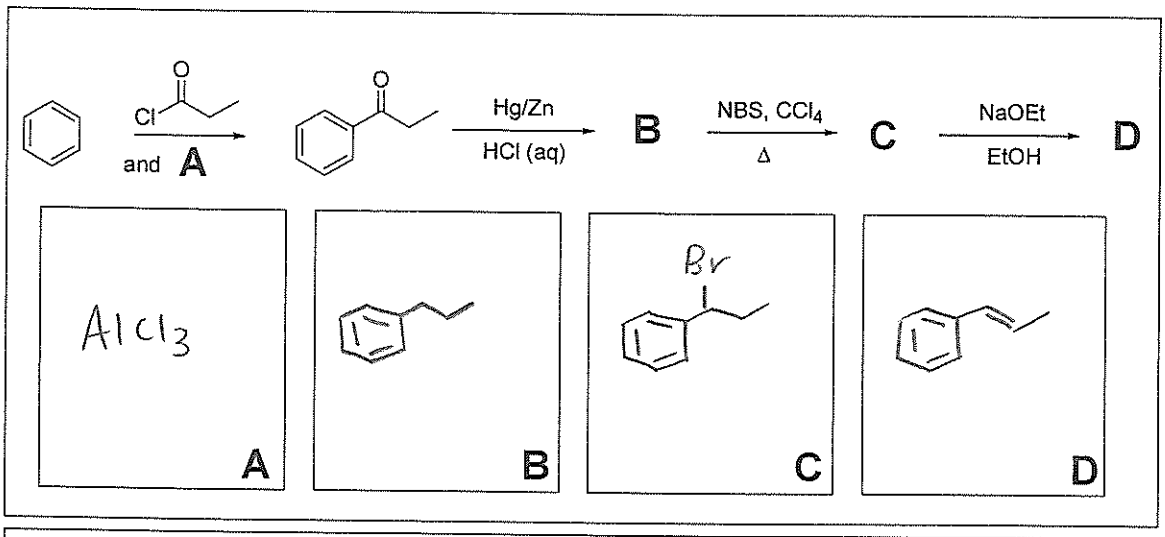
Key Exam 1 Summer 08
Minger - CHEM 3331

1. Supply the missing organic product or reagent(s) for each of the following reactions or synthetic sequences. Use the boxes provided (36 pts).

