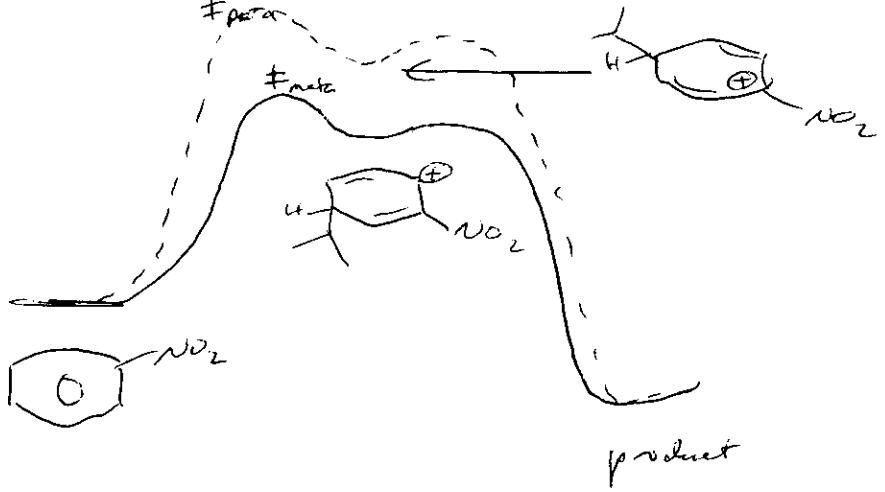


Meta

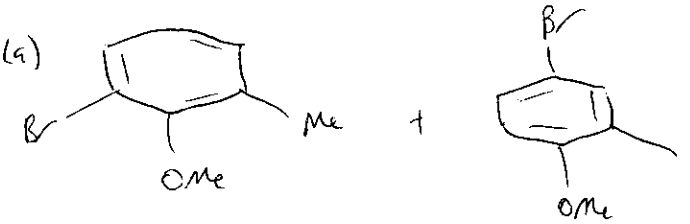


(b)(i) Nitro "directs" to meta because the σ and intermediate of ortho/para addition include a resonance structure which places two ⊕ adjacent to one another (boxed structure), which is very unfavorable. By contrast, meta addition produces no such terrible resonance structure. (ii) NO_2 is electron withdrawing due to the electronegativity of N + O, the presence of a ⊕ charge on the N adjacent to the ring (which draws electron density from the ring, making the aromatic system less nucleophilic), and the absence of a lone pair on the N to donate into the ring (no resonance stabilization of intermediates). ∴ It is deactivating

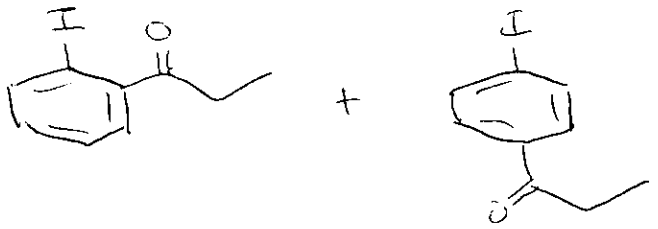
(c)



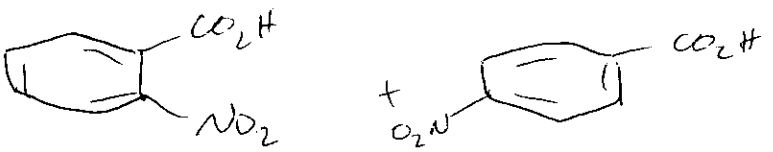
7.(a)



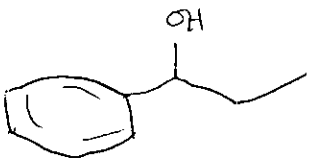
(b)



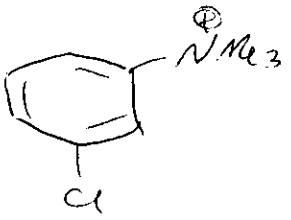
(c)



(d)

