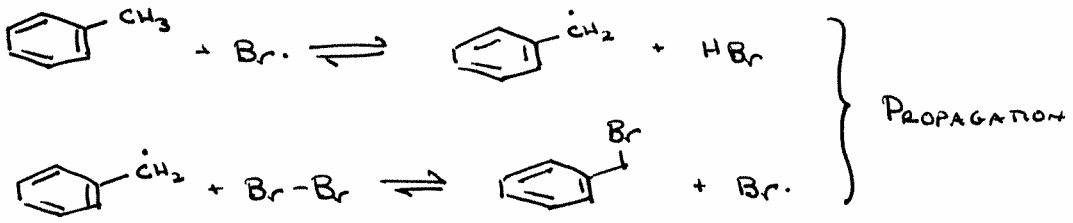
59-235
FINAL 2013
SUGGESTED SOLNS,

$Br_2 + h\nu \rightleftharpoons 2\,Br\cdot$ INITIATION

1.

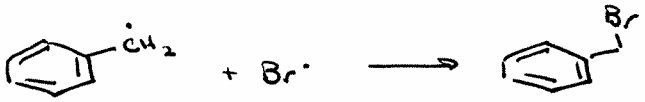


PROPAGATION

FOR EXAMPLE

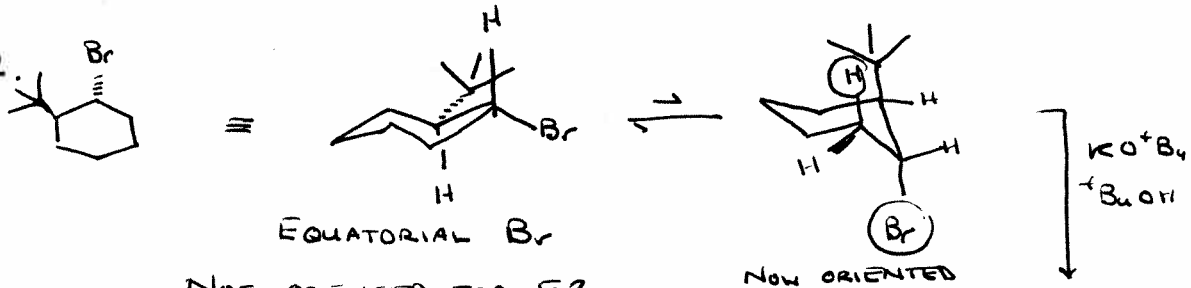
TERMINATION

OR



ANOTHER POSSIBLE TERMINATION

2.