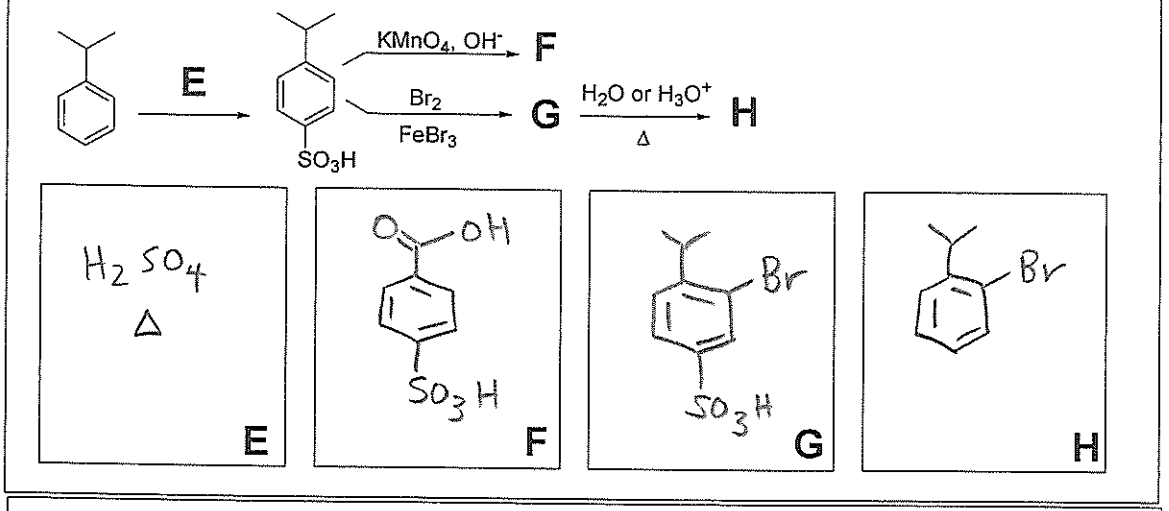


A: $AlCl_3$

B

C

D

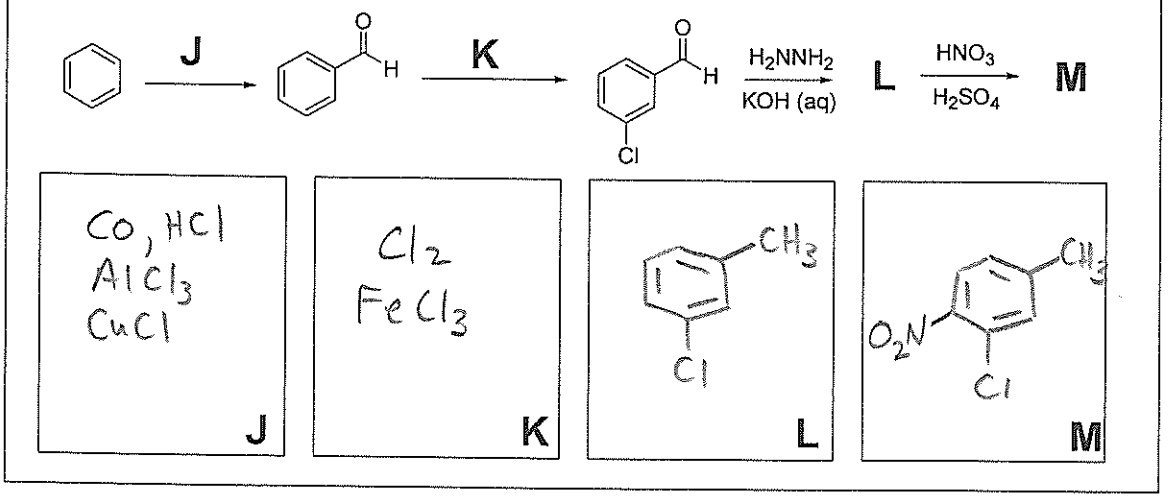


E: H_2SO_4, Δ

F

G

H



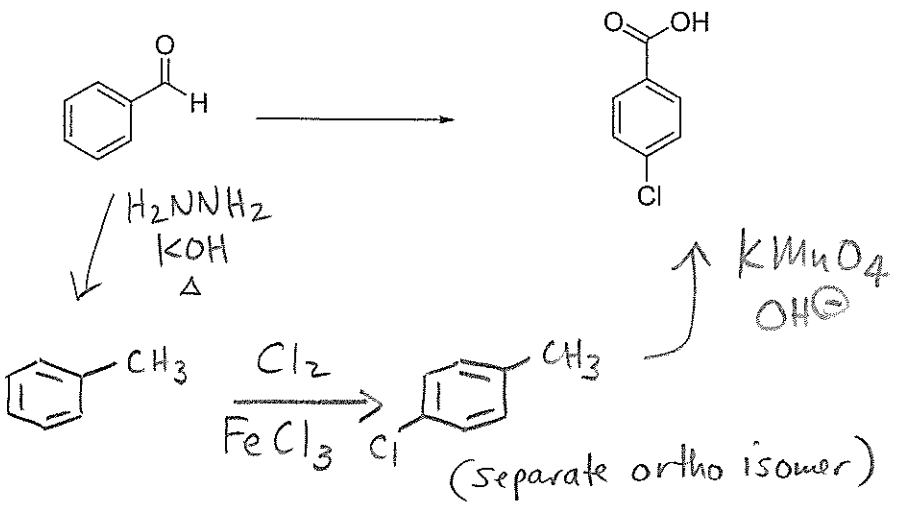
J: CO, HCl, $AlCl_3$, CuCl

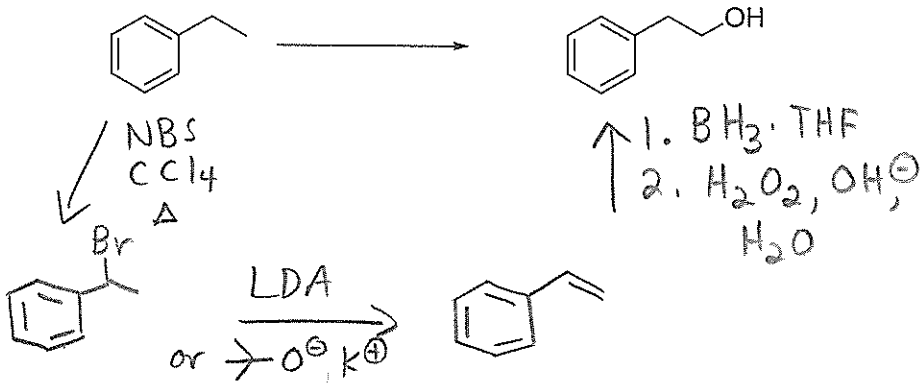
K: Cl_2, $FeCl_3$

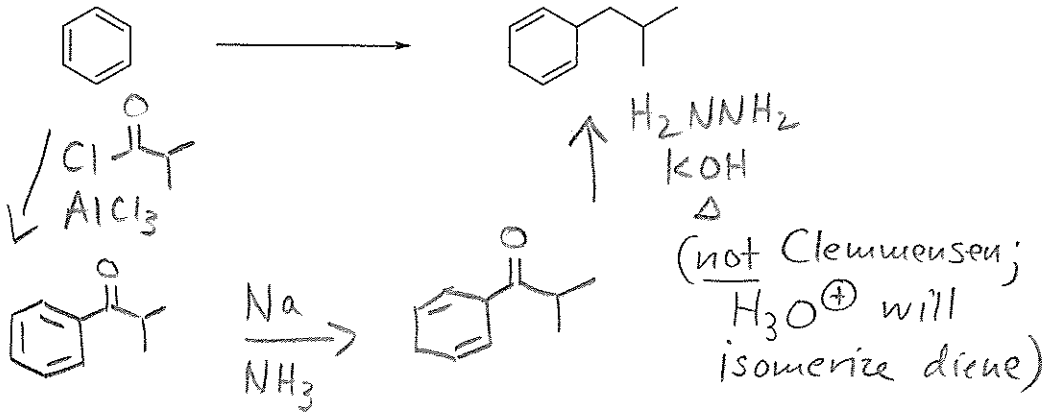
