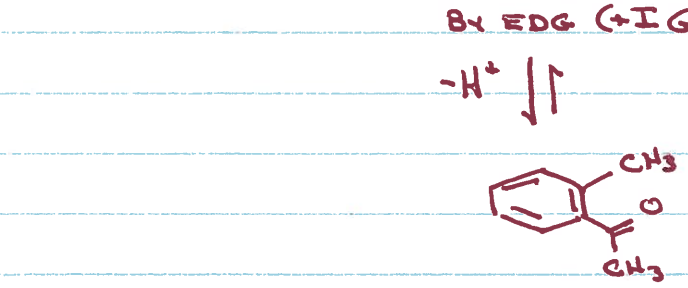
59-235 Final 2017
Suggested Solutions

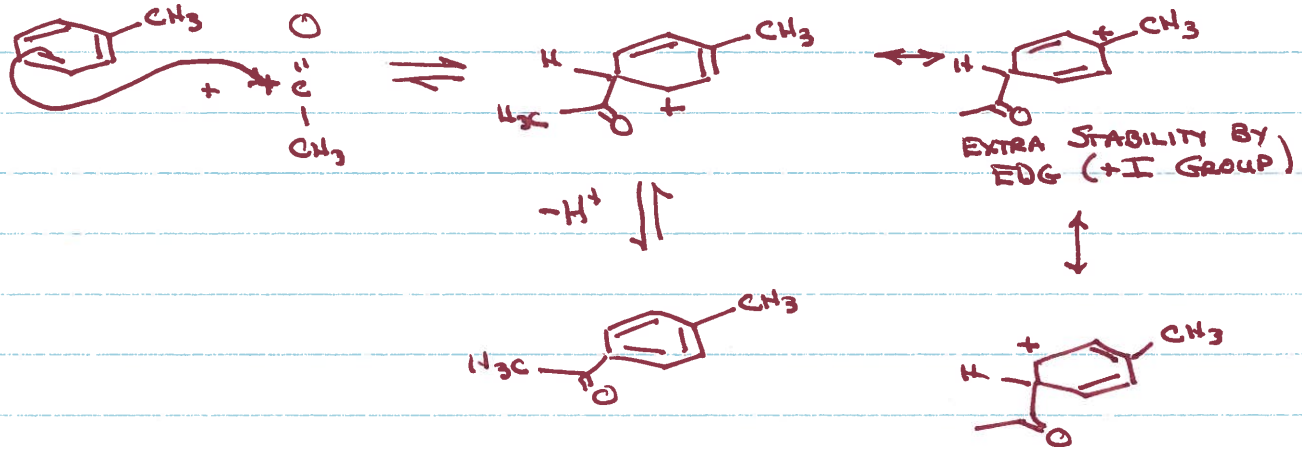
1.

ORTHO

EXTRA STABILITY BY EDG (+I GROUP)

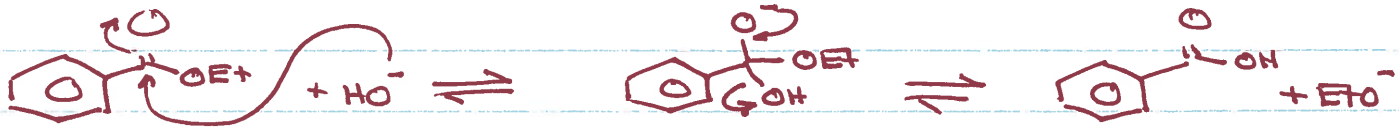


PARA



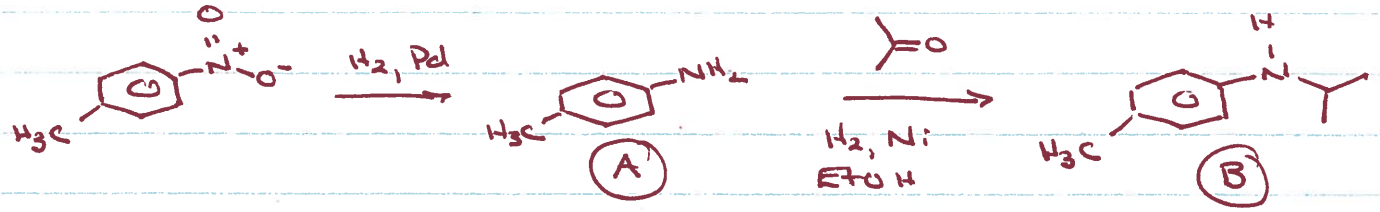
META NOT AS GOOD, SINCE C^+ NEVER ON CARBON ATOM WITH EDG.

