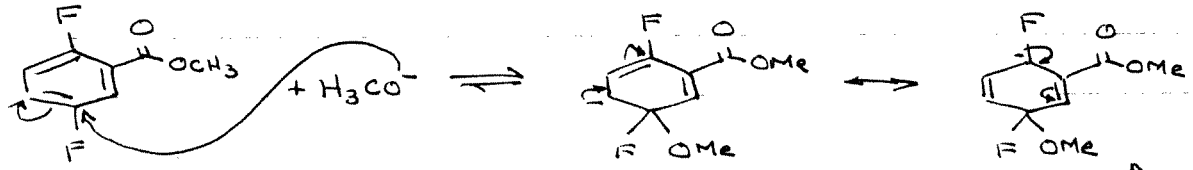
Suggested Solns
59-235
Final

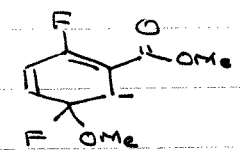
W' 2012

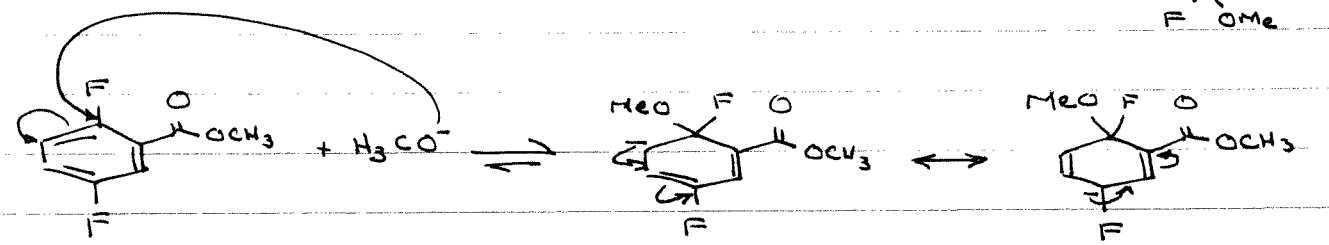
1a)



"−" charge never on C atom with EWG.

∴ Not favoured.

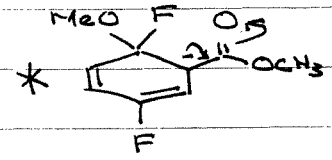




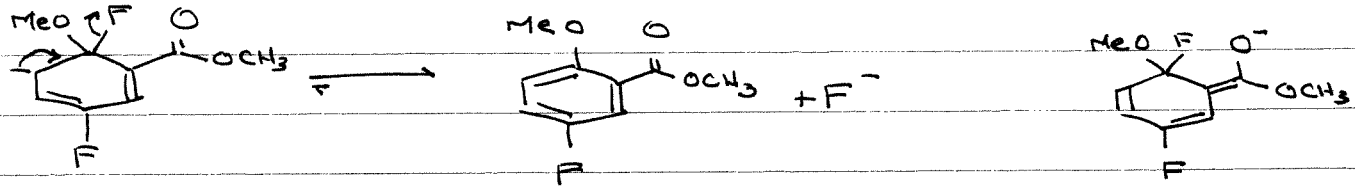
"−" charge is on C atom EWG; in fact 4th.

Resonance form is especially favoured

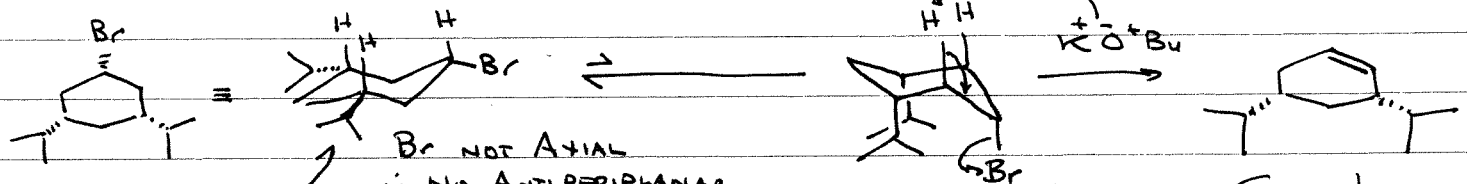
∴ This is a productive pathway; reaction finishes by way of



and.



