UNIVERSITY OF WINDSOR

NAME OF STUDENT ..... FINAL - 1998 ..... Course Name & Number ... 59-235 .....

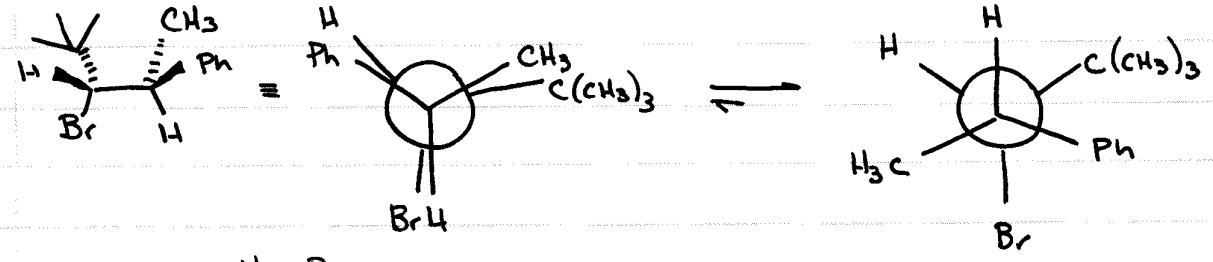
Student I.D. Number ... SUGGESTED SOLNS ..... Course Section .....

Date of Test: ..... NAME OF INSTRUCTOR .....

Book No. .....

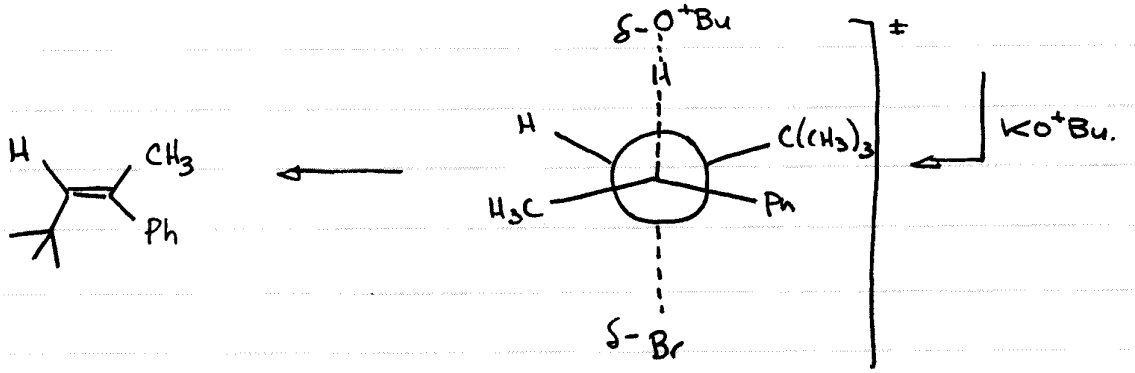
Total No. of Books .....

1.



H + Br NOT ANTIPERIPLANAR

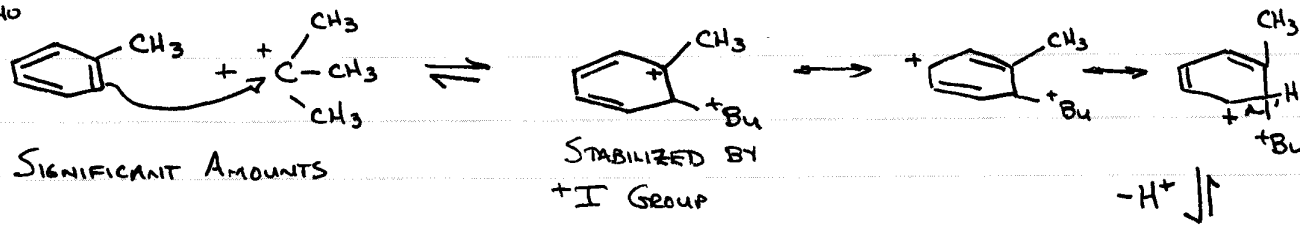
NOW ANTIPERIPLANAR



TRANSITION STATE

2.

