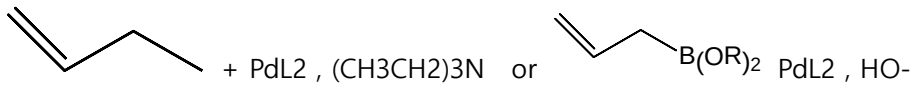
1.

(a) Grub's catalysts and CH2=CH2

(b)

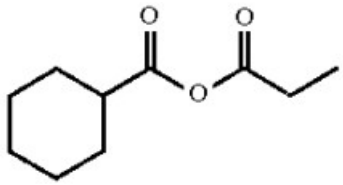


(c) 1. Mg 2. D2O

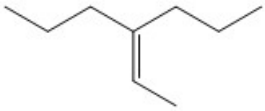
(d) NBS, heat, peroxide

2.

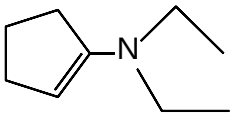
(a)



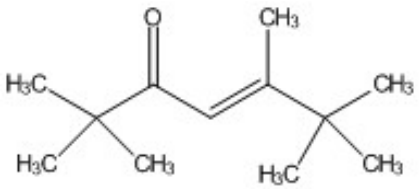
(b)



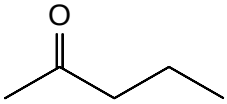
(c)



(d)



(e)



3.

(a) [6 pts] Give **either** the systematic or common name of **A**, **B**, and **D**.

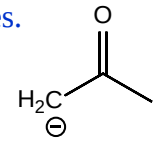
A N,N-dimethylacetamide or N,N-dimethylethanamide

B ethyl acetate or ethyl ethanoate

D acetaldehyde or ethanol

(b) [2 pts] How would you explain the reason why **D** is more acidic than **C**?

The electron donating methyl group of C destabilizes the conjugate base of C more than H of D does.



(c) [2 pts] How would you explain the reason why **B** is less acidic than **C**?

The carboxyl oxygen of B donates electron by resonance to destabilize the conjugate base of B.

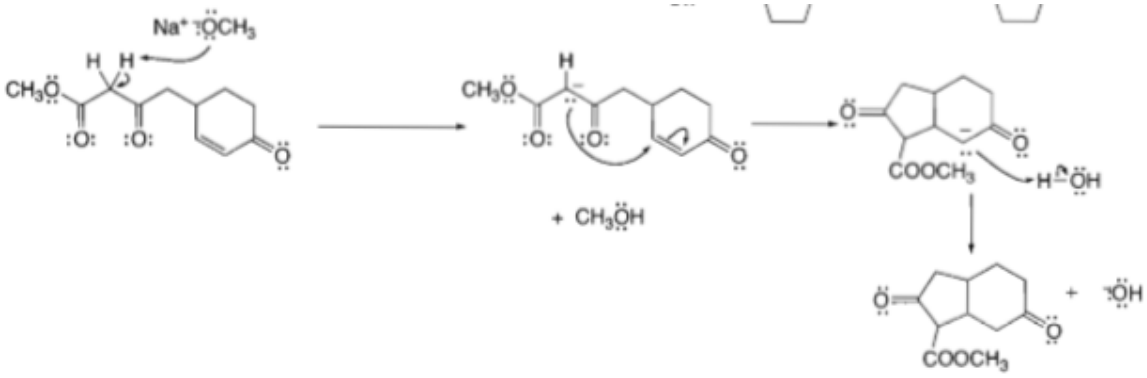
or See the explanation on page 839 of the textbook.

(d) [2 pts] How would you explain the reason why **A** is less acidic than **B**?

The nitrogen of A donates electron by resonance better than the carboxyl oxygen of B due to the smaller electronegativity.

4.

b.



5.

