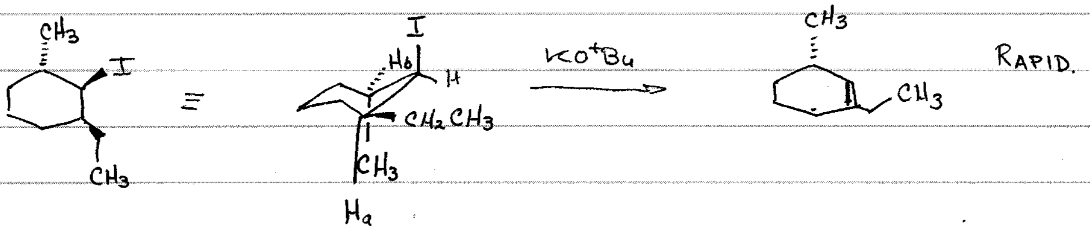
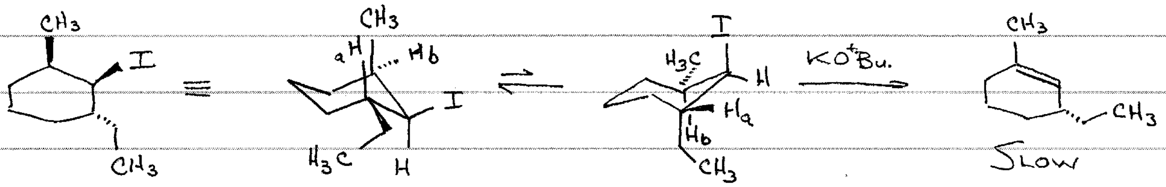
UNIVERSITY OF WINDSOR

NAME OF STUDENT: FINAL '96
Student I.D. Number: 59-235
Date of Test:
Book No.:
Total No. of Books:
Course Name & Number:
Course Section:
NAME OF INSTRUCTOR:

1.

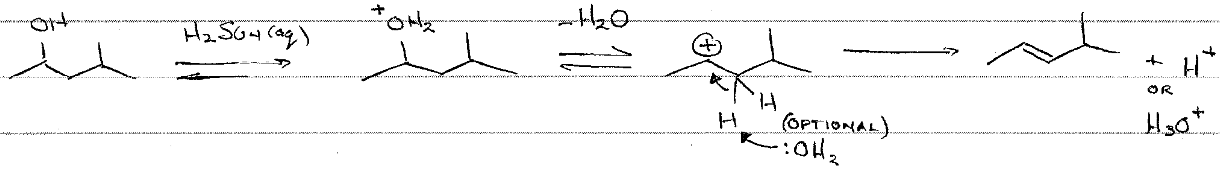


IN PREFERRED CONFORMATION, THE ETHYL IS EQUATORIAL. THERE, THE I AND Ha ARE TRANS DIAXIAL (ANTIPERIPLANAR), AND THEREFORE APPROPRIATE FOR ELIMINATION. THIS IS ALSO, THEREFORE, THE FASTER REACTION

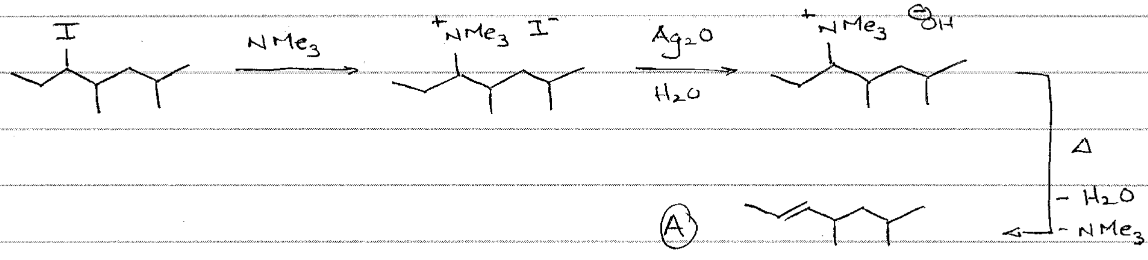


IN PREFERRED CONFORMATION, THE EQUATORIAL METHYL RESULTS IN AN EQUATORIAL IODINE, WHICH IS NOT SUITABLE FOR ELIMINATION. A CHAIR/CHAIR INTERCONVERSION TO THE MORE MINOR CONFORMATION WITH AN AXIAL ETHYL GROUP GIVES A SITUATION WHERE THE I AND Hb ARE TRANS DIAXIAL (ANTIPERIPLANAR). ELIMINATION THEREFORE GOES IN THE OTHER 'DIRECTION', AND IS NOTICEABLY SLOWER.