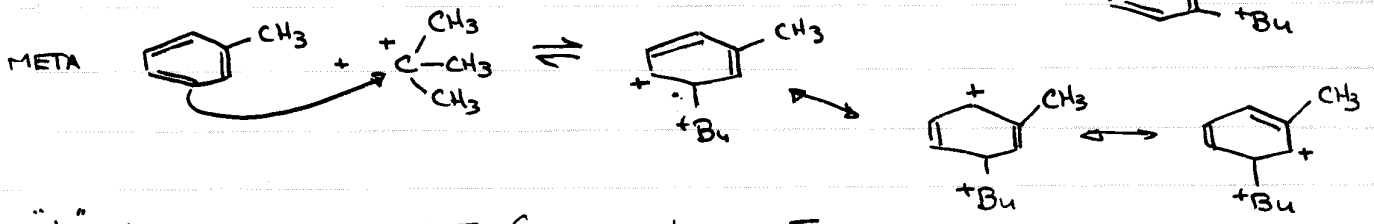
ORTHO



∴ SIGNIFICANT AMOUNTS

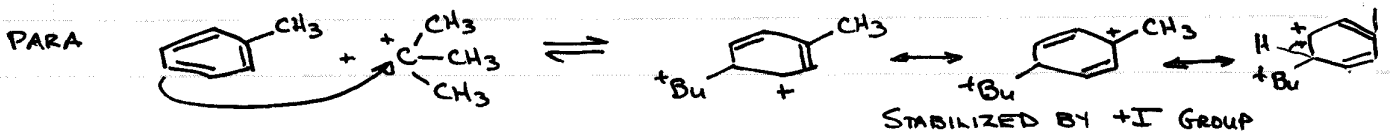
STABILIZED BY +I GROUP