A. 1. NaOEt, 2. (EtO)2CO, 3. HCl

B 1. NaOEt, 2. CH3CH2I

C. H2O, HCl, Δ

D. 1. CH3CH2MgBr 2. H_3O^+

E. 1. LDA, CH3X, X= halogens

F. H_3O^+ or HO^- , Δ

G. 1. LDA, CH3CH2CHO 2. H_3O^+ or HO^- , Δ

H. H2, Pd/C

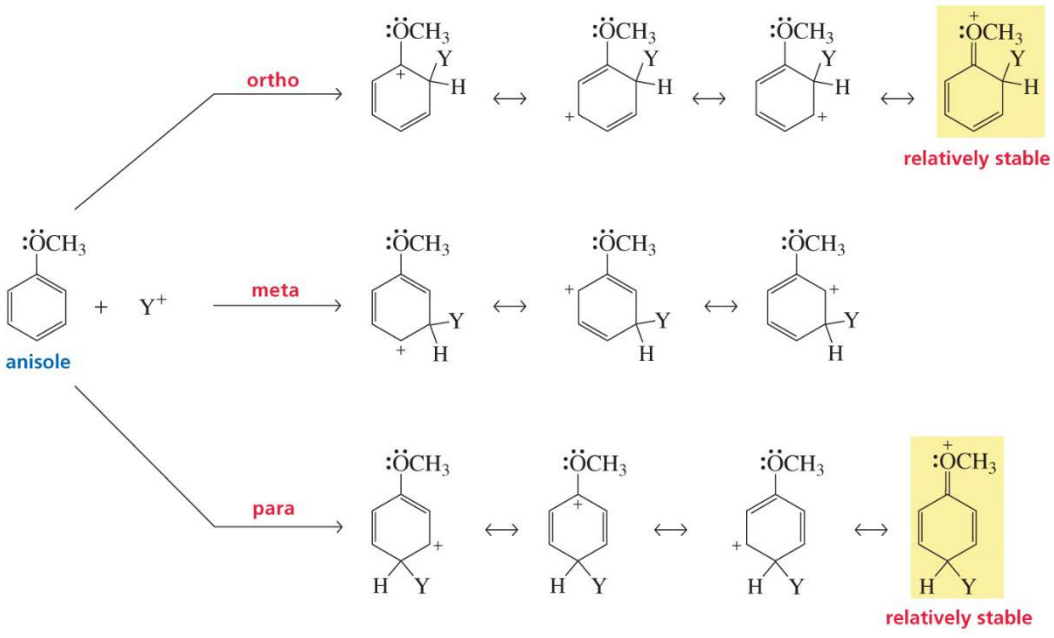
I. 1. LDA, HCO2Et 2. HCl

6.

(a) [4 pts]
A anisole or methoxybenzene
B benzenesulfonic acid

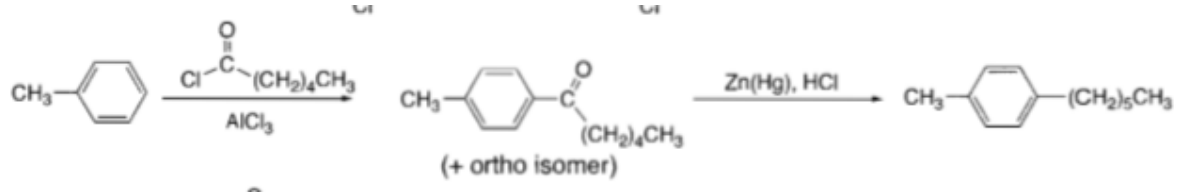
(b) [2 + 4 pts] ___A__ is more reactive and ___B__ is less reactive than benzene [2 pts]
The methoxy of A donates electron by resonance and withdraws electron inductively. Since the resonance effect is more significant than inductive effect in this case, the methoxy group donates electron to the ring to enhance the nucleophilicity of the ring and also stabilize the arenenium ion intermediate, which increases the reactivity of the ring. [2 pts]
The sulfonic acid group withdraws electron inductively and by resonance from the ring, which results in the decrease in nucleophilicity of the ring, stability of the arenium ion intermediate, and hence the reactivity of the ring. [2 pts]

(c) [2 + 6 points] ___A__ is the ortho-para director [2pts]
The methoxy group donates electron by resonance, and the intermediate with an electrophile attached to ortho or para position has one more resonance contributor. As these intermediates are better resonance-stabilized than that of meta intermediate, the substitution to ortho and para position is faster than that to meta position. [2 pts]
drawing resonance forms [2 pts]
As the methoxy group withdraws electron inductively, it destabilizes the resonance contributor with the positive charge at the ring carbon directly bonded to the methoxy group. As this type of resonance form is part of ortho and para intermediate, the inductive effect favors meta direction. However, the inductive effect is outweighed by the resonance effect in this case. [2 pts]