2.

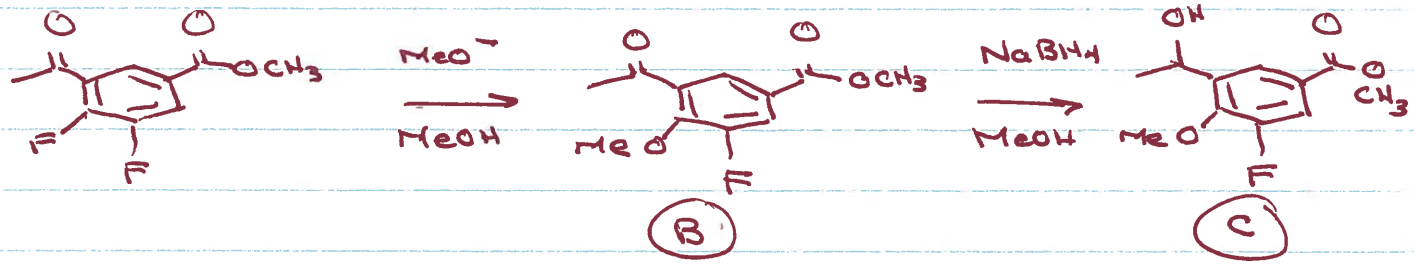


DRIVES RXN TO COMPLETION

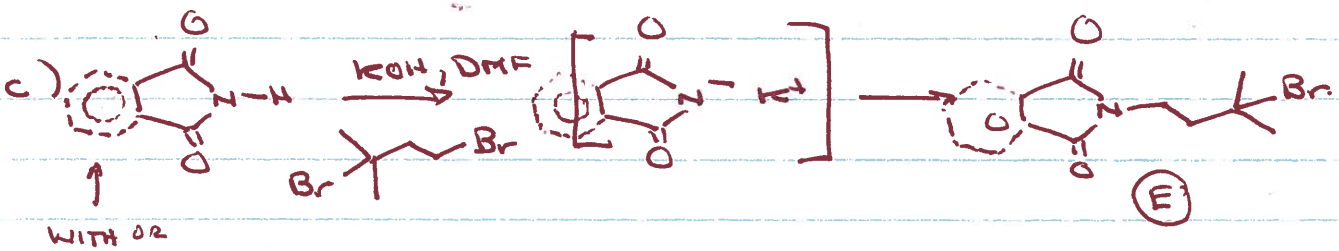
3a)



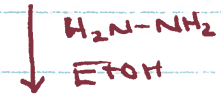
b)



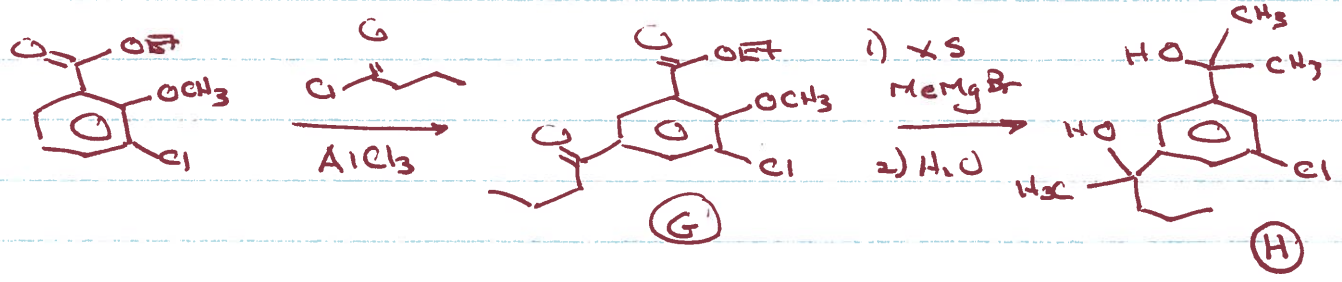
c)



