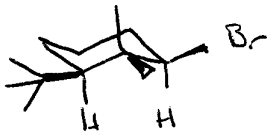
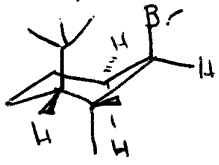
59-235

Final 2001 - Suggested Solutions

1. 

≡


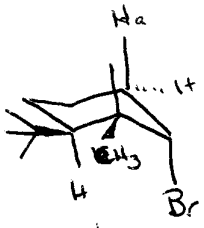
Equatorial t-Bu makes Br equatorial ∴ can't have antiperiplanar arrangement of H + Br until



KO^tBu

- but only occurs to very small equilibrium extent

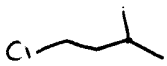
∴ Very Slow

≡


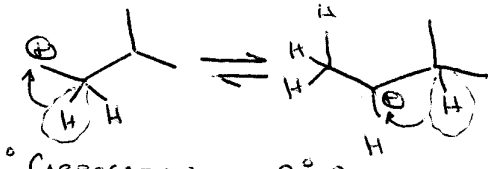
Equatorial tBu allows axial Br ∴ antiperiplanar arrangement with Ha present

∴ Eliminates Rapidly

KO^tBu

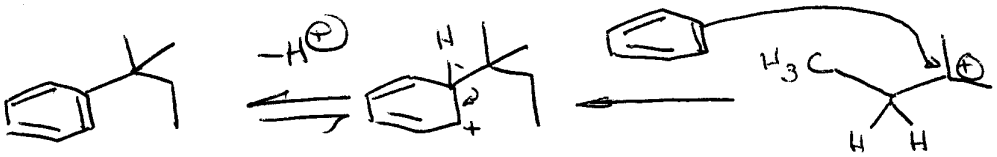
2. 

$\xrightarrow{AlCl_3}$


≡


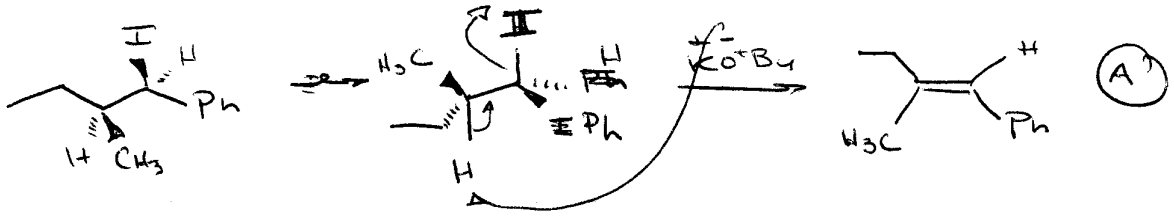
1° Carbocation

2° Carbocation - more stable

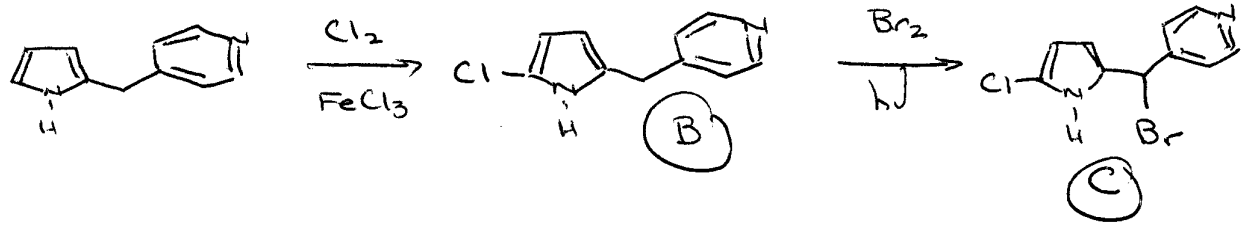


3° Carbocation - most stable

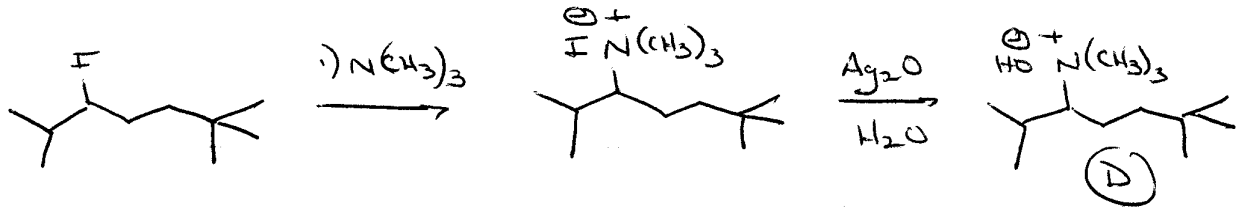
3a)

