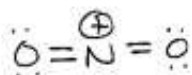
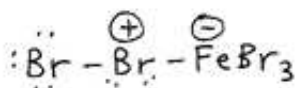
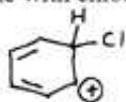


Name: Key

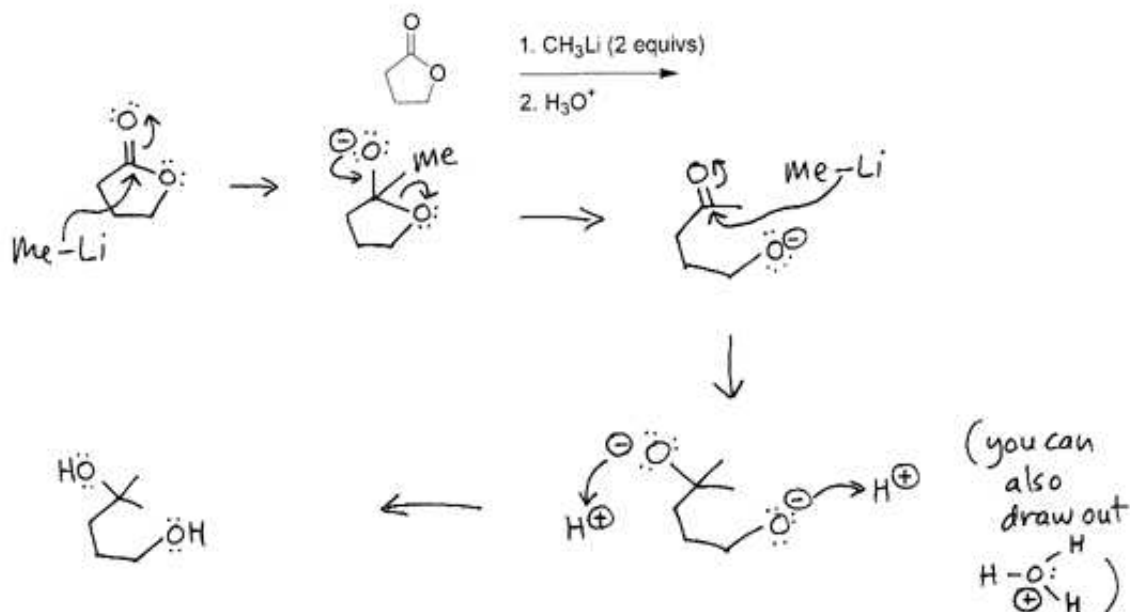
1a) Draw the Lewis structure of the electrophile in the nitration of benzene (3 pts):

1b) Draw the Lewis structure of the electrophile in the bromination of benzene under FeBr_3 catalysis (3 pts):

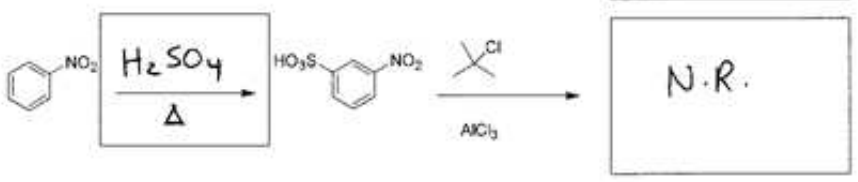
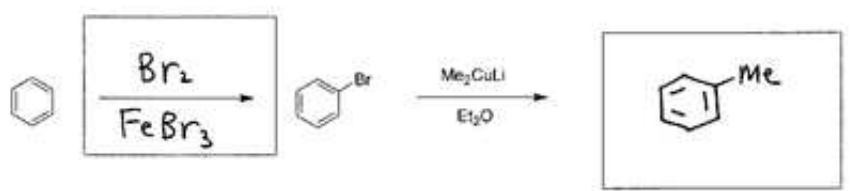
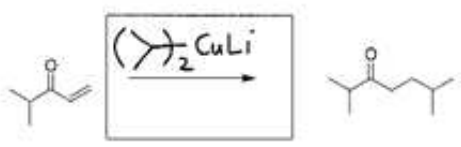
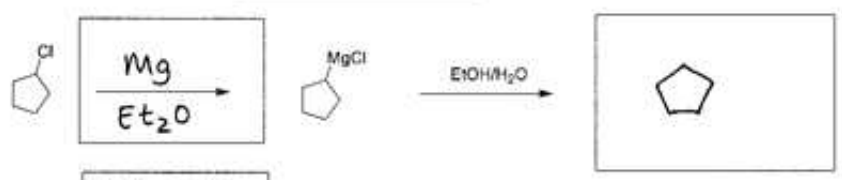
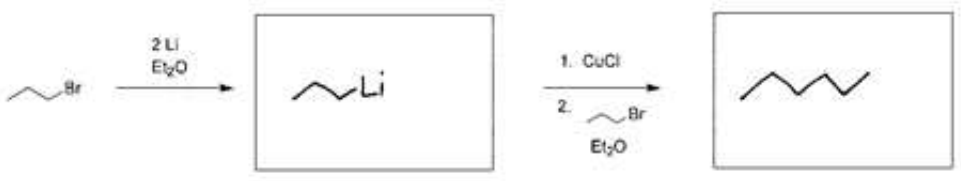
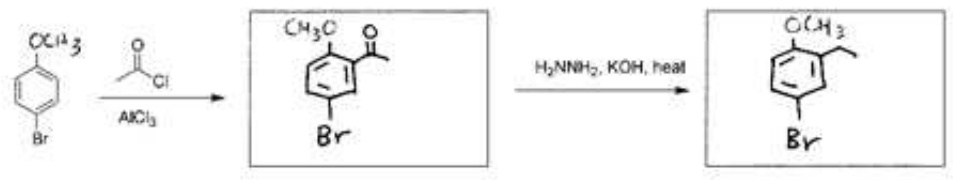
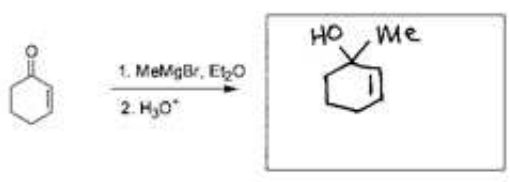
1c) Draw the Lewis structure of the intermediate formed in the rate determining step of the reaction of benzene with chlorine and aluminum trichloride (3 pts):