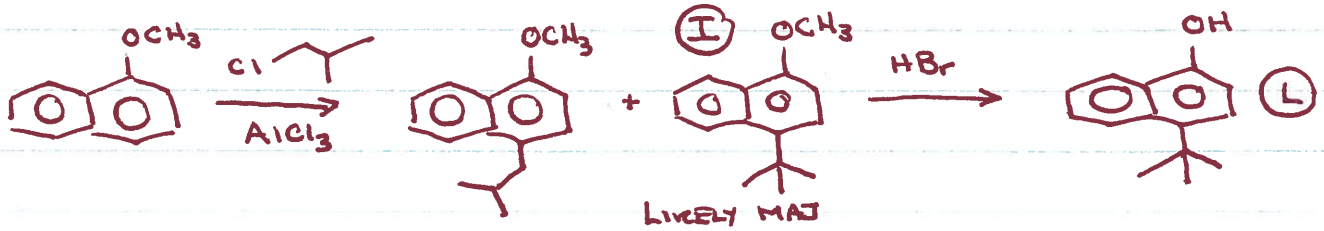
WITH OR WITHOUT THE BENZENE RING



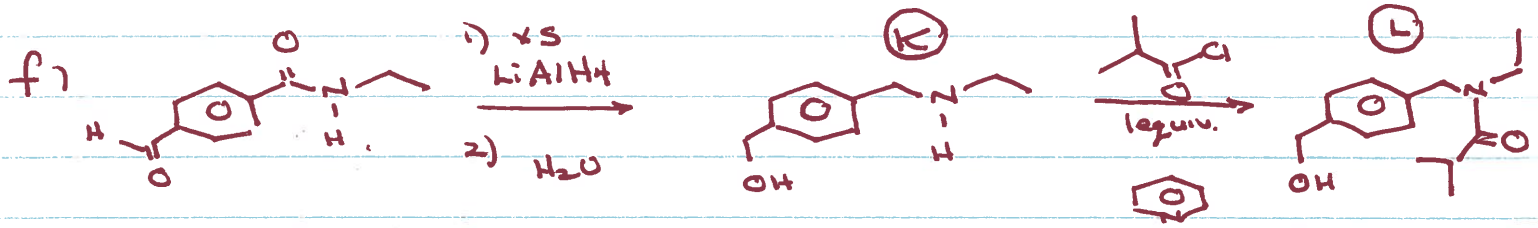
d)



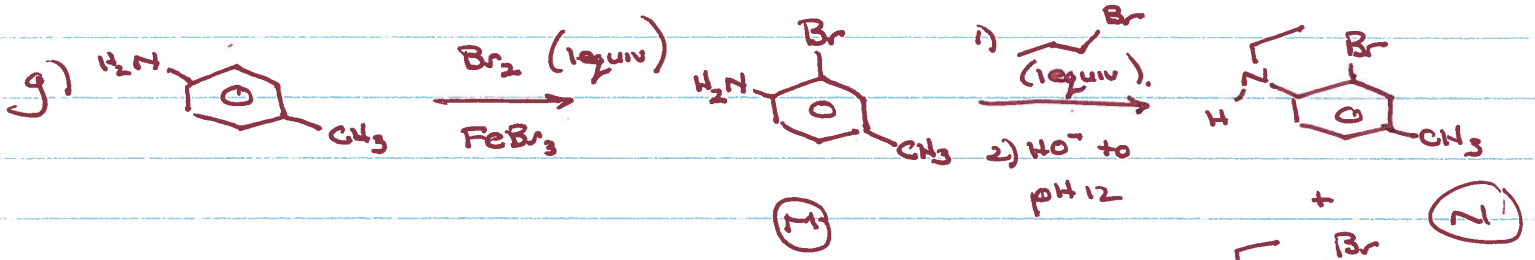
e)



f)