2. Left Compound



Br not axial

∴ no antiperiplanar H available

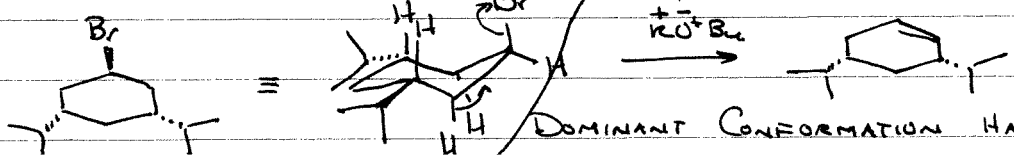
Isopropyls equatorial ∴ favoured

Now anti H's available

Slow!

Slow because molecule spends v. little time in reactive conformation (isopropyls are forced axial)

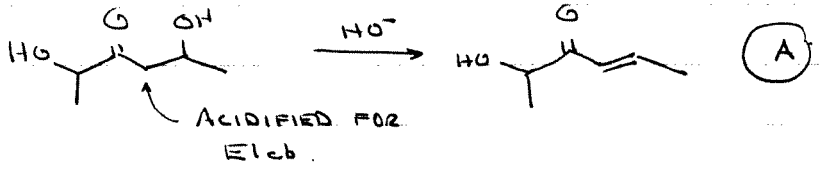
Right Compound



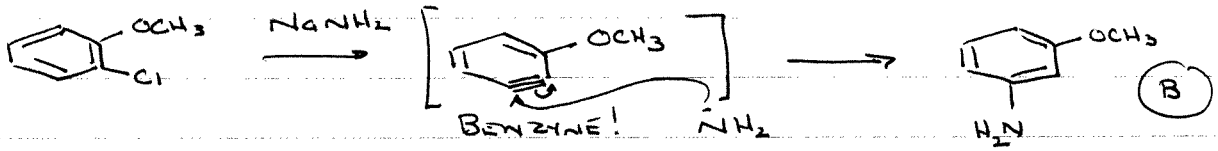
Fast!

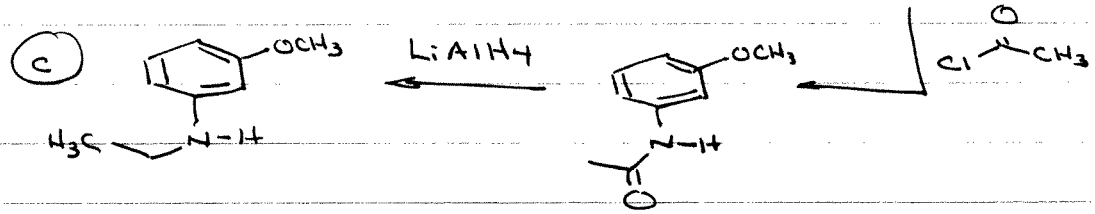
Dominant conformation has H & Br antiperiplanar

3a)

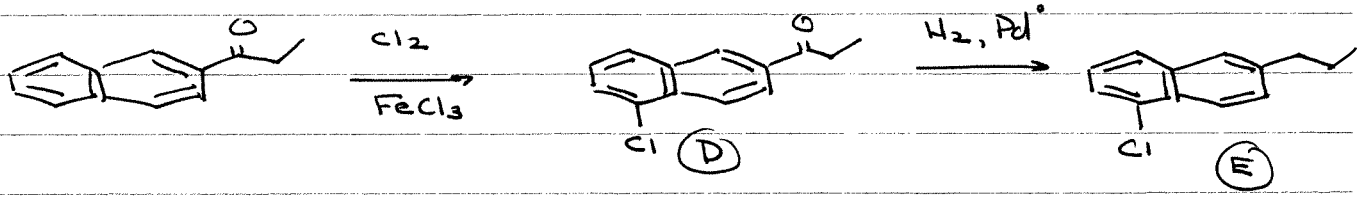


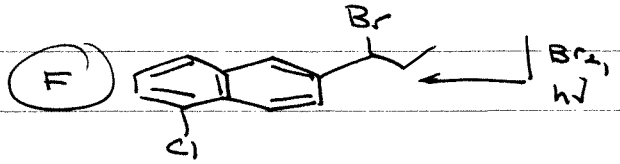
b)