2. E1 MECHANISM. ZAITSEV PRODUCT.

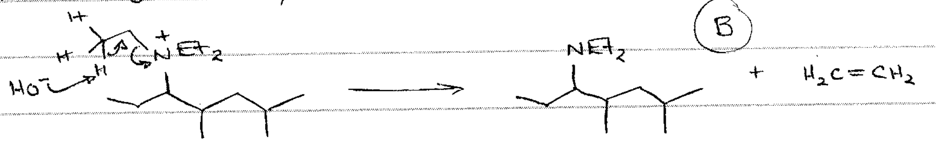


3a)

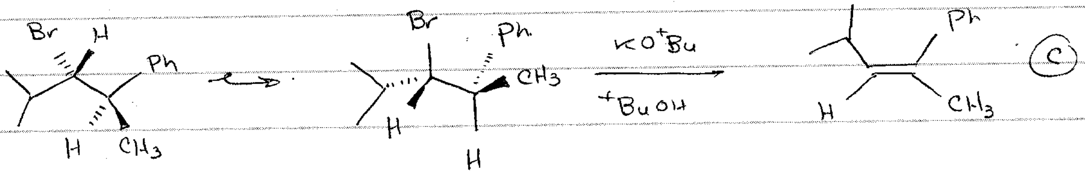


3a, CONT'D.

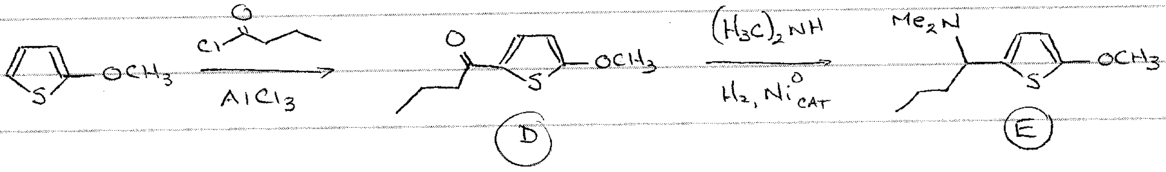
IF NEt3 INSTEAD, WOULD GET COMPETITIVE ELIMINATION OF ETHYL GROUP.



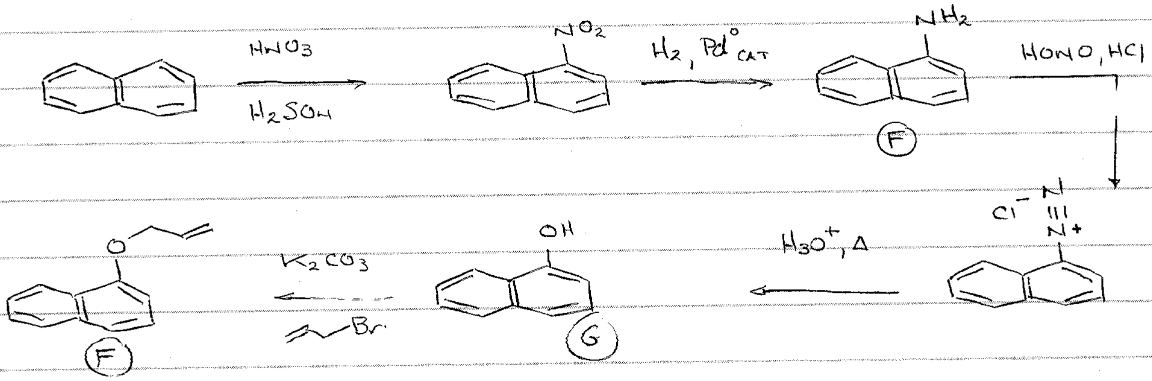
b)