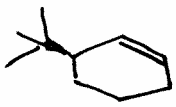


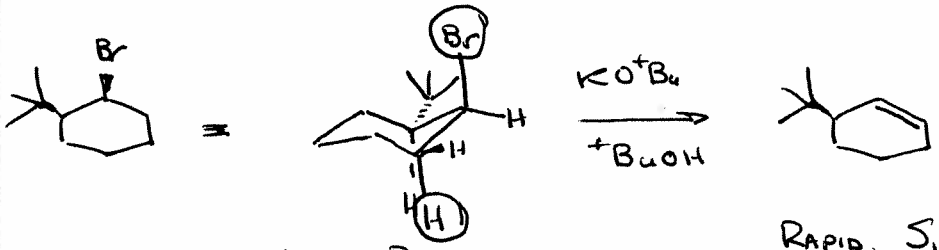
EQUATORIAL Br

NOT ORIENTED FOR E2

NOW ORIENTED PROPERLY

SLOW, BECAUSE Br WAS ORIENTED PROPERTY IN DISFAVOURED CONFORMER

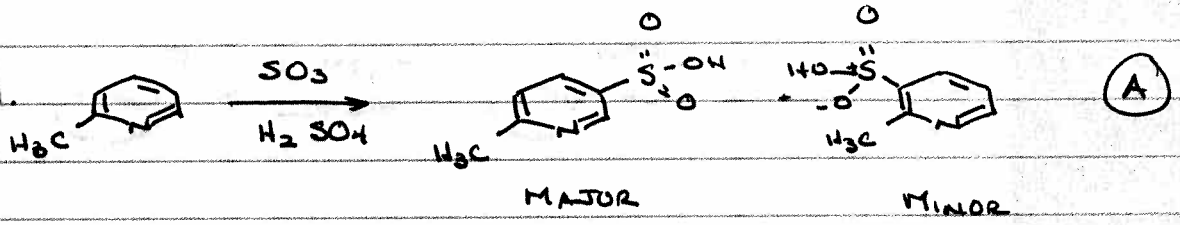




AXIAL Br ALREADY PROPERLY ORIENTED

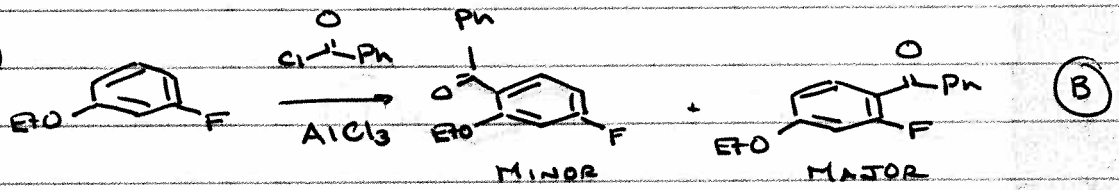
RAPID, SINCE Br IS CORRECTLY ORIENTED IN FAVOURED CONFORMER

3a.

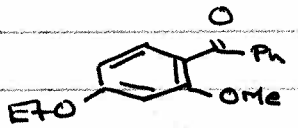


A

b)

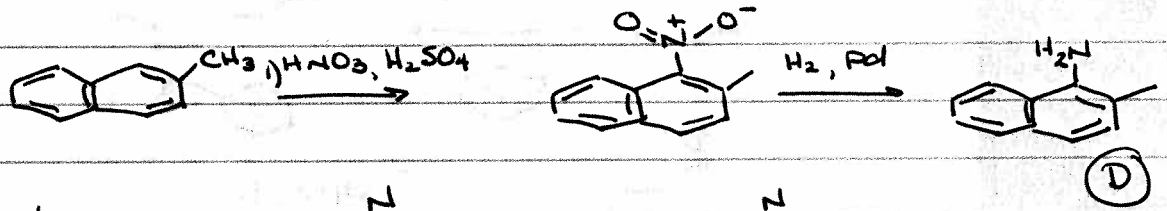


B

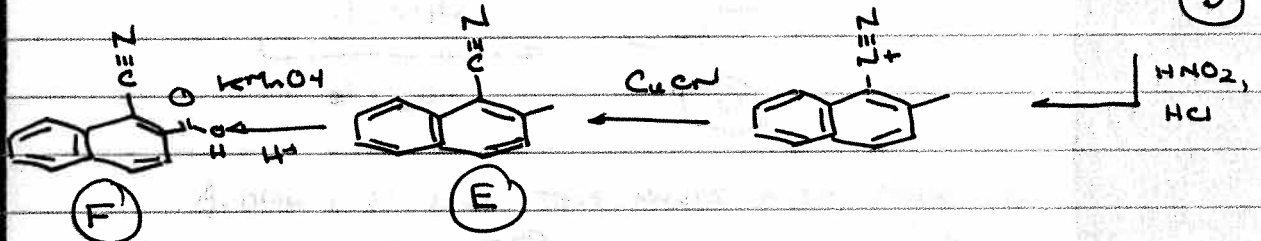


C

c).

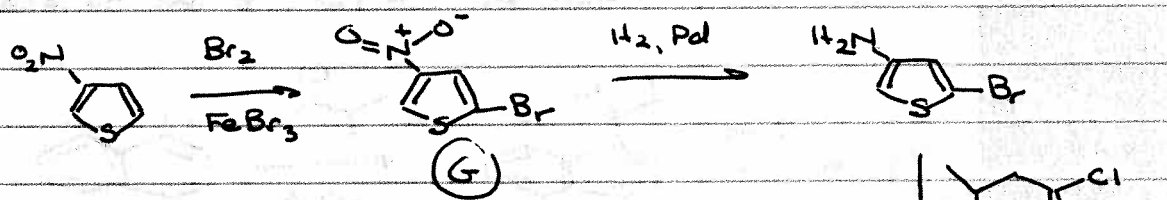


D

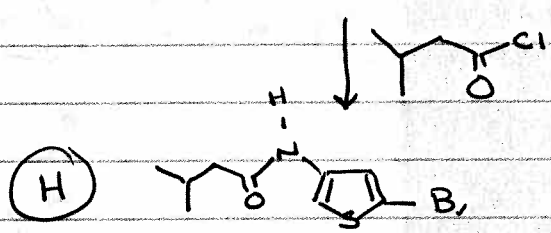


F E

d)