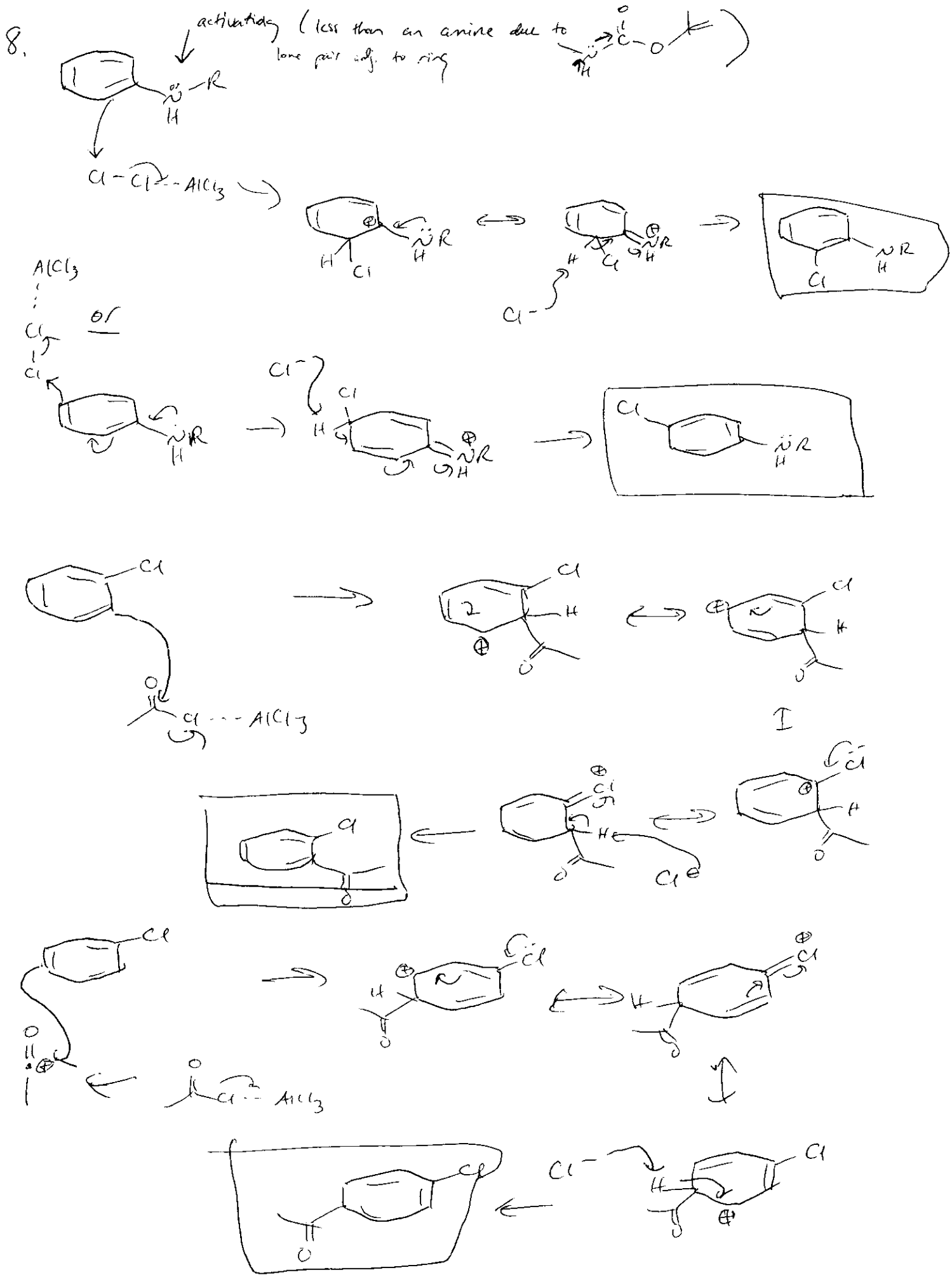


(e)