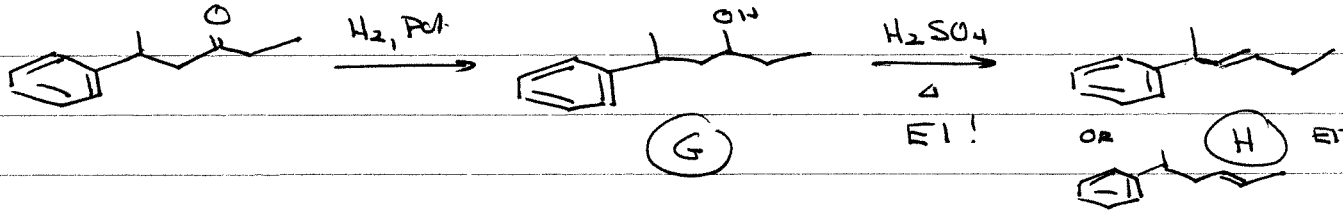


c)

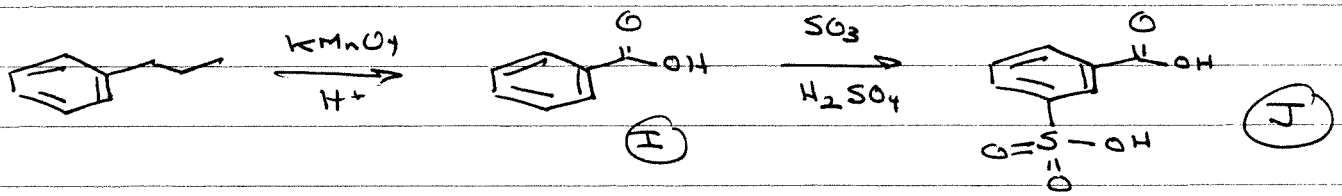




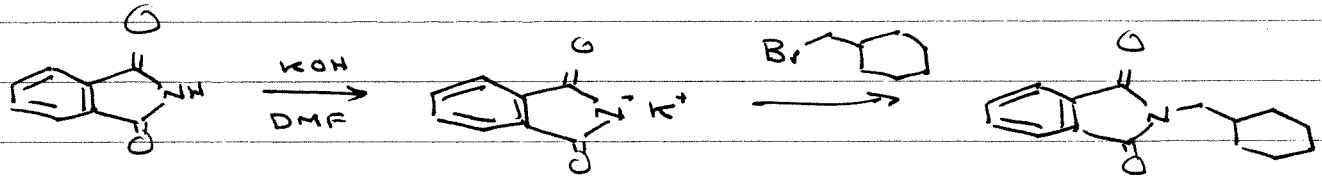
d)



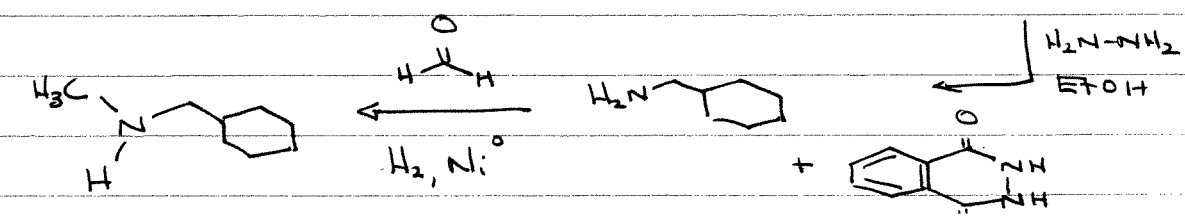
e)