META

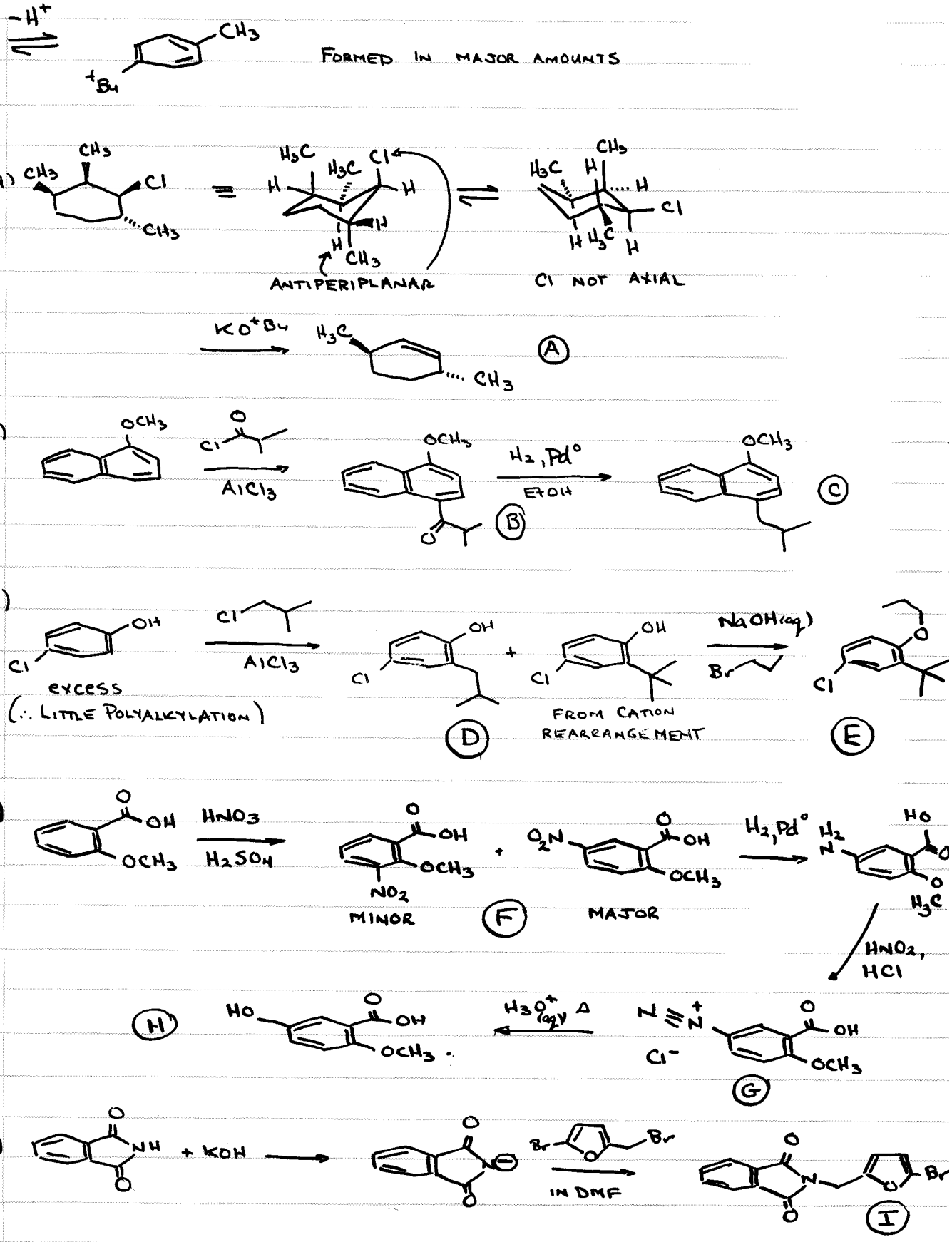


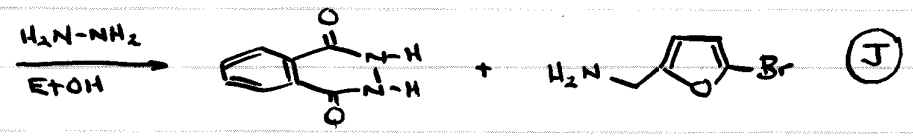
"+" NEVER AT SITE OF +I GROUP ∴ LITTLE FORMED