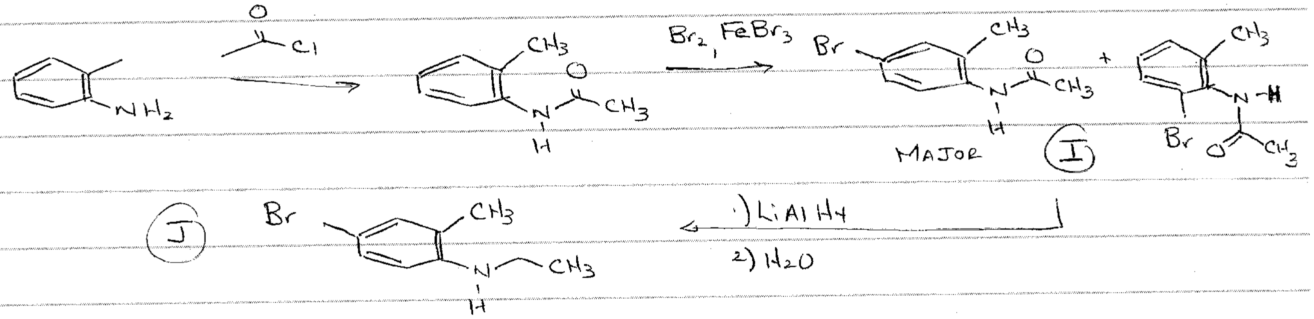
c)



d)

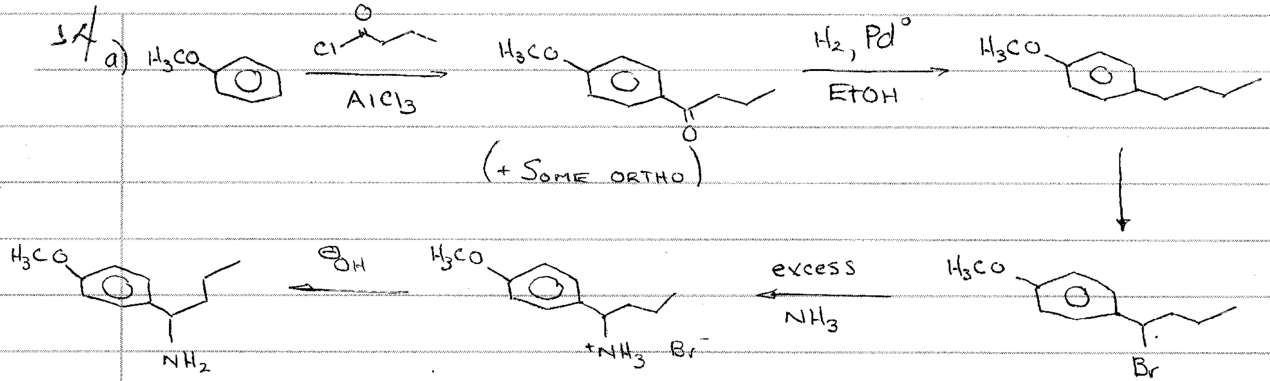


e)