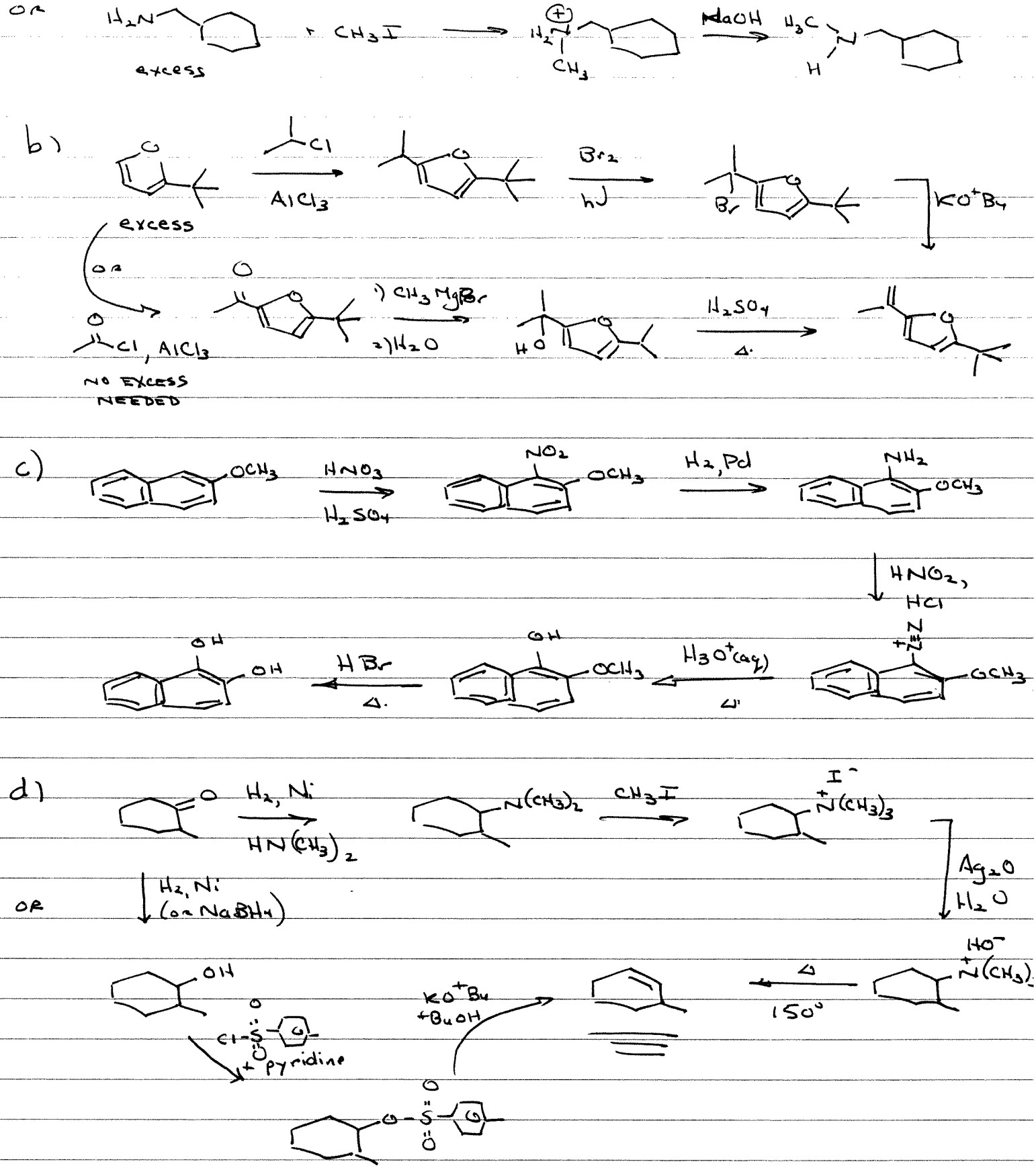


4a)