L

M

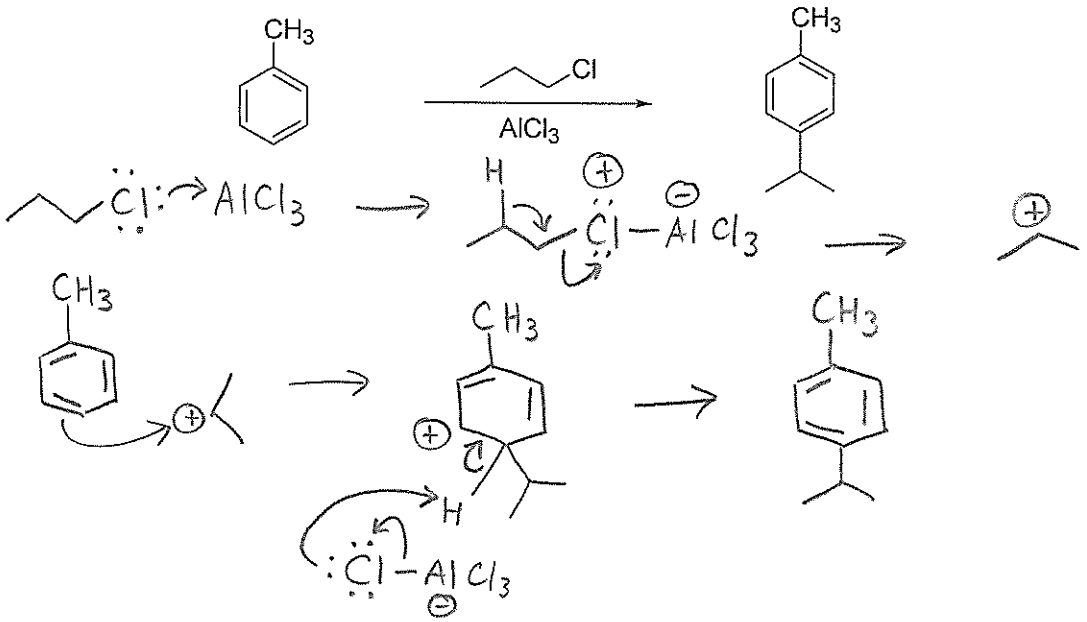
2. Provide reasonable multi-step syntheses for each of the following target molecules from the given starting material. Do not write any mechanisms, just the reagents needed for each step and the product of each step. (27 pts)