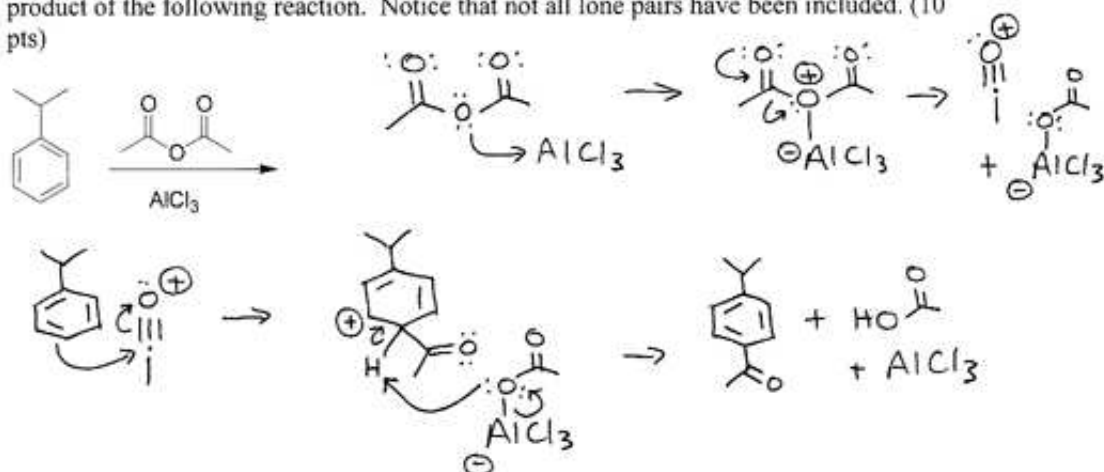
1d) Provide the product and an arrow-pushing mechanism for the following transformation. Show all intermediates, formal charges, necessary lone pairs, and all arrows required for the mechanism (6 pts)



2. Predict the products of the following reactions or supply the reagents needed to accomplish the indicated transformation. If no reaction occurs, write "N.R." (24 pts)

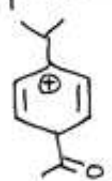


3a) Draw an arrow-pushing mechanism for the formation of the *para* substituted product of the following reaction. Notice that not all lone pairs have been included. (10 pts)



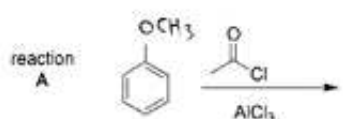
3b) Explain why the isopropyl substituent in the starting material in question 3a is an *ortho*, *para* director instead of a *meta* director. Just focus on a *para* vs. *meta* argument for the purposes of this question, *i.e.*, you don't have to go into details about *ortho*. Your answer should include relevant chemical structures and a clear, logical explanation of why the *para* product is favored (5 pts).