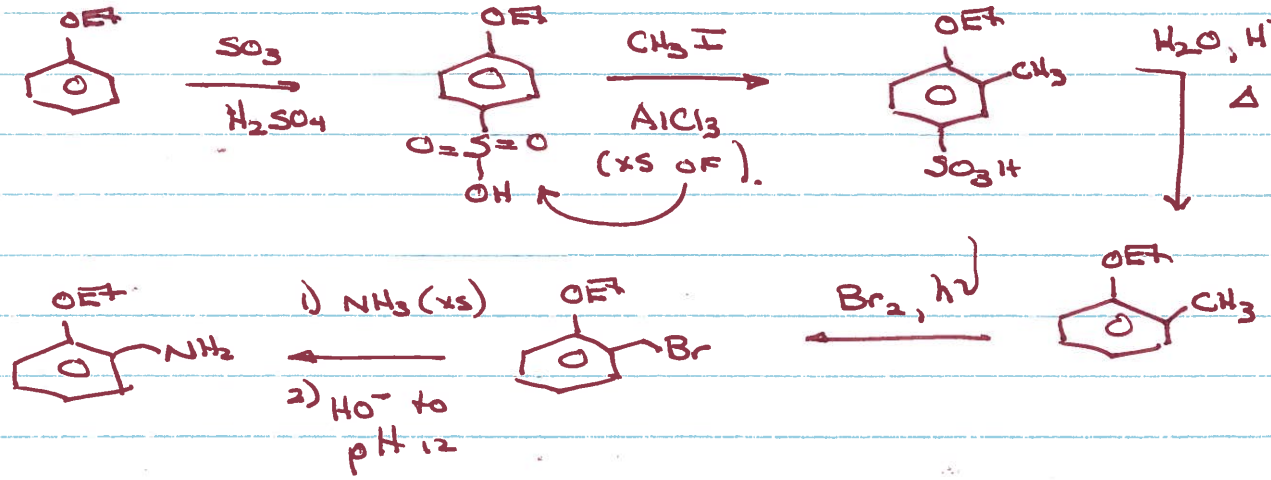


g)

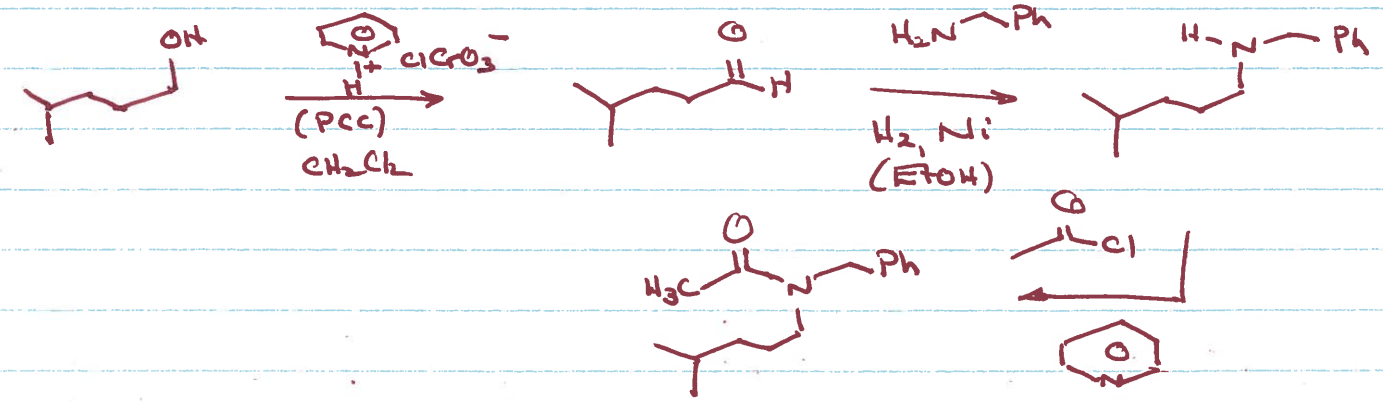


SOME SIGN OF POLYALKYLATION

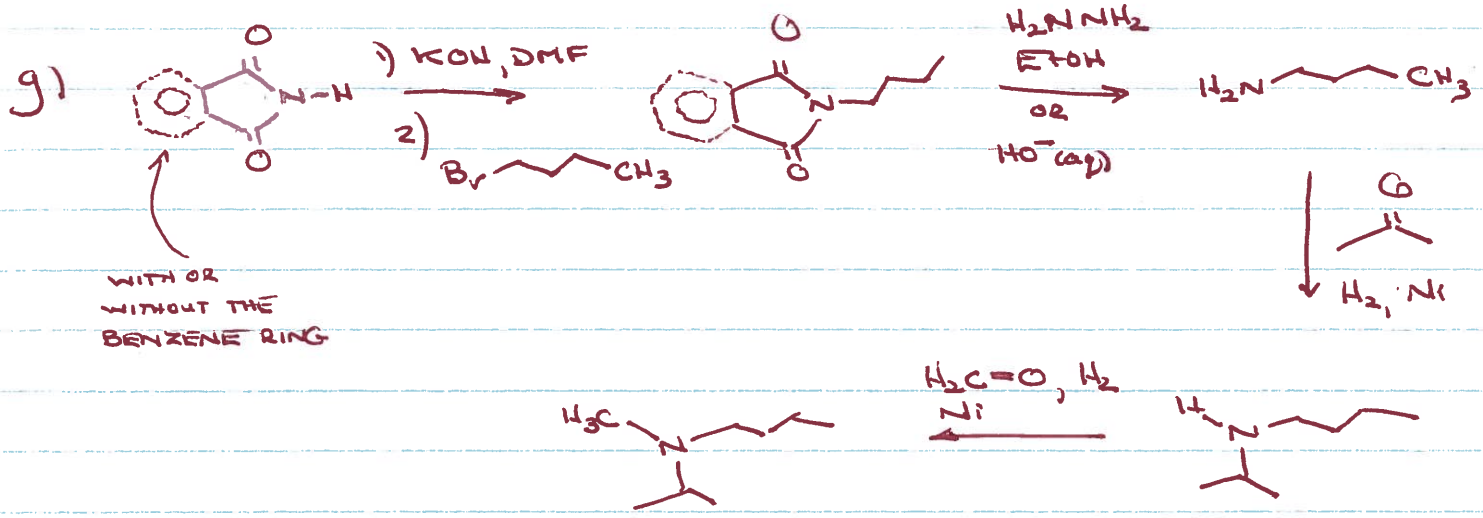
4 a)