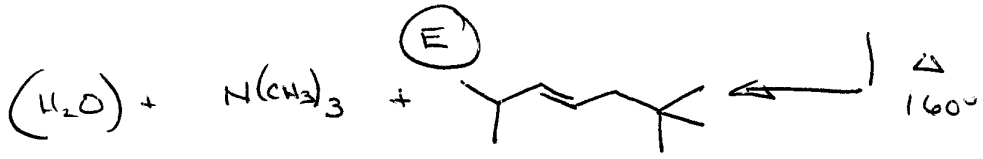

I
H
Ph
H
CH3
II
H3C
H
Ph
H
KO+Bu
H3C
H
Ph
A

b)

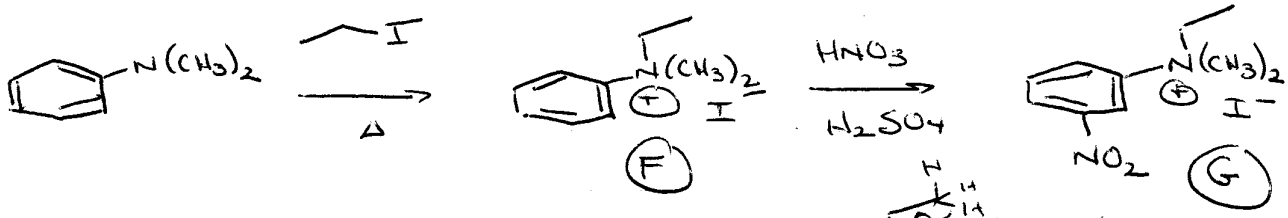

N
H
Cl2
FeCl3
Cl
N
H
B
Br2
hν
Cl
N
H
Br
C

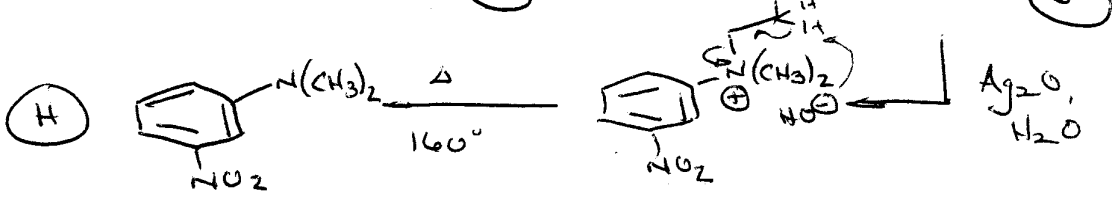
c)


I
1) N(CH3)3
I⊖ +N(CH3)3
Ag2O
H2O
HO⊖ +N(CH3)3
D

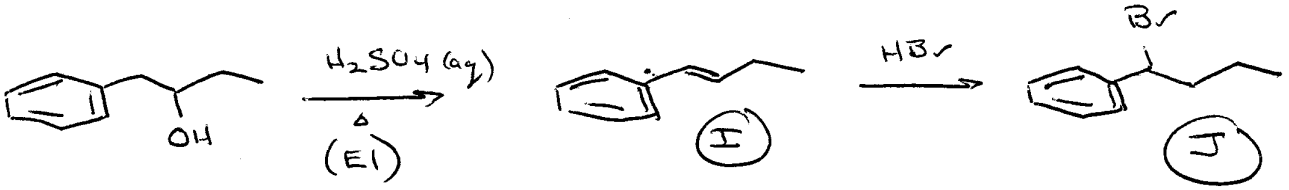

E
(H2O) + N(CH3)3 +
Δ
160°

d)