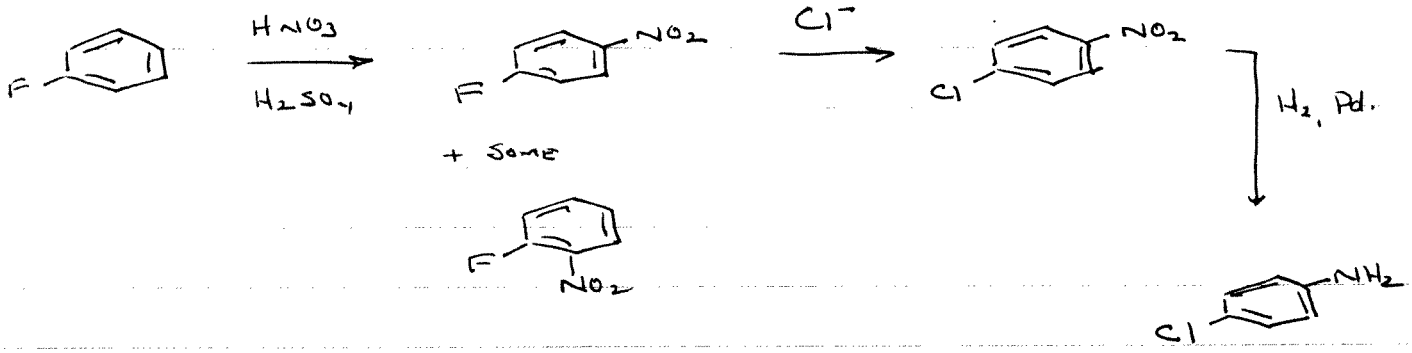


OTHER METHODS FOR THIS LAST STEP




or
excess
+ CH3I
NaOH
b)
excess
or
AlCl3
Br2
hν
KO+Bu
1) CH3MgBr
2) H2O
H2SO4
Δ
NO MORE EXCESS NEEDED
c)
HNO3
H2SO4
H2, Pd
HNO2,
HCl
HBr
Δ
H3O+(aq)
Δ
d)
H2, Ni
HN(CH3)2
CH3I
Ag2O
H2O
or
H2, Ni
(or NaBH4)
pyridine
KO+Bu
+BuOH
Δ
150°

e)



5.

E2 PROD. + E1 PROD.

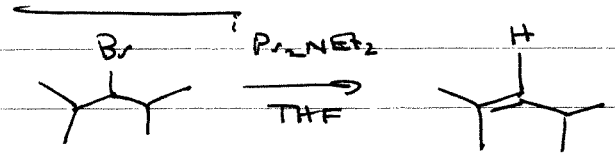
LEAVING GROUP EXCELLENT - E1 OR E2

BASE MEDIOCRE - COULD BE E1 OR E2.

SUBSTRATE 2° - COULD DO E1 OR E2

SOLVENT - NOT V. POLAR - PROBABLY PUSHES IT TOWARDS E2.

∴ CLEARLY IN THE MIDDLE SOMEWHERE



LEAVING GROUP - SAME EXCELLENT ONE AS BEFORE ∴ E1 OR E2

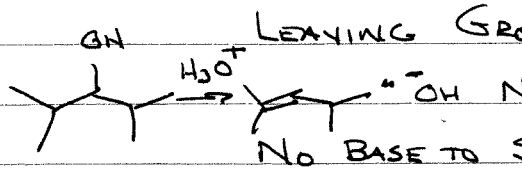
BASE - MEDIOCRE AS BEFORE - E1 OR E2.

SUBSTRATE 2°, BUT HAS ADDITIONAL β-ALKYL SUBSTITUENTS

∴ SLOWS E2 AND FAVOURS E1 MORE BY DEFAULT

SOLVENT - NOT V. POLAR - PUSHES SLIGHTLY TOWARDS E2

∴ ROUGHLY STILL A MIDDLE CASE, BUT MORE E1 CHARACTER THAN ABOVE



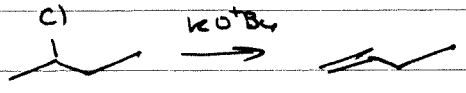
LEAVING GROUP - EXCELLENT FOR E1 ONCE IT BECOMES $^{+}OH_2$

NO BASE TO SPEAK OF (H_2O ACTUALLY) ∴ E1 FAVOURED.

SOLVENT H_2O IS POLAR ∴ E1 FAVOURED.

SUBSTRATE 2° W β-ALKYLS FAVOURS E1 A BIT, BUT COULD DO E2

∴ CLEARLY WAY OVER IN THE E1 REALM



LEAVING GROUP IS GOOD.