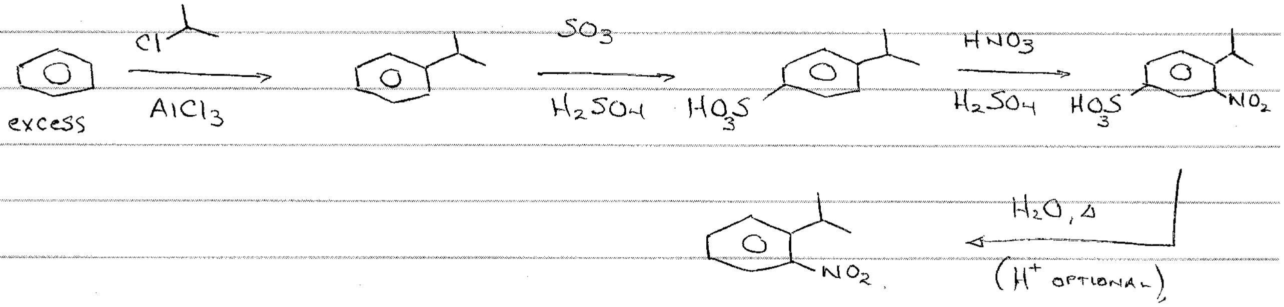


14

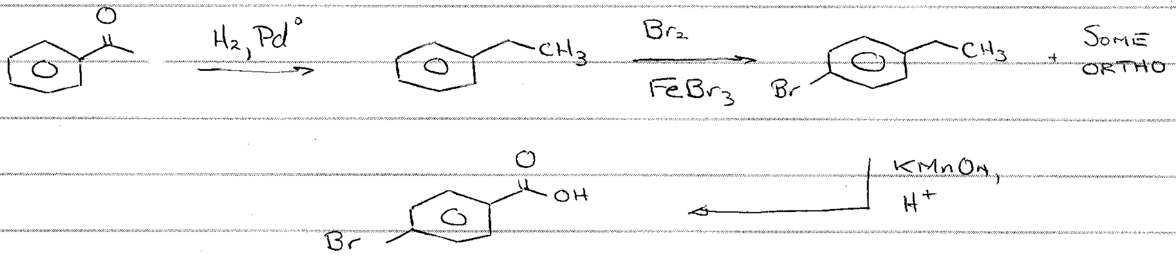
a)


H3CO
Cl
AlCl3
H3CO
(+ Some ortho)
H2, Pd°
EtOH
H3CO
H3CO
Br
excess
NH3
H3CO
+NH3 Br−
⊖OH
H3CO
NH2

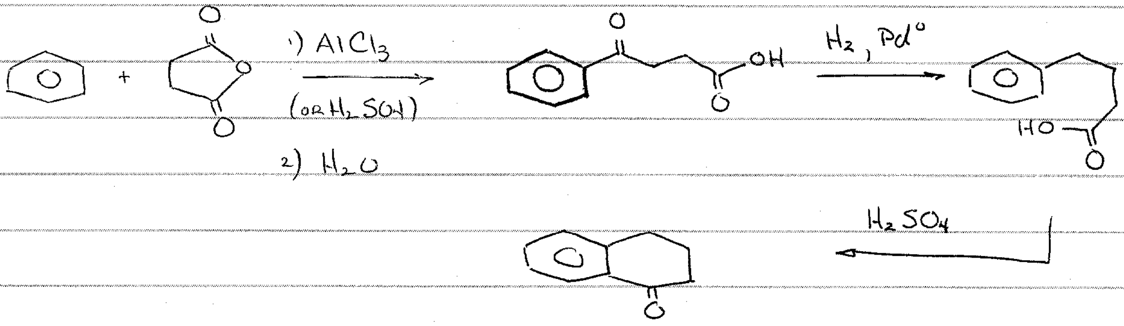
b)


excess
Cl
AlCl3
SO3
H2SO4
HO3S
HNO3
H2SO4
HO3S
NO2
H2O, Δ
(H+ optional)
NO2

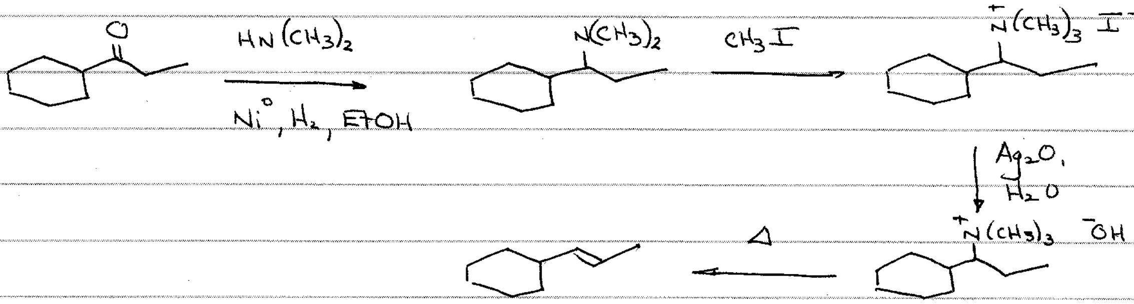
c)