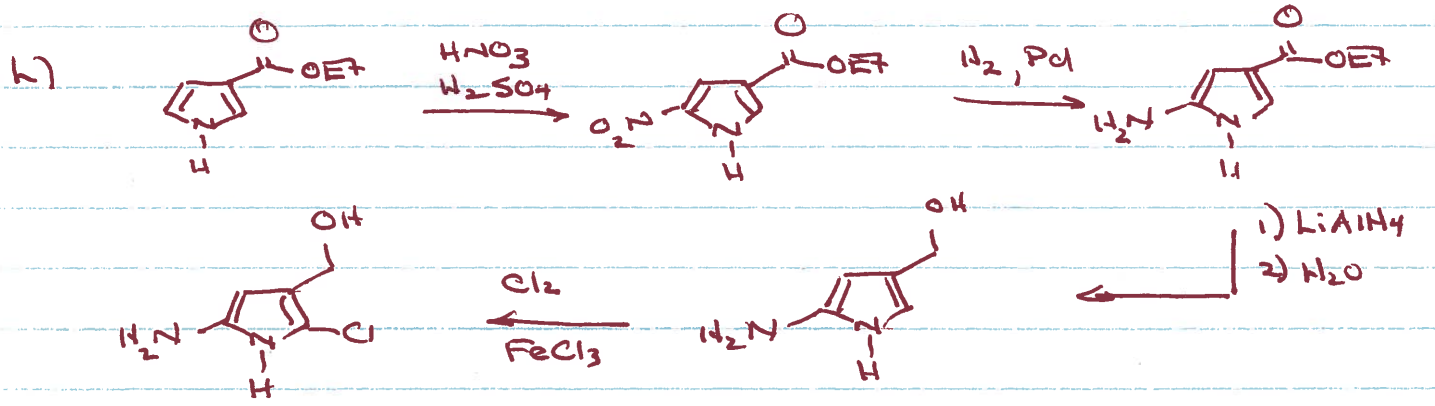
b)



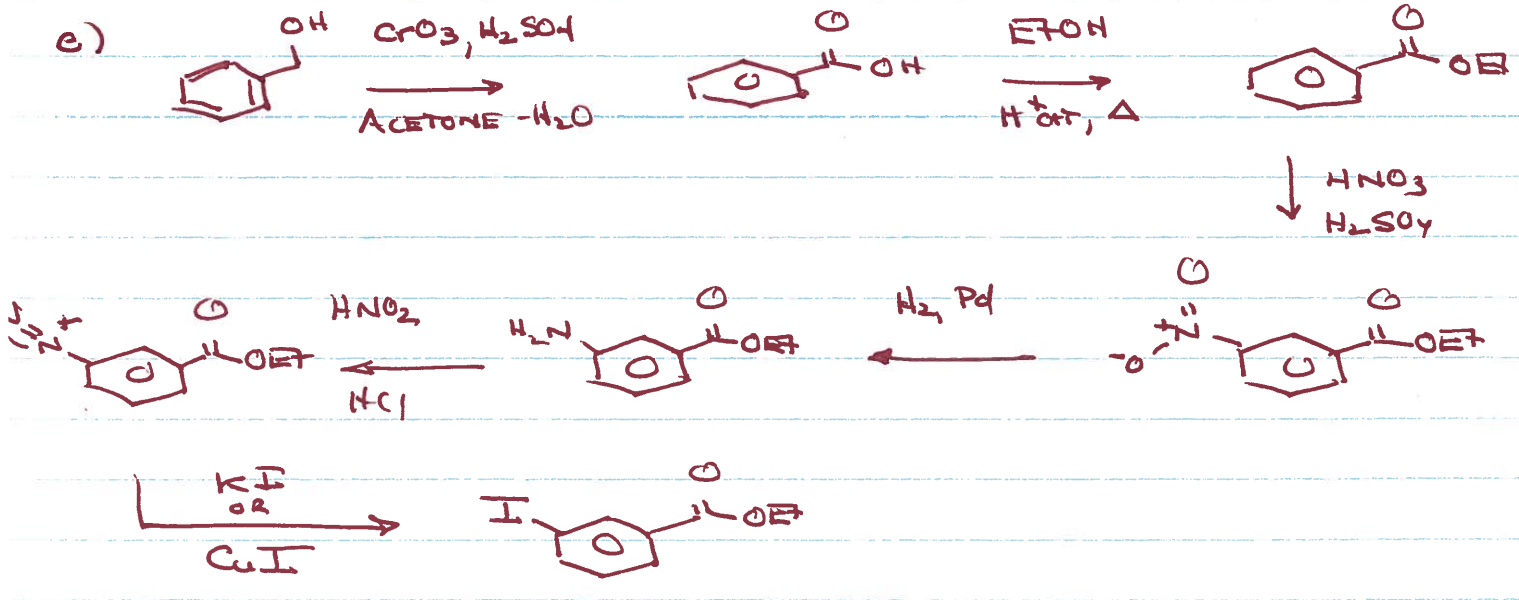
g)