- COULD BE EITHER, BUT A BIT MORE E2 CHARACTER THAN OTHER CASES

BASE IS GREAT - THIS PUSHES IT WELL OVER TOWARDS E2

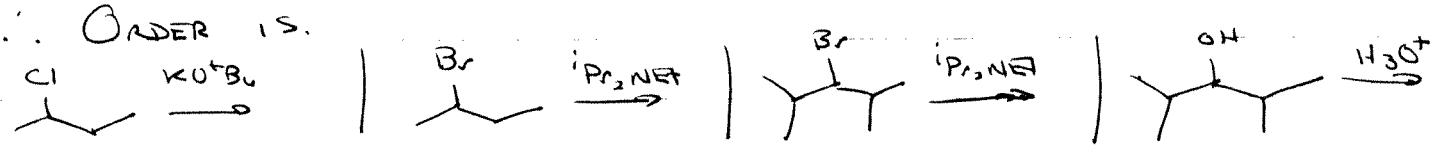
SUBSTRATE - 2° - COULD DO E1 OR E2

- PROBABLY PUSHES IT TOWARDS E2

CONT'D

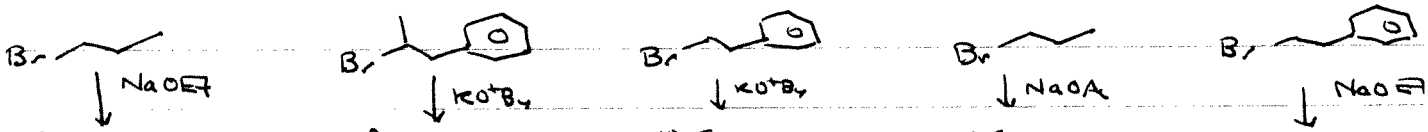
- SO THIS LAST CASE IS WAY TOWARDS E2.

∴ ORDER IS.



E2 MOST | E2 2ND MOST | E2 3RD MOST | E1 MOST

6.



1° SUBSTRATE
GOOD BASE
GOOD NUCLEOPHILE
2ND MOST S_N2

2° SUBSTRATE ⇒ E2
EXTRA β-ARYL ⇒ E2
GOOD BASE
POOR NUCLEOPHILE ⇒ E2
MOST E2

1° SUBSTRATE
EXTRA β-ARYL
GOOD BASE
POOR NUCLEOPHILE
2ND MOST E2

1° SUBSTRATE
LOUSY BASE
DECENT NUCLEOPHILE
MOST 1 S_N2

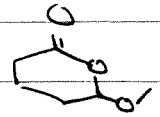
1° SUBSTRATE
GOOD BASE
GOOD NUCLEOPHILE
EXTRA β-ARYL
∴ 3RD MOST E2
(MIDDLE CASE)

7.

	C	H	O
	54.53	9.15	36.32
÷	12.011	1.008	15.999
=	4.54	9.08	2.27
÷	2.27	2.27	2.27
=	2	4	1

BUT $C_2H_4O_1$ = 44 AND m/e IS 3× THIS (132)

∴ MOLECULAR FORMULA IS $C_6H_{12}O_3$!

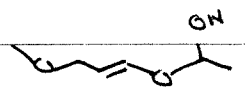
FROM CHOICES, ALL ARE OK EXCEPT  THIS IS $C_6H_{10}O_3$

∴ ELIMINATE!

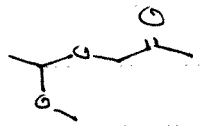
TO IR.

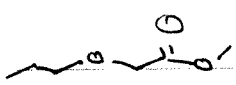
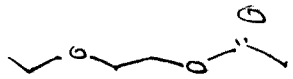
MAIN BANDS 2978 cm^{-1} C-H STRETCH OF sp^3 C-H'S.

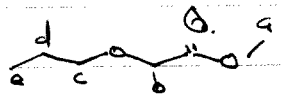
1742 cm^{-1} C=O STRETCH OF ESTER!

THIS ELIMINATES  SINCE WE EXPECT O-H STRETCH AT 3300 cm^{-1}, AND C=C STRETCH AT 1600-1650 cm^{-1} - MISSING

ALSO, NO ESTER.