PARA

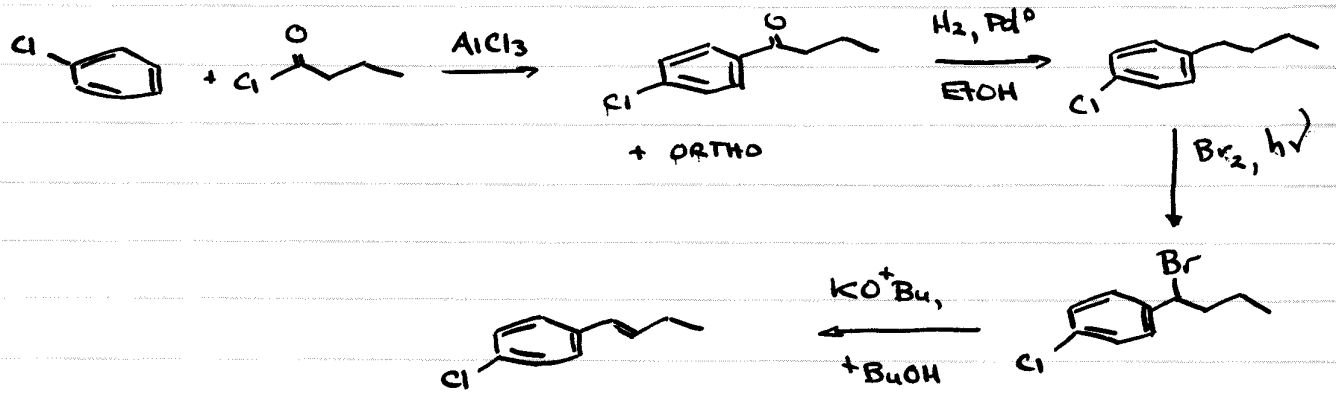


STABILIZED BY +I GROUP

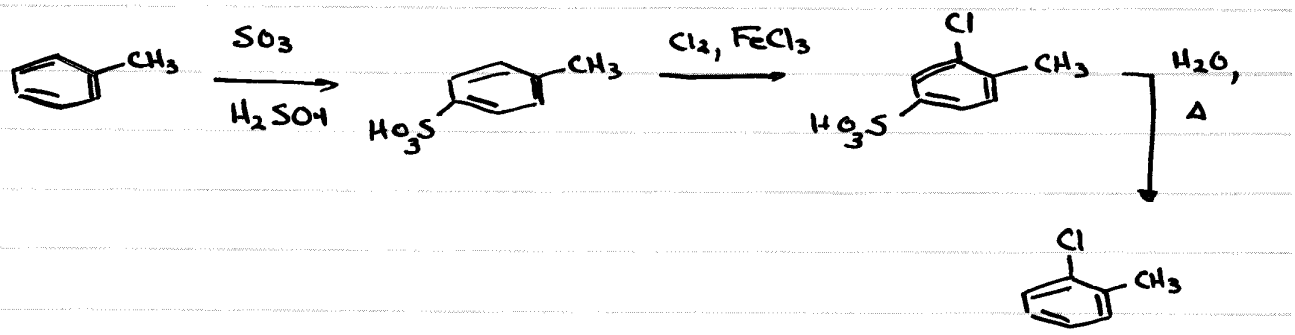

-H+
CH3
+BuH
FORMED IN MAJOR AMOUNTS
3a)
CH3
CH3
Cl
CH3
H3C
H3C
Cl
H
H
H
H
CH3
ANTIPERIPLANAR
CH3
H3C
H
H
Cl
H H3C
H
Cl NOT AXIAL
KO+Bu
H3C
CH3
A
b)
OCH3
O
Cl
AlCl3
OCH3
O
B
H2, Pd°
EtOH
OCH3
C
c)
OH
Cl
excess
(∴ LITTLE POLYALKYLATION)
Cl
AlCl3
OH
Cl
OH
Cl
FROM CATION REARRANGEMENT
NaOH(aq)
Br
O
Cl
D
E
d)
O
OH
OCH3
HNO3
H2SO4
O
OH
OCH3
NO2
MINOR
F
O2N
O
OH
OCH3
MAJOR
H2, Pd°
H2N
HO
O
H3C
HNO2,
HCl
H
HO
O
OH
OCH3
H3O+ (aq) Δ
N≡N+
Cl-
O
OH
OCH3
G
e)
O
NH
O
+ KOH
O
N
O
Br
Br
IN DMF
O
N
Br
O
I


H2N-NH2
EtOH
+
Br
J

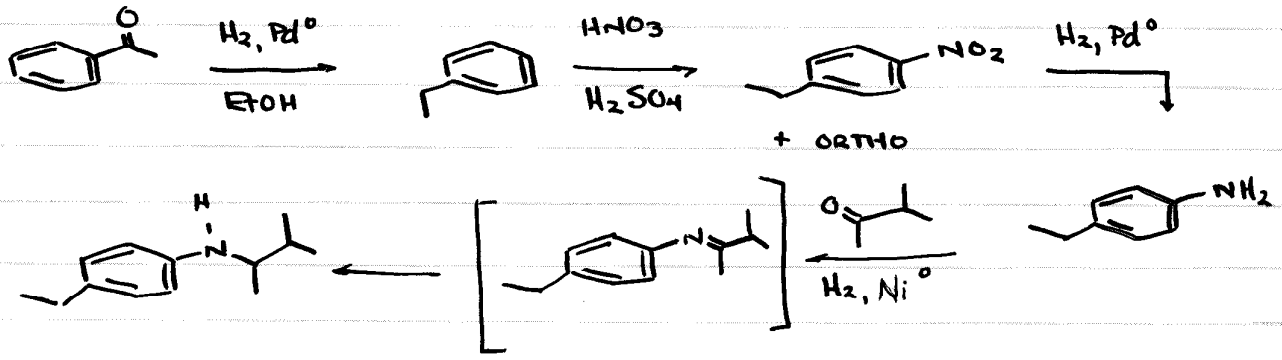
4a)