1) KOH, DMF
2)
H_2NNH_2
EtOH
OR
HO^- (aq)
H_2, Ni
$H_2C=O$, H_2
Ni
WITH OR WITHOUT THE BENZENE RING

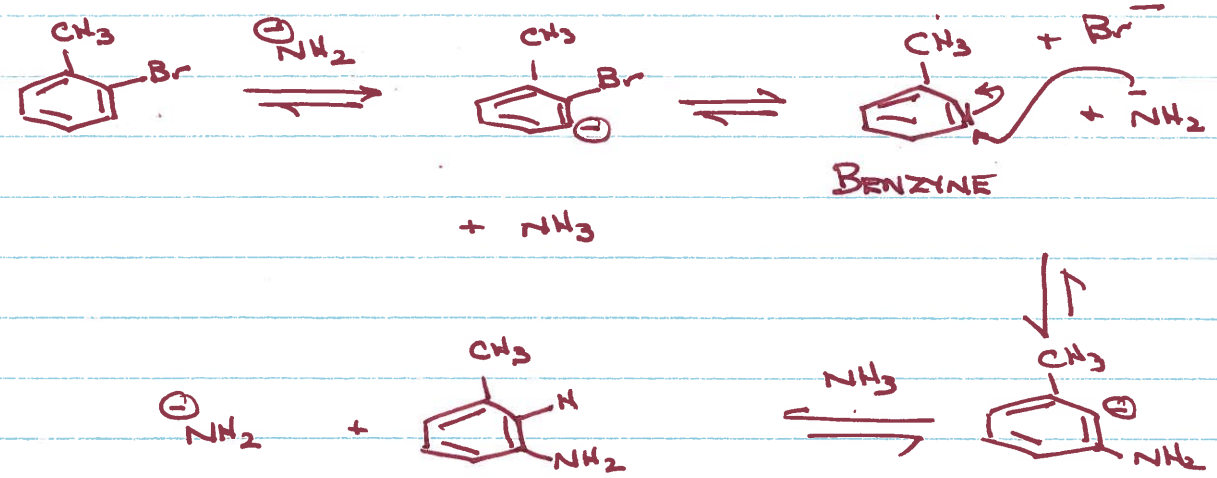
h)