O
H2, Pd°
CH3
Br2
FeBr3
Br
CH3
+ Some ortho
KMnO4,
H+
O
OH
Br

d)

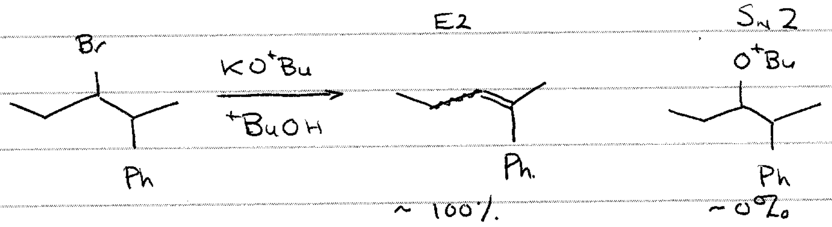

+
1) AlCl3
(or H2SO4)
2) H2O
O
OH
O
H2, Pd°
HO
O
H2SO4
O

e)


O
HN(CH3)2
Ni°, H2, EtOH
N(CH3)2
CH3I
+N(CH3)3 I−
Ag2O,
H2O
+N(CH3)3 −OH
Δ

JAMES

5.



- BULKY, STRONG BASE FAVOURS E2 OVER S_N2
- β-ARYL GROUP ACIDIFIES ADJACENT PROTON, ENHANCES E2 RATE
- 'ALWAYS' CONJUGATED TO Ph.

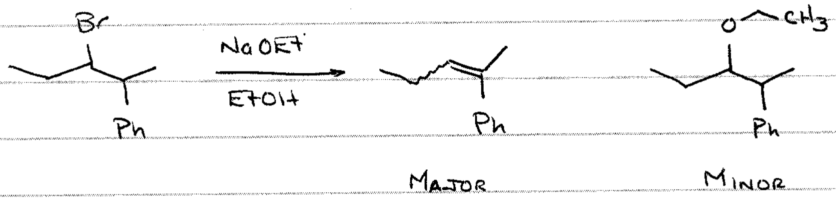
MORE

↑

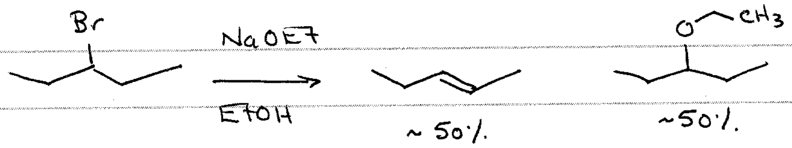
E2

↓

LESS.



- STRONG BASE, BUT NOT SO BULKY ∴ MORE S_N2
- β-ARYL GROUP ACIDIFIES ADJACENT PROTON, ENHANCES E2
- 'ALWAYS' CONJUGATED TO Ph

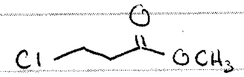


- STRONG BASE, BUT NOT SO BULKY ∴ MORE S_N2 THAN TOP CASE
- NOT β-ARYL GROUP (ONE ALKYL), SO THAT PROTON ISN'T ACIDIFIED ∴ MORE S_N2 THAT 2^{ND} CASE

no\. 6. START WITH ANALYSIS

	C	H	Cl	O
	43.97	6.64	25.96	23.43
÷	12.011	1.008	35.453	15.999
	3.66	6.59	0.732	1.46
÷SMALLEST ÷	0.732	0.732	0.732	0.732
	5.00	9.00	1	1.99

$\equiv C_5H_9ClO_2$ IS EMPIRICAL FORMULA

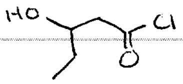
 IS $C_4H_7ClO_2$ ∴ DOESN'T FIT .... ELIMINATE

TO IR.