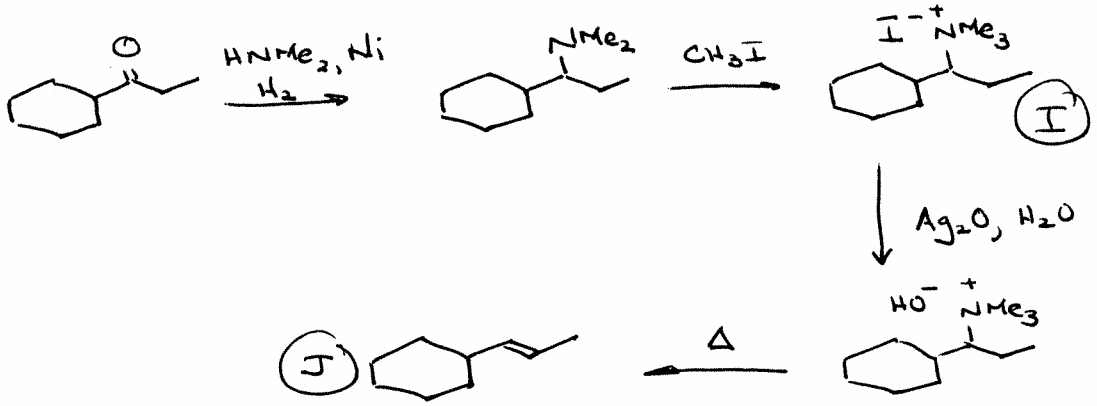


G

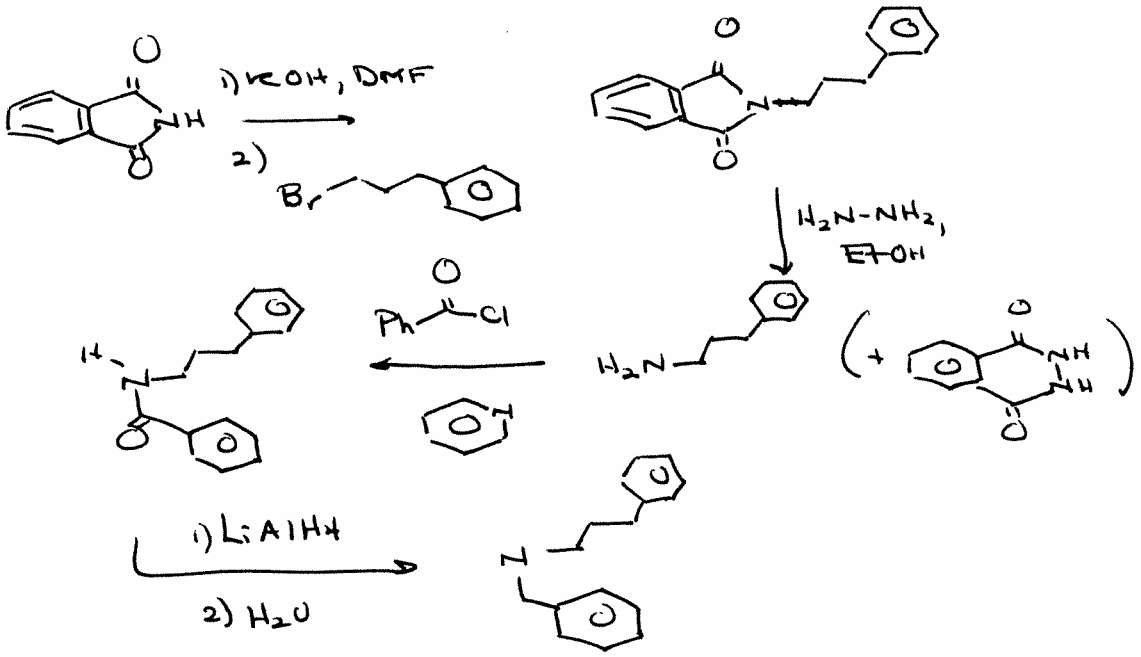


H

e)