HNO_3
H_2SO_4
H_2, Pd
1) $LiAlH_4$
2) H_2O
Cl_2
$FeCl_3$

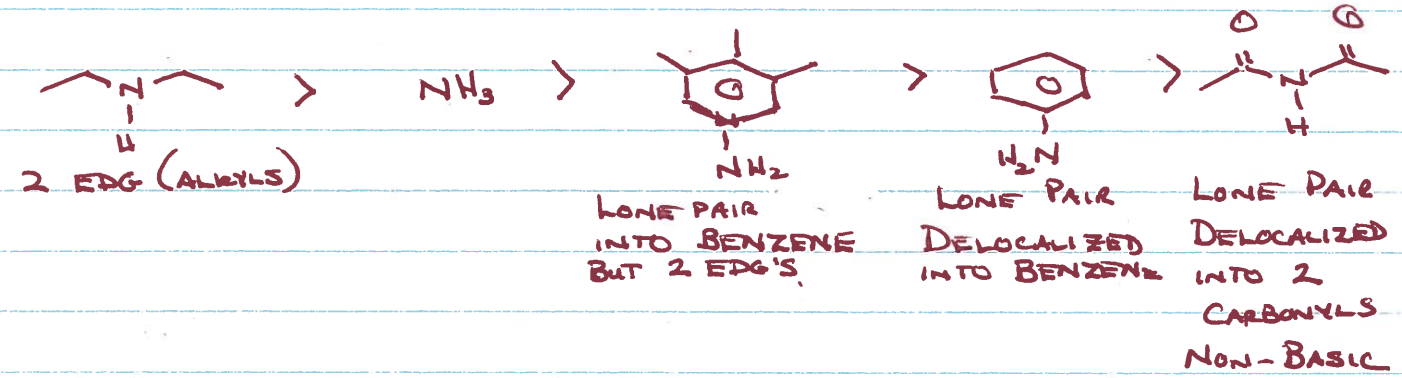
e)


CrO_3, H_2SO_4
ACETONE $-H_2O$
EtOH
H^+ cat, Δ
HNO_3
H_2SO_4
H_2, Pd
HNO_2
HCl
KI
OR
CuI

5.

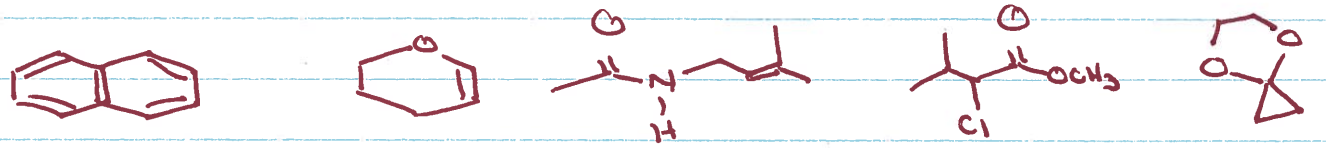


6a)



2 EDG (ALKYLS) > NH_3 > LONE PAIR INTO BENZENE BUT 2 EDG'S > LONE PAIR DELOCALIZED INTO BENZENE > LONE PAIR DELOCALIZED INTO 2 CARBONYLS NON-BASIC

b)



IHD = 7 | 2 | 2 | 1 | 2

c)

10 x e⁻ AROMATIC | 8 x e⁻ ANTIAROMATIC | 6 x e⁻ AROMATIC | 5 π e⁻ NON-AROMATIC | 4x e⁻ ANTI-AROMATIC

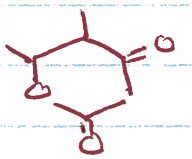
7. C, $\frac{58.32\%}{12.011}$ = $\frac{4.856}{2.081}$ = 2.33 ; H, $\frac{8.39\%}{1.008}$ = $\frac{8.32}{2.081}$ = 4 ; O, $\frac{33.29\%}{15.999}$ = $\frac{2.081}{2.081}$ = 1

RATHER OBVIOUSLY MUST MULTIPLY BY 3 TO GET WHOLE #'S

∴ $C_7H_{12}O_3$ IS EMPERICAL FORMULA

GIVES M = 144 MATCHES m/e FROM MASS SPECTRUM

MOLECULAR FORMULA IS $C_7H_{12}O_3$



FAILS $C_7H_{10}O_3$ AND IHD = 3

ALSO FAILS $C_8H_{14}O_3$

NOT NEEDED, BUT $IHD = \frac{2c+2-h-x-n}{2}$

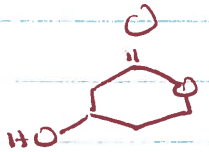
$= \frac{14+2-12}{2} = 2$

ON TO IR SPECTRUM ....

$\nu = 2960\ cm^{-1}$ C-H STRETCH, MOSTLY sp^3 C-H 's.

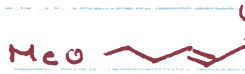
$\nu_{MAX} = 1739\ cm^{-1}$ C=O STRETCH, LIKELY ESTER

$\nu_{MAX} = 1718\ cm^{-1}$ C=O STRETCH, LIKELY KETONE OR CONJUGATED ESTER



FAILS. NO OH IN IR @ $3300\ cm^{-1}$

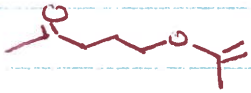
NO KETONE OR CONJUGATED ESTER



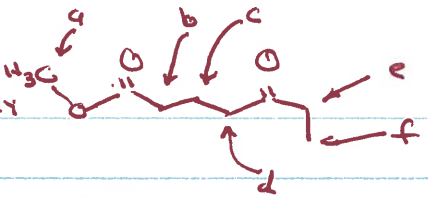
FAILS. NO REASON TO HAVE A $\nu_{MAX} = 1739\ cm^{-1}$

ONLY ESTER IS CONJUGATED.