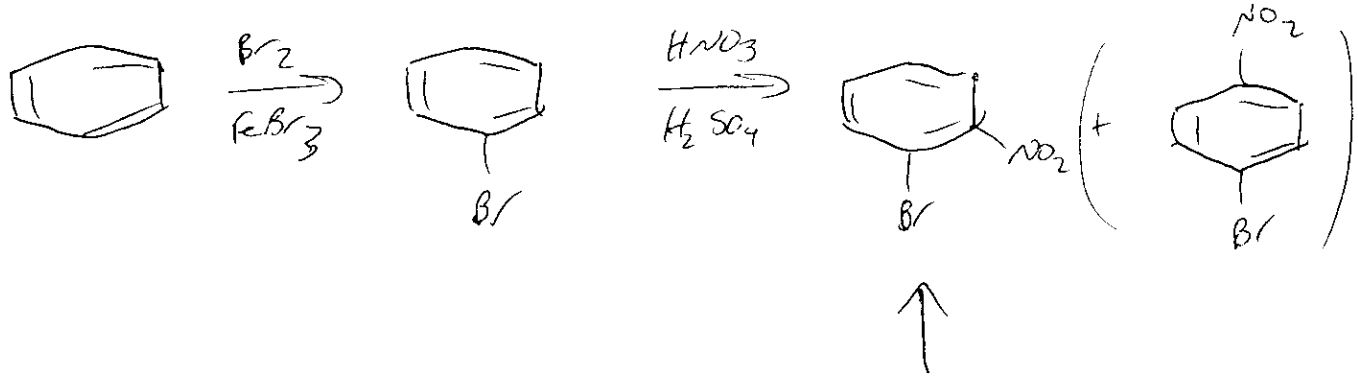


(f) No reaction

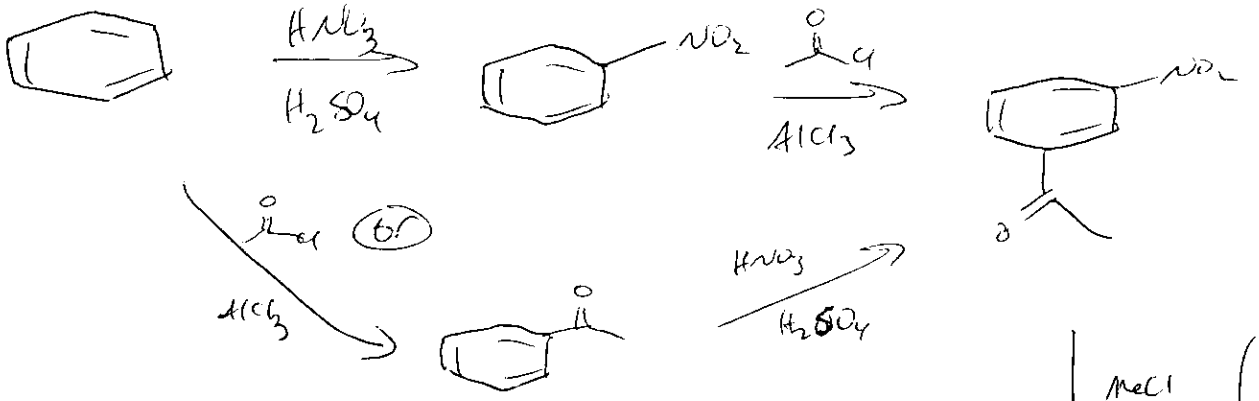
8.

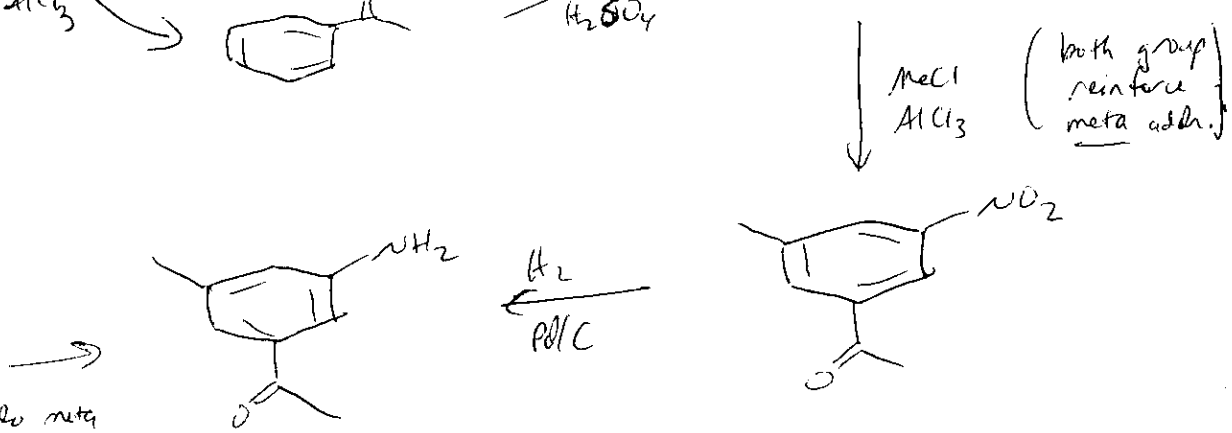

activating (less than an amine due to lone pair adj. to ring
AlCl3
or
I

9.



groups ortho → must add o,p – director first





groups all meta → must do meta directors first

must be last step – NH_2 is a strong o,p director (and also reacts w/ MeCl)