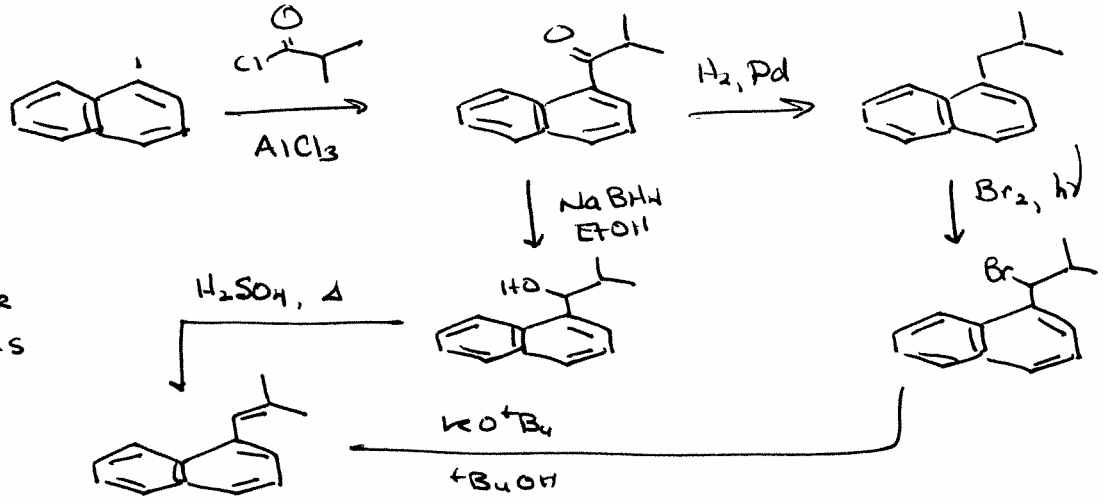


4a)



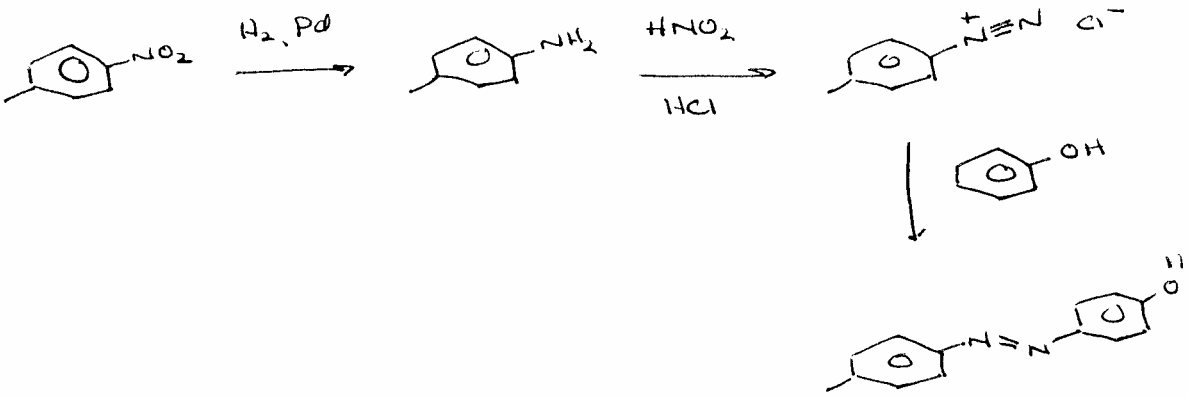
ALTHOUGH I LIKE THIS ROUTE BEST, THERE ARE OTHER WAYS OF DOING THE 2ND N ALKYLATION / BENZYLATION.

b.