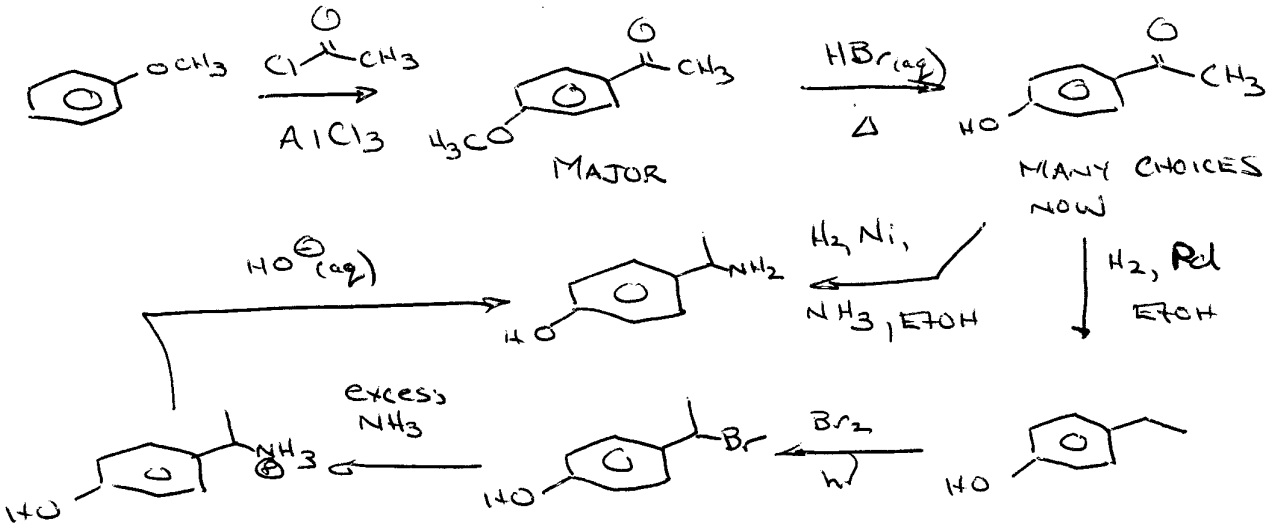

N(CH3)2
I
Δ
N(CH3)2
I⊖
F
HNO3
H2SO4
N(CH3)2
I⊖
NO2
G


H
N(CH3)2
NO2
Δ
160°
N(CH3)2
NO2
Ag2O,
H2O

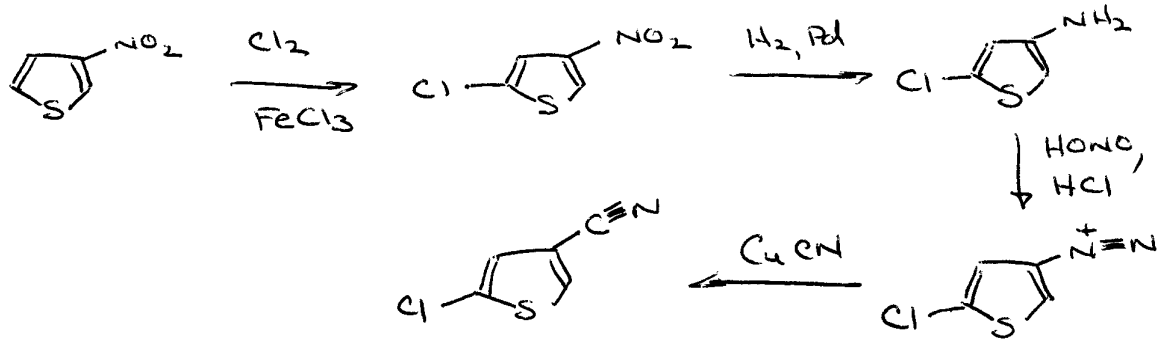
e)