The intermediate cyclohexadienyl cation for *para* attack includes a 3° cation resonance structure:



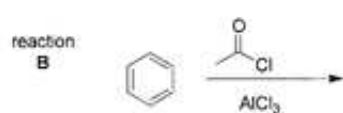
The intermediate formed on *meta* attack can only form 2° carbocation resonance structures. Thus, the formation of the more stable intermediate (*para* situation) has a lower activation energy, and *para* direction is favored over *meta* direction.

3c) Compare the rate determining step for these two reactions:



Which has a higher activation energy (circle one)? (1 pt)

A **B**

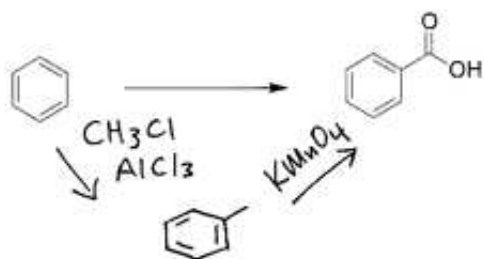


Why? Explain here (3 pts):

Lone pair on O can donate e⁻ density into ring by resonance, "activating" the ring to attack by electrophile relative to benzene.

4) For each of the following, outline a synthesis of the compound from the indicated starting material and reagents of four or fewer carbons and any needed inorganic reagents. Do not show mechanisms, just reagents needed and the product of each step. (20 pts)

4a)

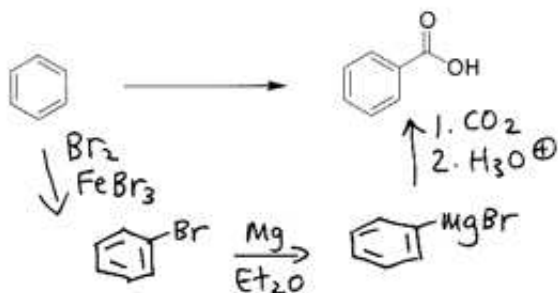


or

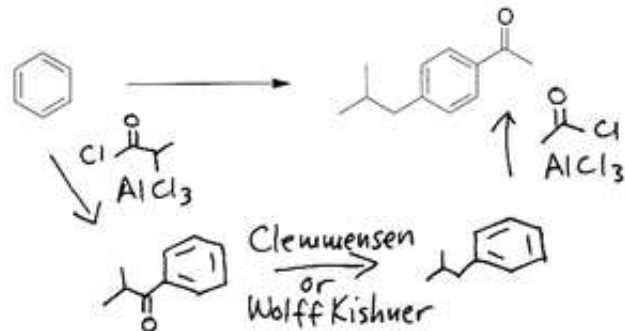
1. CH_3COCl or $\text{CH}_3\text{CO}_2\text{R}$, AlCl_3
2. Clemmensen or Wolff Kishner reduction
3. KMnO_4 or $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{O}$
 Δ

4b)

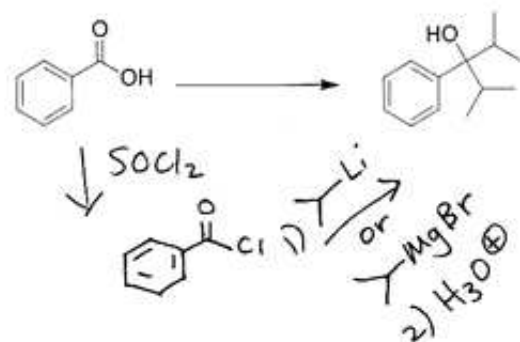
(Use a different method than in 4a)



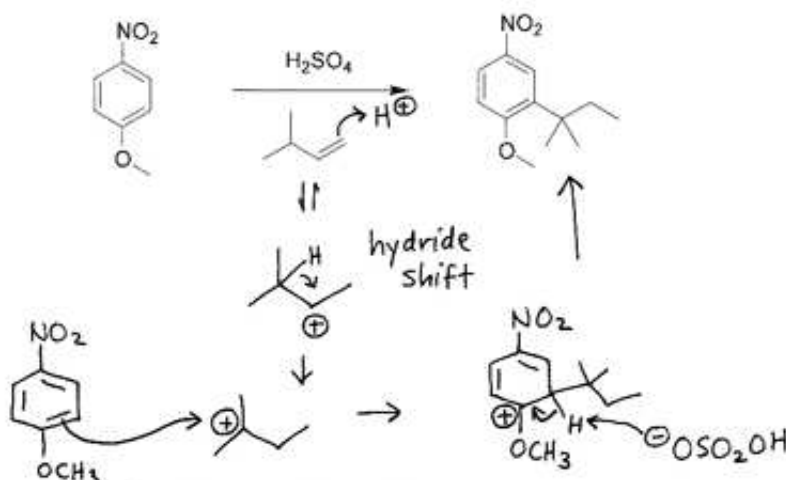
4c)



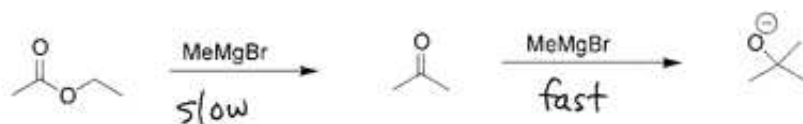
4d)



5. Show a detailed mechanism for the following reaction. Include all arrows, lone pairs, formal charges and key intermediates to receive full credit (8 pts).