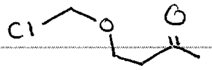
IMPORTANT BANDS ARE ν_{MAX} 2983 cm^{-1} C-H ALKYL

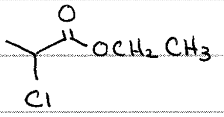
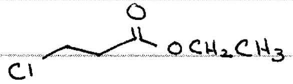
1739 cm^{-1} C=O CARBONYL .... COULD BE ESTER,

AND THAT'S ABOUT IT.

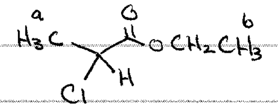
∴  WOULD HAVE $\nu_{C=O}$ 1800 cm^{-1} AND A ν_{O-H} OF ~3400 cm^{-1}

NEITHER ARE THERE ∴ NOT THIS ONE

 WOULD HAVE $\nu_{C=O}$ 1710 cm^{-1} ∴ NOT THIS ONE.

∴ LEFT WITH  AND 

TO 'H NMR.

FOR  CH_3^a $\delta_{CALC} = \overset{\text{BASE}}{0.8} + \overset{\text{M-Cl-Cl}}{0.7} + \overset{\text{M-C-CO}_2\text{R}}{0.3} = 1.8$, DOUBLET,

AREA = 3 NO DOUBLET ANYWHERE!

CH $\delta_{CALC} = \overset{\text{BASE}}{1.6} + \overset{\text{CH-Cl}}{2.4} + \overset{\text{CH-CO}_2\text{R}}{0.9} = 4.9$, QUARTET, AREA = 1

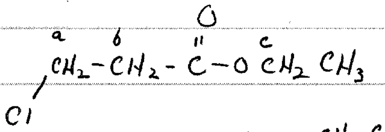
NO AREA = 1 QUARTET IN SPECTRUM

CH_2 $\delta_{CALC} = \overset{\text{BASE}}{1.2} + \overset{\text{CH}_2\text{-O}\overset{O}{\overset{\|}{C}}\text{R}}{2.9} = 4.1$, QUARTET, AREA = 2 FITS WITH δ 4.15 ppm

CH_3^b $\delta_{CALC} = \overset{\text{BASE}}{0.8} + \overset{\text{CH}_3\text{-C-O}\overset{O}{\overset{\|}{C}}\text{R}}{0.5} = 1.3$, TRIPLET, AREA = 3 FITS WITH δ 1.28 ppm

NOTHING CORRESPONDS TO OBSERVED δ 3.76 ppm (TRIPLET- OR δ 2.77 ppm TRIPLET

∴ THIS ISN'T THE COMPOUND.

AND  ?

$\underset{\text{Cl}}{\overset{a}{CH_2}}-\overset{b}{CH_2}-\overset{O}{\overset{\|}{C}}-O\overset{c}{CH_2}CH_3$

CH_2^a $\delta_{CALC} = \overset{\text{BASE}}{1.2} + \overset{\text{CH}_2\text{-Cl}}{2.2} + \overset{\text{CH}_2\text{-C-CO}_2\text{R}}{0.5} = 3.9$ SHOULD BE TRIPLET, AREA = 2

DECENT MATCH WITH 3.76 ppm TRIPLET

$\overset{b}{CH_2}$ $\delta_{CALC} = \overset{BASE}{1.2} + \overset{CH_2-C-Cl}{0.6} + \overset{CH_2-CO_2R}{1.0} = 2.8$ ppm, EXPECT TRIPLET, AREA = 2

EXCELLENT MATCH WITH 2.77 ppm TRIPLET.

$\overset{c}{CH_2}$ $\delta_{CALC} = \overset{BASE}{1.2} + \overset{CH_2-O-\overset{\overset{O}{\|}}{C}R}{2.9} = 4.1$ ppm EXPECT QUARTET, AREA = 2

EXCELLENT MATCH WITH 4.15 ppm QUARTET.

CH_3 $\delta_{CALC} = \overset{BASE}{0.8} + \overset{CH_3-C-O-\overset{\overset{O}{\|}}{C}R}{0.5} = 1.3$ ppm EXPECT TRIPLET, AREA = 3

EXCELLENT MATCH WITH 1.28 ppm QUARTET.

∴ COMPOUND IS CLEARLY