Cl
+
Cl
AlCl3
Cl
+ ORTHO
H2, Pd°
EtOH
Cl
Br2, hν
Br
Cl
KO+Bu,
+BuOH
Cl

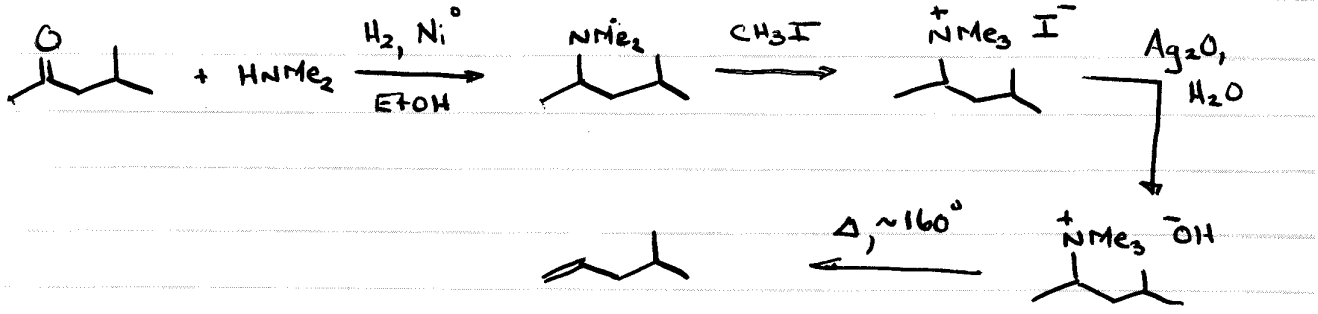
b)


CH3
SO3
H2SO4
HO3S
CH3
Cl2, FeCl3
Cl
HO3S
CH3
H2O,
Δ
Cl
CH3

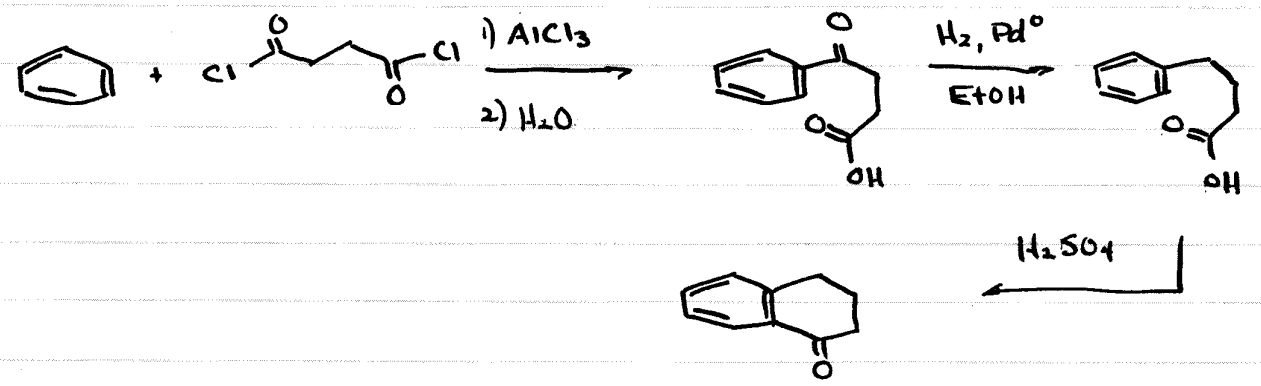
c)


O
H2, Pd°
EtOH
HNO3
H2SO4
NO2
+ ORTHO
H2, Pd°
NH2
O
H2, Ni°
N
H
N

d)


O
+ HNMe2
H2, Ni°
EtOH
NMe2
CH3I
+
NMe3 I−
Ag2O,
H2O
Δ, ~160°
+
NMe3 −OH

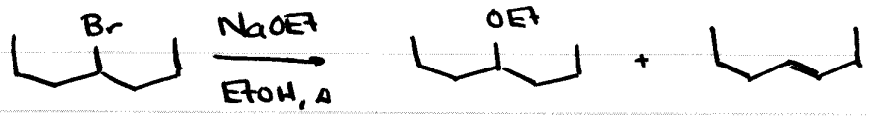
e)



5.

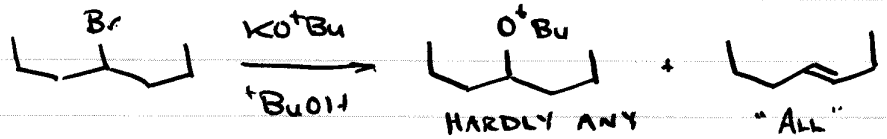
- 1° ALKYL HALIDE - FAVOURS SUBSTITUTION
- NON-BULKY BASE / NUCLEOPHILE - FAVOURS SUBSTITUTION

∴ MOST SUBSTITUTION OF THE GIVEN CASES



- 2° ALKYL HALIDE - FAVOURS MORE ELIMINATION RELATIVE TO ABOVE CASE
- NON-BULKY BASE / NUCLEOPHILE ∴ STILL GIVES SIGNIFICANT SUBSTIT.