6. In the reaction of ethyl acetate with methyl Grignard shown below, the Grignard reagent adds to the ester in the first step to give the ketone, then adds to the ketone to provide the alkoxide ion. (The magnesium bromide attached to the alkoxide is not shown.) The alkoxide becomes the alcohol product after acidic aqueous workup.



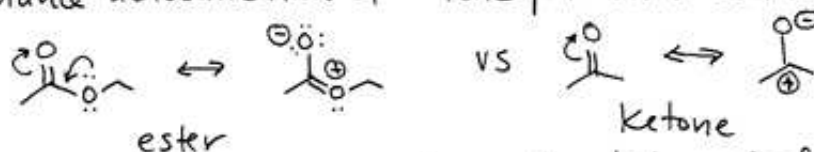
- 6a) As the reaction progresses, which accumulates more rapidly: the ketone or the alkoxide? (Circle one) (1 pt)

Ketone

Alkoxide

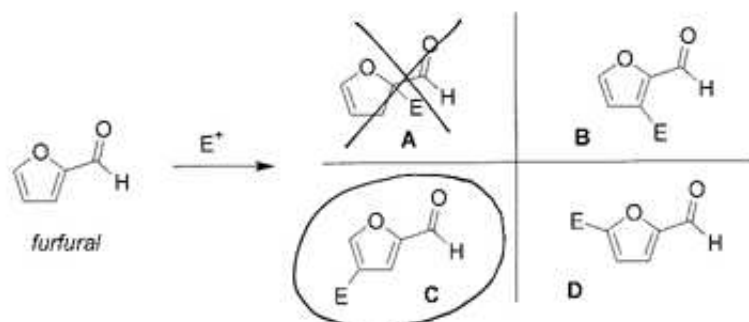
- 6b) Explain your answer to 6a here. Be concise, logical, and brief. Include any relevant chemical structures to help you explain (6 pts).

The ester is less electrophilic than the ketone because of resonance delocalization of a lone pair on the ester oxygen:



Therefore the first step is slow - the ketone is formed slowly and reacts rapidly once it is formed, resulting in a more rapid accumulation of the alkoxide.

7. In the electrophilic aromatic substitution reaction of furfural with a generic electrophile E^+ , four possible products (A, B, C and D) can be envisioned:

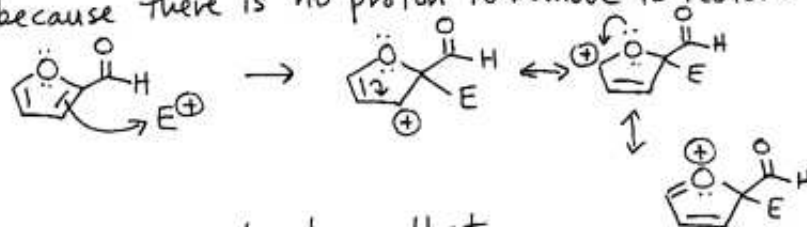


7a) One of these products cannot be formed. Put an "X" through the product that *cannot* be formed (1 pt).

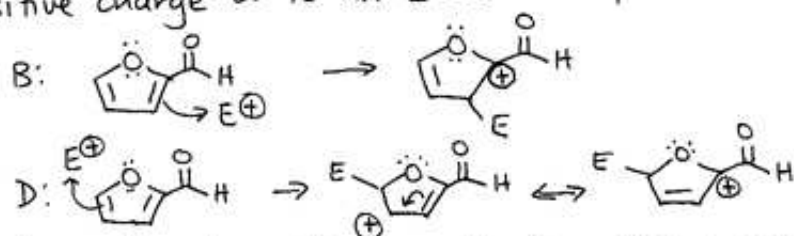
7b) One of these products is much more likely than the others to form. Which of these products is most likely to form? Circle it (1 pt).

7c) Explain your answers to 7a and 7b here. Why did you make the choices you did? Be brief, concise and logical. Use chemical structures to support your reasoning (5 pts).

A cannot form because there is no proton to remove to restore aromaticity:



B and D both have resonance structures that place positive charge α to an EWG - very unstable!



C doesn't have the destabilizing situation of B and D, and is stabilized by a resonance contributor where all atoms have octets of e^- .