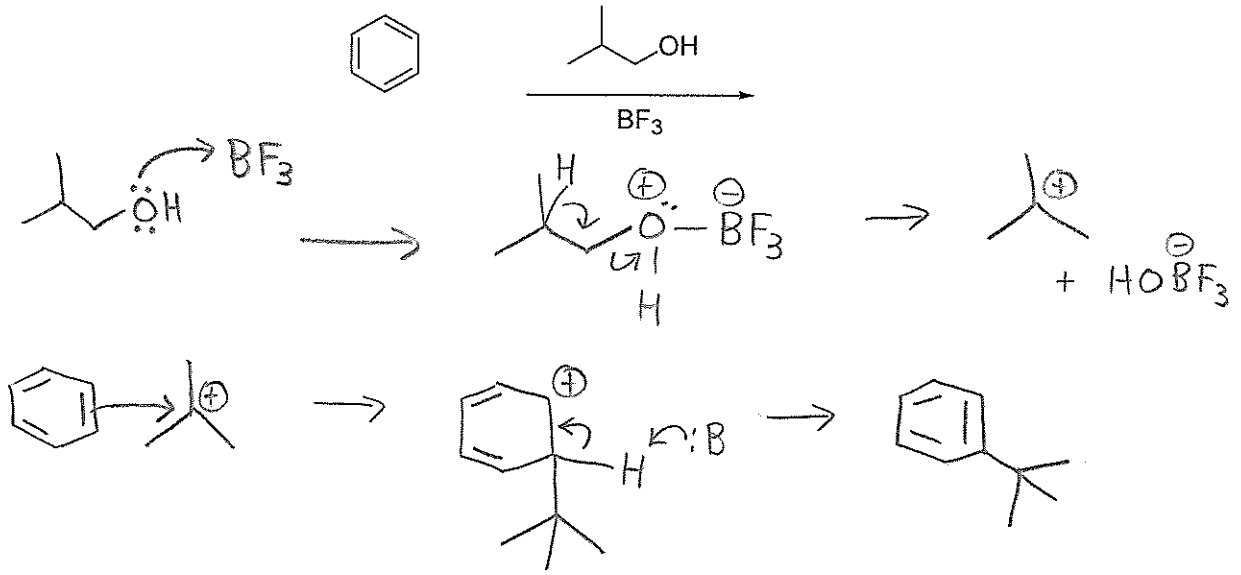




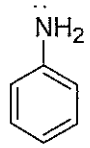
3a. Draw an arrow-pushing mechanism to rationalize the formation of the product of the following transformation. Show all bonds, curved arrows, non-zero formal charges, necessary lone pairs and intermediates clearly to receive full credit (10 pts).



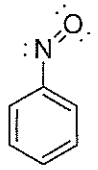
3b. Predict the product and draw an arrow-pushing mechanism to rationalize its formation under the conditions shown below. Show all bonds, curved arrows, non-zero formal charges, necessary lone pairs and intermediates clearly to receive full credit (10 pts).



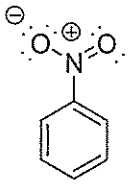
4a. Amino groups are *ortho, para* directing and activating toward EAS. In contrast, nitro groups are *meta* directors and deactivating toward EAS. The nitroso group is *ortho, para* directing but deactivating toward EAS.



amino group
o,p directing
activating



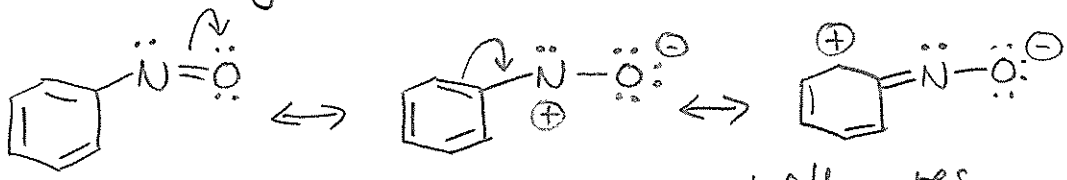
nitroso group
o,p directing
deactivating



nitro group
m directing
deactivating

Explain why the nitroso group is deactivating toward EAS, using appropriate structure(s). (10 pts)

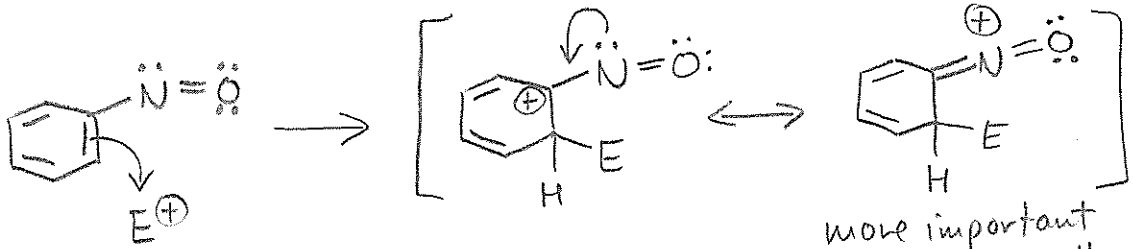
The nitroso group withdraws e⁻ density from the ring by resonance, thus diminishing its nucleophilicity and slowing rate of EAS.



+ other res. structures

4b. Explain why the nitroso group is an *ortho, para* director, using appropriate structure(s). (7 pts)

Using the ortho pathway as an example, we can stabilize the carbocation formed in the rate-determining step (attack by ring on E⊕) via resonance. This stabilization is also available in the para pathway, but not in the meta pathway. Thus, o,p pathways are favored (lower Ea, faster rates) over meta.



more important contributor - all atoms have octets