∴ MIDDLE CASE OF THE THREE



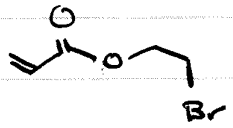
- 2° ALKYL HALIDE - FAVOURS MORE ELIMINATION RELATIVE TO TOP CASE
- VERY BULKY BASE ∴ FAVOURS ELIMINATION OVER SUBSTITUTION

∴ GREATEST AMOUNT OF ELIMINATION OF THE THREE

6. C 33.17 % H 5.01 % Br 44.14 % O 17.68 %

	C	H	Br	O
÷ Atomic Weight	÷ 12.011	÷ 1.008	÷ 79.904	÷ 15.999
	2.762	4.970	0.552	1.105
÷ Smallest	÷ 0.552	÷ 0.552	÷ 0.552	÷ 0.552
	5.00	9.00	1	2.00

∴ Emperical Formula is $C_5H_9BrO_2$

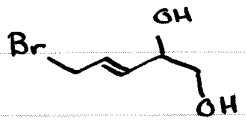
- This eliminates  only has 7 H's.

Now to ir.

Key Bands V. Broad absorption centred at 3000 cm^{-1}
O-H Stretch of Carboxylic Acid.

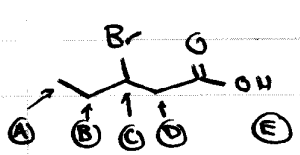
1708 C=O Stretch, Probably for $-\overset{O}{\overset{\|}{C}}-OH$ (not Conjugated)

∴ Eliminates  ν_{max} Predicted ~ 1735 cm^{-1} (ester)

 - no Carbonyl whatsoever.

∴ Leaves  and  as possibilities

Now to NMR

Consider 

(A) Predict CH_3 + M-C-Br (Nothing) = 0.8 + 0 = 0.8 ppm, triplet, Area = 3 ⇒ NO!

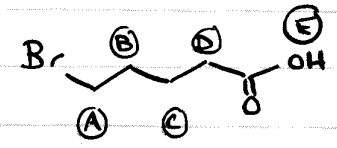
(B) Predict 1.2 + M-Br + M-C-CO_2R = 1.2 + 0.7 = 1.9, q of d, Area = 2 = NO!

(C) Predict 1.6 + M-C-Br + M-CO_2H = 1.6 + 2.5 + 0.3 = 4.4 ppm, t of t, Area = 1 NO!

(D) Predict 1.2 + 0.7 + 0.1 = 2.0 ppm, d, Area = 2 NO!

(E) Predict 12-14 ppm, broad s, Area = 1 11.6 is OK.

CLEARLY, THIS DOESN'T FIT THE ^1H NMR SPECTRUM

LET'S TRY 

PREDICTIONS

(A) = 1.2 + 2.2 ($M-Br$) = 3.4 ppm, triplet, Area = 2

CORRESPONDS WELL WITH OBSERVED 3.43 ppm, t, Area = 2 peak

(B) = 1.2 + 0.7 ($M-C-Br$) = 1.9 ppm, triplet of triplets, Area = 2

CORRESPONDS WELL WITH OBSERVED 1.93 ppm, m (multiplet), Area = 2 peak

(C) = 1.2 + 0.5 ($M-C-CO_2R$) = 1.7 ppm, triplet of triplets, Area = 2

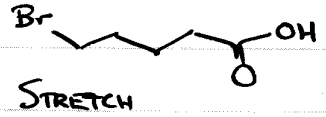
CORRESPONDS WELL WITH OBSERVED 1.81 ppm, m (multiplet), Area = 2 peak

(D) = 1.2 + 1.1 ($M-CO_2H$) = 2.3 ppm, triplet, Area = 2

CORRESPONDS WELL WITH OBSERVED 2.40 ppm, t, Area = 2 peak

(E) = 12-14 ppm, broad singlet, Area = 1

CORRESPONDS OK WITH 11.6 ppm, br s, Area = 1 peak

∴ STRUCTURE IS CLEARLY 

ν_{MAX} 1708 WAS THE ACID C=O STRETCH

ν_{MAX} 3000, broad WAS THE O-H STRETCH

BONUS