CAN'T SEE ANY C=C STRETCH @ $1650\ cm^{-1}$ EITHER

WE ONLY HAVE  LEFT. BUT SOME MAY STILL HAVE

IF THEY ONLY DID IHD.

LET'S TRY 

a) CALC $\delta = 0.8 + (2.8) = 3.6$ ppm, A=3, S — NOTHING ON NMR SPECTRUM, ANYTHING LIKE THIS

b) CALC $\delta = 1.2 + (1.0) = 2.2$, A=2, t — MAYBE, THAT 2.4 A=2, t IS CLOSE ENOUGH

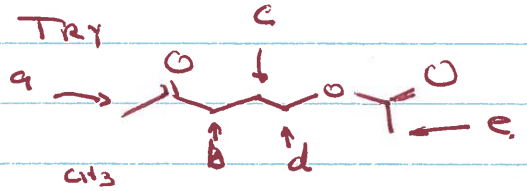
c) CALC $\delta = 1.2 + (0.4) + (0.5) = 2.1$, A=2, tt (OR m) — MAYBE... THAT m @ 1.95, A=2 IS CLOSE ENOUGH

d) CALC $\delta = 1.2 + (1.1) = 2.3$, A=2, t — NOPE, - COULD USE 2.4 RESONANCE, BUT IT'S ALREADY ASSIGNED.

e) CALC $\delta = 1.2 + (1.1) = 2.3$, A=2, q — NOPE - NO q's, A=3 AT ALL - FAIL.

f) CALC $\delta = 0.8 + (0.3) = 1.1$, A=3, t — NOPE NOTHING TO MATCH THIS

ANY TWO FAILING MATCHES, OR JUST COMPARING THE # OF RESONANCES, AREAS, AND MULTIPLICITIES RESULTS IN CALLING THIS POSSIBILITY A FAILURE.

SO LET'S TRY 

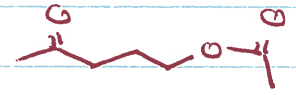
a) $\delta_{CALC} = {}^{CH_3}0.8 + (1.3) = 2.1$, A=3, S — MATCHES W/ EITHER THE $\delta = 2.1$ OR $\delta = 2.2$, A=3, S IN SPECTRUM

b) $\delta_{CALC} = {}^{CH_2}1.2 + (1.1) = 2.3$, A=2, t — MATCHES W/ $\delta = 2.4$, A=2, t PEAK IN SPECTRUM

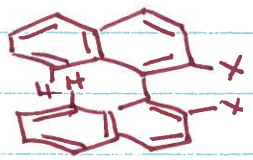
c) $\delta_{CALC} = {}^{CH_2}1.2 + (0.4) + (0.5) = 2.1$, A=2, tt — MATCHES OR W/ $\delta = 1.95$, A=2, m IN SPECTRUM

d) $\delta_{CALC} = {}^{CH_2}1.2 + (2.9) = 4.1$, A=2, t — MATCHES NICELY WITH THE $\delta = 4.15$ A=2, t IN SPECTRUM,

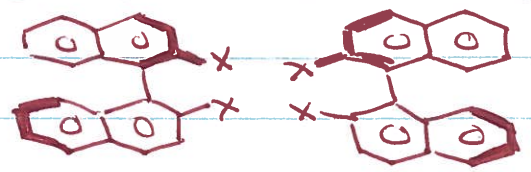
e) $\delta_{CALC} = {}^{CH_3}0.8 + (1.2) = 2.0$, A=3, S — MATCHES WITH THE δ 2.1, A=3, S IN SPECTRUM, SO WE'LL ASSIGN THE δ 2.2 TO "a"

- EVERYTHING MATCHES - STRUCTURE IS 

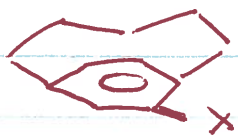
BONUS



CHIRAL BECAUSE NAPHTHALENES CAN'T ROTATE PAST EACH OTHER

S. 

ARE NON-SUPERIMPOSABLE MIRROR IMAGES - ENANTIOMERS

SO THE SAME CAN APPLY TO 

AND