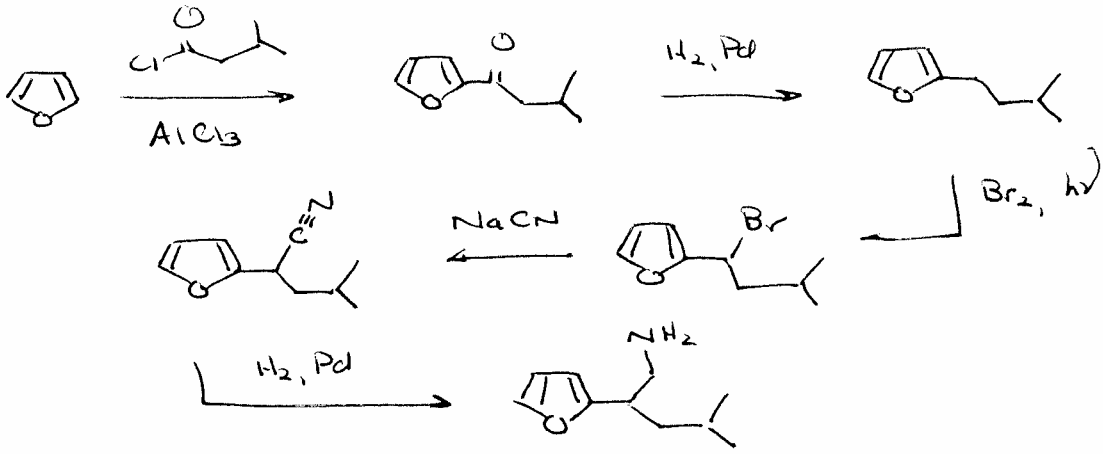


EITHER WAY IS OK.

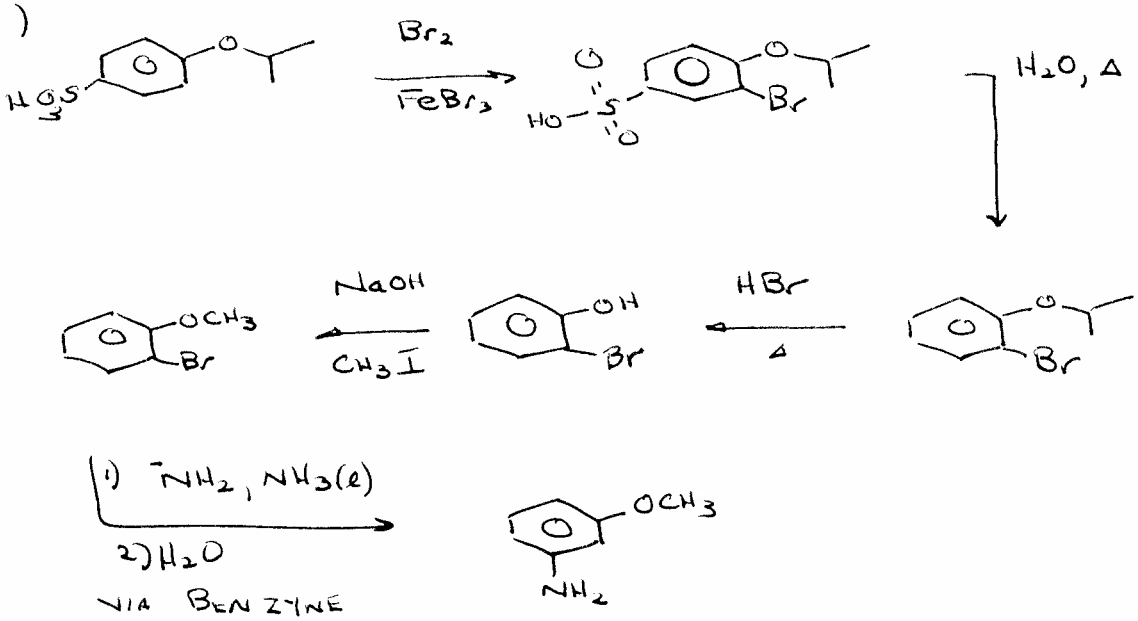
c)

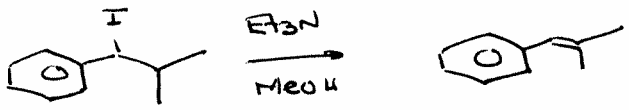

NO_2
H_2, Pd
NH_2
HNO_2
HCl
$N\equiv N^+$ Cl^-
OH
N=N
O

d)


O
Cl
$AlCl_3$
H_2, Pd
Br_2, hν
Br
NaCN
C≡N
H_2, Pd
NH_2

e)