ALSO ELIMINATES  , SINCE THIS IS A KETONE, SO WE'D EXPECT $\nu_{MAX} = 1710\ cm^{-1}$ FOR THIS C=O

∴ LEAVES US WITH  AND 

LET'S PREDICT FOR 

FOR a) A=3, S, δ = 3.6 ppm NOTHING CLOSE TO IT
ONLY AREA = 3, S AT δ = 2.3 ppm

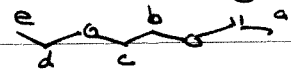
FOR b) A=2, S, δ = 2.2 + 2.2 = 4.4 ppm
NO WAY ... THERE IS NO A=2 SINGLET ANYWHERE

FOR c) A=2, t, δ = 3.4 ppm. ~~STILL NOT GOOD~~ MAYBE
NEAREST A=2, t IS δ = 3.7 ppm. (M-C-OR)

FOR d) A=2, t of q (or m), δ_{CALC} = 1.5 ppm NOPE
NOTHING TO MATCH THAT - I THINK WE CAN GIVE UP ON THIS ONE

FOR THE RECORD e) A=3, t, δ_{CALC} = 0.8 ppm COULD BE MATCHED WITH δ 1.15 ppm A=3, t

BUT IT'S NOT THIS CPD.

MUST BE  , SO LET'S SEE

FOR a) A=3, S, δ_{CALC} = 2.0 ppm
DECENT MATCH W A=3, S, AT δ 2.3 ppm.

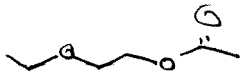
b) A=2, t, δ_{CALC} = 4.1 (M-OCR) + 0.3 (M-C-OR) = 4.4 ppm.
DECENT MATCH W A=2, t AT δ 4.2 ppm.

c) A=2, t, δ_{CAL} = 3.4 (M-OR) + 0.4 (M-C-O-C) = 3.8 ppm
DECENT MATCH W A=2, t AT δ 3.65 ppm

d) A=2, q, δ_{CALC} = 3.4 ppm ; DECENT MATCH W A=2, q, AT δ 3.5 ppm

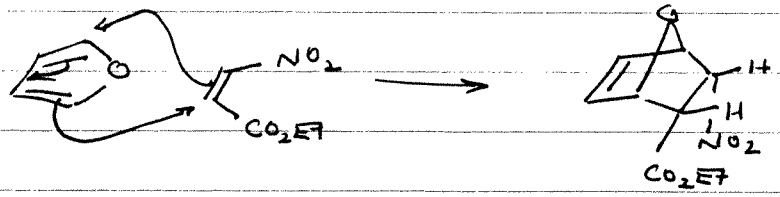
e) A = 3, t, δ_{CALC} = 1.2 ppm

GOOD MATCH IS A = 3, t, δ 1.15 ppm.

THIS WORKS FOR ALL DATA; THE CPD IS  !

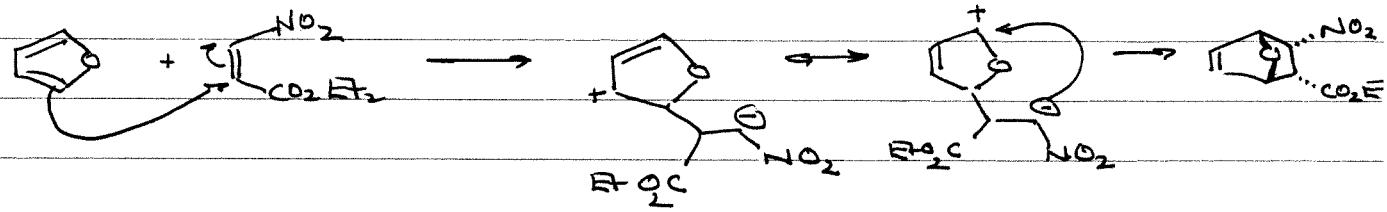
BONUS:

THIS IS A DIELS-ALDER RXN., WHICH IS CONCERTED



ELECTRON WITHDRAWING GROUPS B PREFER TO BE UNDERNEATH FURAN π-SYSTEM, OR ENDO!

IT IS <u>NOT</u> STEPWISE, BUT A STEPWISE RATIONALE CAN HELP



RXN GOES WITH FURAN AND NOT BENZENE BECAUSE FURAN DOES NOT HAVE <u>AS MUCH</u> AROMATIC STABILIZATION.