OH
H2SO4 (aq)
Δ
(E1)
I
HBr
Br
J

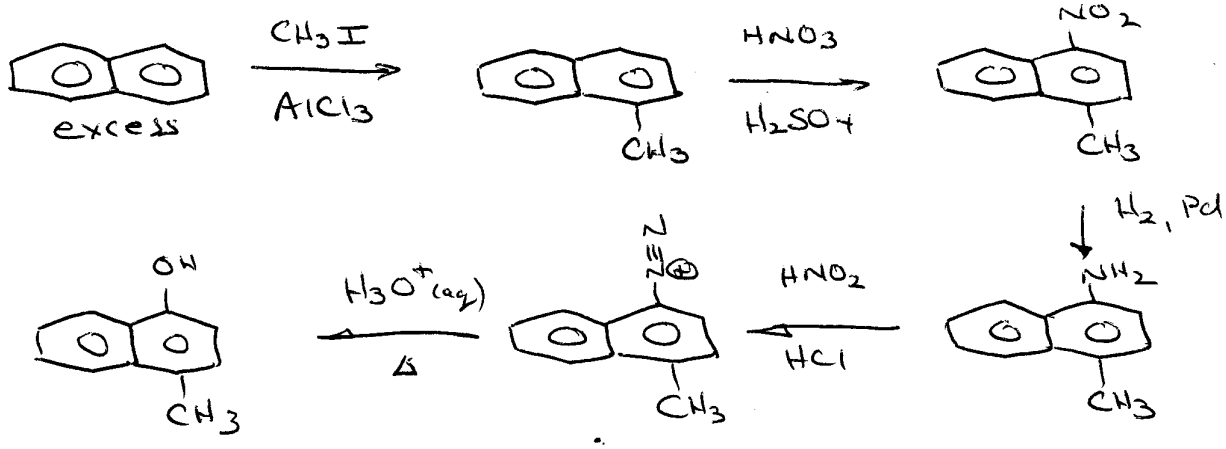
4. a)


OCH3
Cl
CH3
O
AlCl3
H3CO
MAJOR
HBr(aq)
Δ
HO
MANY CHOICES NOW
H2, Ni,
NH3, EtOH
H2, Pd
EtOH
HO(aq)
NH2
excess NH3
NH3
Br2
hν
Br

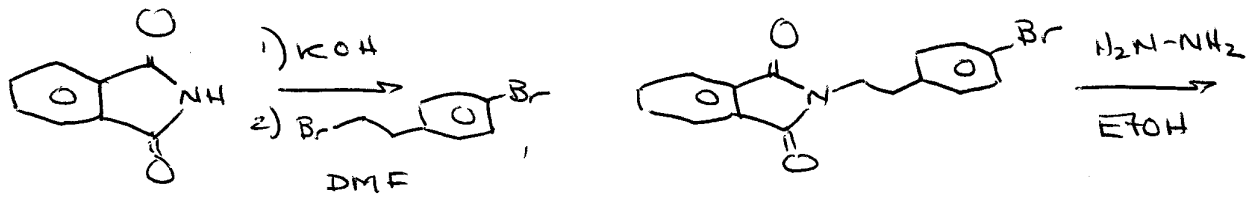
b)


NO2
Cl2
FeCl3
S
Cl
H2, Pd
NH2
HONO, HCl
N+≡N
CuCN
C≡N

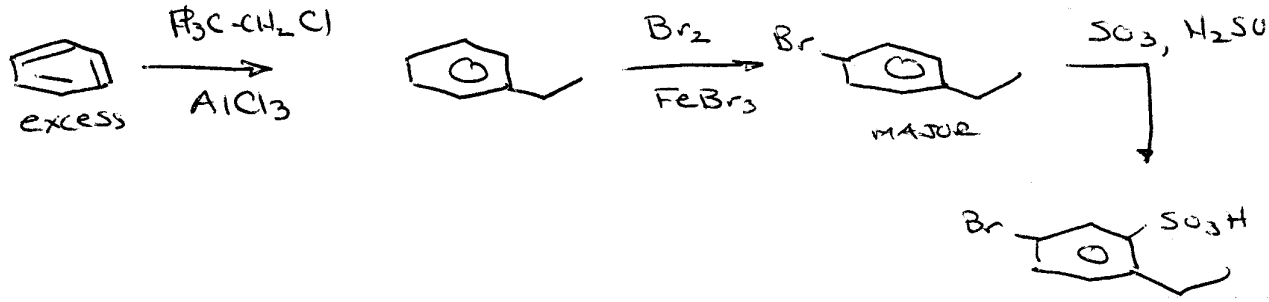
c)