H_3CO_2S
Br_2
$FeBr_3$
HO
O
S
Br
H_2O, Δ
OCH_3
NaOH
CH_3I
OH
HBr
Δ
1) $^-NH_2$, $NH_3(\ell)$
2) H_2O
VIA BENZYNE
NH_2

5 

I^- LEAVING GROUP - EXCELLENT - COULD BE E1 OR E2, BUT MORE E1 THAN W CORRESPONDING CHLORIDE

EXTRA β- CH_3 GROUP WILL PUSH TREND TOWARDS E1

BASE IS A REAL ONE, BUT NOT THAT STRONG - E1 OR E2

- WILL BE MOST E1 OF ALL.

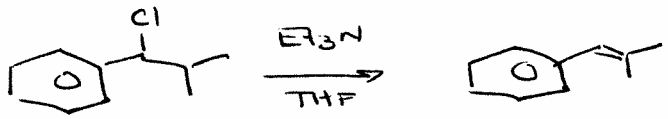
Cl^- LEAVING GROUP - GOOD - MORE TOWARDS E2 THAN ABOVE CASE

STILL β- BRANCHING ⇒ TOWARDS E1

STILL POLAR SOLVENT ⇒ TOWARDS E1

BASE STILL So-So ⇒ E1 OR E2

- 2ND MOST E1 CHARACTER



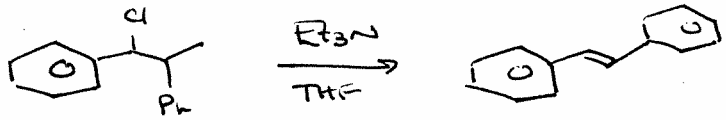
Cl^- LEAVING GROUP - GOOD - SAME AS CASE #2 : MORE E2 THAN CASE #1

STILL β- ALKYL BRANCHING ⇒ TOWARDS E1

BASE STILL So-So ⇒ E1 OR E2

NOW A NON-POLAR SOLVENT ⇒ DISFAVOURS CARBOCATION, SO PUSHES THIS CASE TOWARDS E2

- 2ND MOST E2 CHARACTER (2ND LEAST E1)



Cl^- LEAVING GROUP - GOOD. SAME AS #2 & #3 ; LESS E1 THAN #1

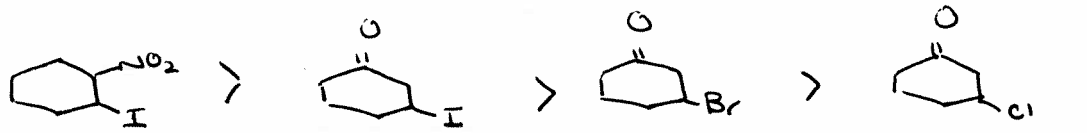
BASE STILL So-So ⇒ E1 OR E2

NON-POLAR SOLVENT ⇒ FAVOURS E2

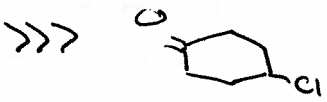
NOW ONLY β- ARYL GROUP ⇒ FAVOURS E2

∴ MOST E2 CHARACTER OF ALL

6a)

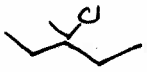


FASTEST E1cb 2ND FASTEST E1cb 3RD FASTEST E1cb 4TH FASTEST E1cb

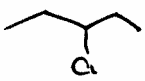


WON'T DO E1cb AT ALL

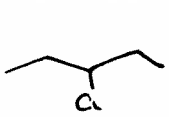
b)