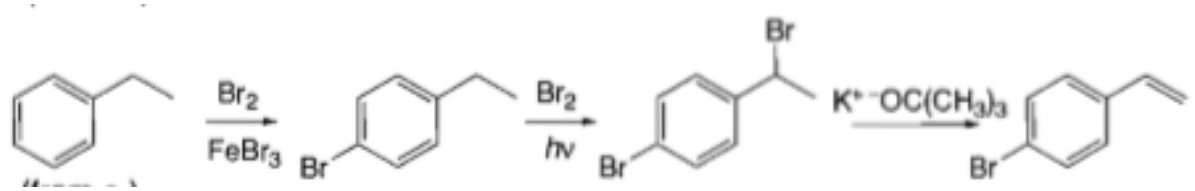
7.

(a)



or . H2, Pd/C for reduction

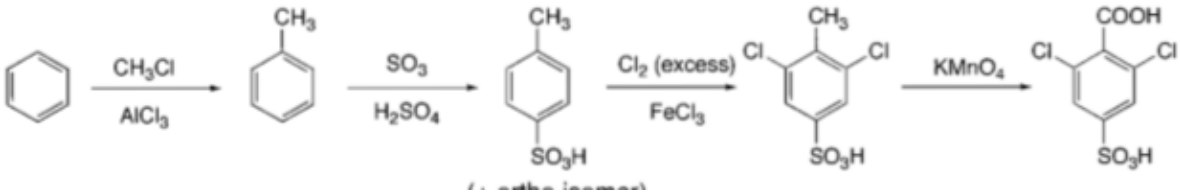
(b)



(c)

1. H2SO4, HNO3, 2. H2, Pd/C 3. NaNO2, HCl, 0 °C 4. $H3O^+$, Δ

(d)



8.

(a) [4 pts] No point for misspelling!

A pyrrole

B furan

C thiophene

D pyridine

(b) [3 pts]

As N, O, and S of A, B, and C, respectively, can donate electron to the rings by resonance, the nucleophilicity of the rings and stability of the intermediates are enhanced to give higher reactivity of the rings.

In pyridine N withdraws electron inductively from the ring, lowers the nucleophilicity of the ring, makes the intermediate less stable, and hence the ring less reactive than benzene.

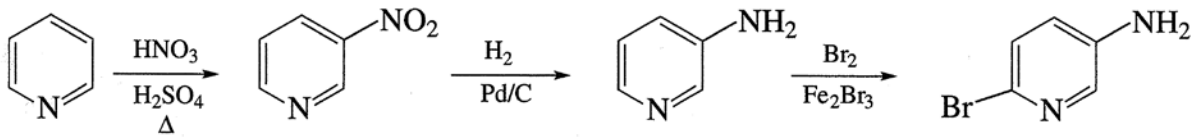
In the former case resonance effect wins, and in the latter inductive effect wins. (No need to mention in your answer.)

(c) [2 pts]

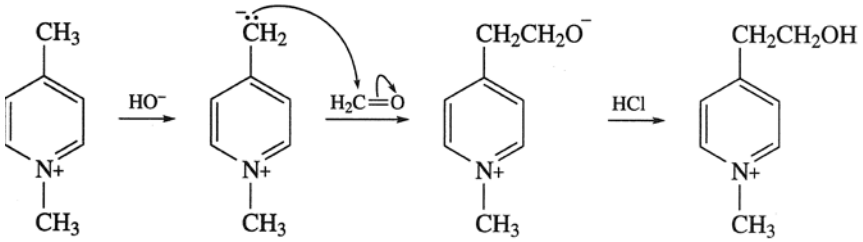
As S of thiophene has to use its 3p orbital to overlap with 2p orbital of carbon, the electrondonation by resonance is less effective than in furan.

9.

(a) Problem 44(b), Chapter 19, textbook



(b) Problem 40(e), Chapter 19, textbook



10.