excess
CH3I
AlCl3
CH3
HNO3
H2SO4
NO2
H2, Pd
NH2
HNO2
HCl
N≡N
H3O+(aq)
Δ
OH

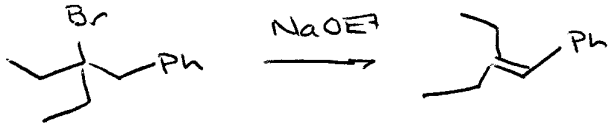
d)


NH
1) KOH
2) Br
Br
DMF
N
H2N-NH2
EtOH

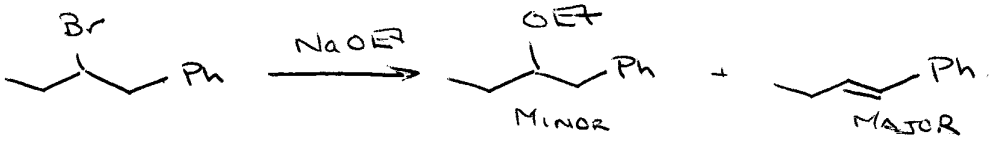
e)



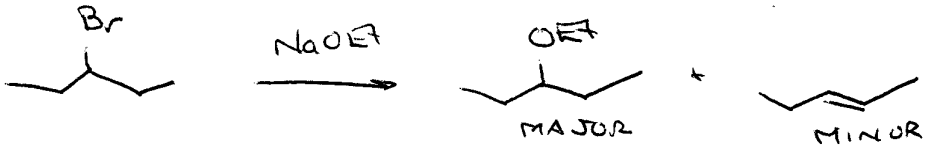
5.



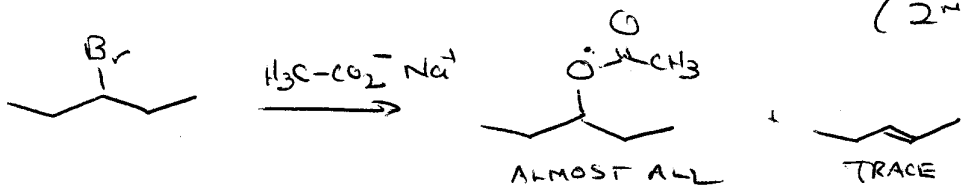
3° ALKYL HALIDE 'FORBIDS' S_N2
β-ARYL GROUP ENCOURAGES E2, BY ACIDIFYING H ATOM.
∴ MOST E2.



2° ALKYL HALIDE ALLOWS S_N2.
β ARYL STILL ENCOURAGING E2 ∴ 2ND MOST E2



2° ALKYL HALIDE ALLOWS S_N2
β-ALKYL ONLY INHIBITS E2 SLIGHTLY ∴ 3RD MOST E2
(2ND MOST S_N2)



2° ALKYL HALIDE ALLOWS S_N2
β-ALKYLS INHIBITS E2 SLIGHTLY ∴ LEAST E2
$H_3CCO_2^-$ IS NOT VERY BASIC ∴ INHIBITS E2 MOST S_N2

6. ANALYSIS

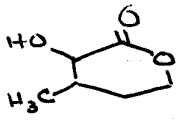
	C	H	O
	54.53 %	9.15 %	36.32 %
÷	12.011	1.008	15.999
	4.54	9.08	2.27
÷ SMALLEST	2.27	2.27	2.27
	2	4	1

∴ EMPERICAL FORMULA IS C_2H_4O

MOLECULAR FORMULA IS THIS, OR MULTIPLE OF IT.