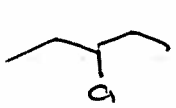
MOST ELIMINATION



2ND MOST ELIMINATION



3RD MOST ELIMINATION



MOST SUBSTITUTION

c AT END OF 7

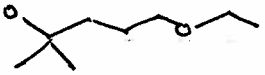
7. C 66.63% / 12.011 = 5.55 ÷ 1.39 = 4

H 11.18% / 1.008 = 11.09 ÷ 1.39 = 8

O 22.19% / 15.999 = 1.39 ÷ 1.39 = 1

EMPERICAL FORMULA IS C_4H_8O GIVES M = 72

m/e IS 144 ∴ MOLECULAR FORMULA IS $C_8H_{16}O_2$

THIS ELIMINATES  SINCE IT IS $C_8H_{18}O_2$

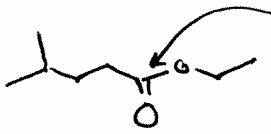
IR SPECTRUM

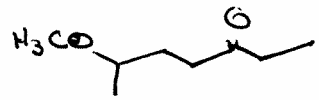
3415 cm^{-1} ν_{O-H} STRETCH, ALCOHOL

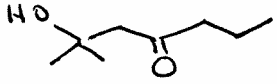
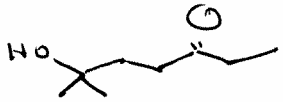
2902 cm^{-1} ν_{C-H} STRETCH, C-H (sp^3)

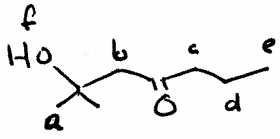
1715 cm^{-1} $\nu_{C=O}$ OF KETONE, ALDEHYDE, CONJUGATED ESTER OR MAYBE ACID

CHOICES AVAILABLE SUGGEST IT'S A KETONE

THIS ELIMINATES  $\nu_{C=O}$ SHOULD BE 1735-1740 cm^{-1} (NOT CONJUGATED) also, no O-H

ELIMINATES  WOULD HAVE NO ν_{O-H}

LEAVES  AND 

LET'S TRY 

a, predict A=6, s, δ= 1.2

GOOD MATCH @ δ=1.2, A=6, s

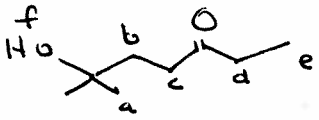
b, PREDICT A=2, s, δ= 2.3 + (0.3) = 2.6 NO MATCH AT ALL.

c, PREDICT A=2, t, δ= 2.3 GOOD MATCH @ δ= 2.4, t, A=2

d, PREDICT A=2, t of q, δ= 1.6 NOPE, A=2 @ 1.65 IS A t,

NOTHING ~~ELSE~~ ELSE WORKS

THIS FAILS.

HOW ABOUT 

a, predict A=6, s, δ= 1.2 GOOD MATCH @ δ=1.2, A=6, s.

b, predict A=2, ~~s~~, δ= 1.6 + (0.3) = 1.9 GOOD MATCH @ δ= 1.7, A=2, t

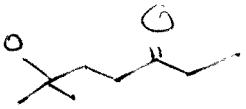
c, predict A=2, t, δ= 2.3 GOOD MATCH @ δ= 2.4, A=2, t

d, predict A=2, q, δ= 2.3 GOOD MATCH @ δ= 2.45, A=2, q

e, predict A=3, t, δ= 1.1 GOOD MATCH @ δ= 1.1, A=3, t

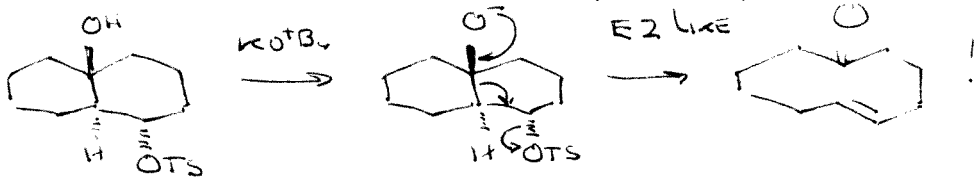
f, predict A=1, s, δ=0.5-5.5 OR @ δ= 4.6, A=1, s (br) ↓

THIS FITS EVERYTHING REASONABLY

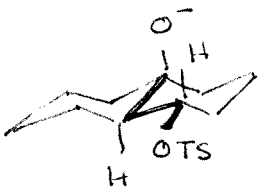
∴  IS IT

AND.....

6c. IHD OF COMPOUND IN 7 = 1

BONUS: 

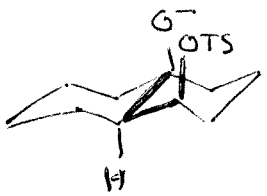
AND



NOTICE: BREAKING C-C BOND IS ANTI PERIPLANAR TO C-OTS BOND.

* AS IS NEEDED IN E2'S

OTHER DIASTEREOMER



NOT ANTI PERIPLANAR

∴ GIVES MANY PRODUCTS.