SINCE ALL PROPOSED STRUCTURES HAVE 3 O'S, MUST BE

$C_6H_{12}O_3$

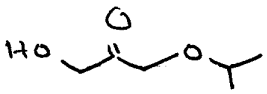
ALL FIT, EXCEPT  $C_6H_{10}O_3$ ∴ ELIMINATED FROM CONSIDERATION

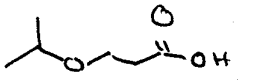
GO TO IR

MAJOR BANDS 3433 cm^{-1} (broad) MOST LIKELY O-H STETCH OF ALCOHOL

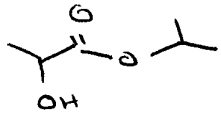
2983 cm^{-1} C-H STRETCH OF sp^3 HYBRIDIZED C-H

1738 cm^{-1} C=O STRETCH OF ESTER

∴  FAILS - THIS IS A KETONE ($\nu_{C=O}$ 1710 cm^{-1}) - ELIMINATE

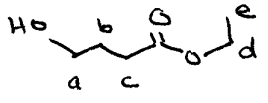
 FAILS - ACID HAS $\nu_{C=O}$ 1700 cm^{-1}, ν_{O-H} EVEN MORE BROAD, CENTRED AT 3000 cm^{-1}

THIS LEAVES

 AND 

POSSIBLE
BOTH ARE ESTERS AND ALCOHOLS

GO TO ^1H NMR.

FOR 

PREDICT a = CH_2 ⇒ 3.4 ppm, triplet, A=2

HMM NO TRIPLETS AT ALL IN SPECTRUM - ONLY THING NEAR 3. ppm IS broad singlet

b CH_2 δ_{CALC} = 1.5 + 0.4 (OR 0.3 + 1.6 OR 1.2 + 0.4 + 0.6) = 1.9 ppm, triplet of triplets, A = 2

Looks like multiplet

NOTHING LIKE THIS AT ALL PRESENT

AFTER TWO I'D SAY THIS DOESN'T WORK

c CH_2 δ_{CALC} = 2.3 ppm, triplet, A = 2

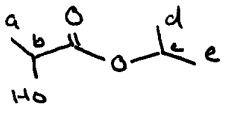
NOTHING TO MATCH THIS EITHER

d CH_2 δ_{CALC} = 4.1 ppm, quartet, A = 2

A QUARTET IS NEAR THERE, BUT AREA IS WRONG

e CH_3 δ_{CALC} = 1.3 ppm, triplet, A = 3

PEAKS NEAR 1.3 ppm ARE NOT TRIPLETS.

LET'S TRY 

a CH_3 δ_{CALC} = 1.2 + 0.3 (OR 0.4 + 1.1 OR 0.8 + 0.4 + 0.3) = 1.5 ppm, DOUBLET, AREA = 3

MATCHES PRETTY WELL WITH δ 1.4 ppm DOUBLET

b) CH δ_{CALC} = 3.8 + 1.0 (OR 2.2 + 2.6 OR 1.6 + 2.2 + 1.0) = 4.8 ppm, QUARTET, A = 1

THERE'S A QUARTET AT 4.25 ppm, MATCH IS 'FAIR'

c CH δ_{CALC} = 4.5 ppm, QUARTET OF QUARTETS, A = 1

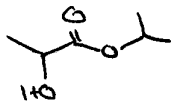
THERE'S A MULTIPLET (WHICH LOOKS LIKE SEPTET) AT 5.1 ppm, MATCH IS 'FAIR'

d CH_3 δ_{CALC} = 1.3 ppm, DOUBLET, A = 3

THERE ARE TWO DOUBLETS AT 1.27 & 1.28 ppm; EITHER ONE IS GOOD

e $\delta_{CALC} = 1.3$ ppm, DOUBLET, A=3

MATCHES WELL WITH EITHER DOUBLET AT 1.26 OR 1.27 ppm, WHOSE TOTAL A=6

∴ MATCH IS PRETTY GOOD FOR  IN ALL RESPECTS

-THIS IS IT

-OOPS - THE REMAINING RESONANCE, IN THE ^{1}NMR, $\delta = 3.1$ ppm, BROAD SINGLET, A=1 IS TH OH PROTON, WHICH CAN BE ANYWHERE BETWEEN 0.5 - 5.5 ppm. FIT IS FINE.

BONUS: