Suggested Solutions
59-235
Assignment #3

W' 2013

1a. C, 76.14% ; H, 11.18% ; O, 12.68%

$\div$ 12.011 ; 1.008 ; 15.999

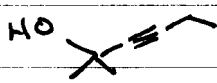
$= \frac{6.34}{0.793} = \frac{11.10}{0.793} = \frac{0.793}{0.793}$

$= 8 \quad : 14 \quad = 1$

∴ Emperical Formula is $C_8H_{14}O$

Gives Molar Mass of 126, which matches m/e

∴ Molecular Formula is $C_8H_{14}O$



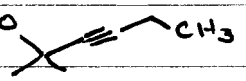
is only 4 ($C_4H_{12}O$) ∴ Eliminate From Consideration

Other 4 Are still Possible

To IR 3350 cm^{-1} Almost Certainly OH Stretch of Alcohol

2975 cm^{-1} C-H Stretch, sp^3 C-H

2220 cm^{-1} Weak - Most Likely C≡C, Since it's weak

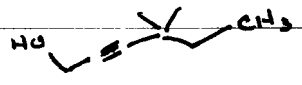
Eliminates 

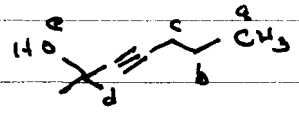
Since this would have no OH Stretch

Eminates 

Since this should have a Carbonyl Stretch at ~1670 cm^{-1}, and the OH should be ~3000 cm^{-1}, and there is NO C≡C

∴ Leaves 

and 

Let's Start $\bar{w}$ 

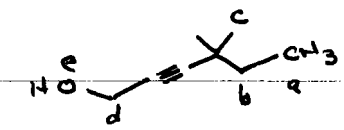
a Predict $\delta = 0.8$, t (triplet), A=3 Good match $\bar{w}$ A=3, t at $\delta = 0.85$

b Predict $\delta = 1.5$, tq (triplet of Quartets), A=2 Nothing here matching that

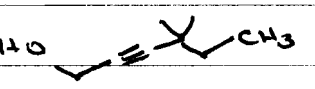
c Predict $\delta = 2.2$, t, A=2 No. Nothing Matching this - not even close

∴ This Fails; it isn't this compound.

You could also do this by saying we need A=3, t; A=2, m · A=2, t; A=6, s; A=1, s and it just doesn't match the pattern.

LET'S TRY 

a	PREDICT	$\delta = 0.8$, A = 3, t	GOOD MATCH w/ A = 3, t AT $\delta = 0.85$
b	PREDICT	$\delta = 1.5$, q, A = 2	GOOD MATCH w/ A = 2, q, AT $\delta = 1.4$
c	PREDICT	$\delta = 1.2$, s, A = 6	GOOD MATCH w/ A = 6, s, AT $\delta = 1.3$
d	PREDICT	$\delta = 3.4 + 1.0 = 4.4$, s, A = 2	GOOD MATCH w/ A = 2, s, AT $\delta = 4.2$
e	PREDICT	$\delta = 0.5$–5.5, s, A = 1	FITS WITH A = 1, s(br), AT $\delta = 2.0$

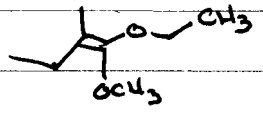
$\therefore$  IS IT!

1b. C, 67.57 % ; H, 9.92 % ; O 22.50 %

	C	H	O
	67.57 / 12.011	9.92 / 1.008	22.50 / 15.999
=	5.63	9.85	1.41
÷	1.41	1.41	1.41
=	4	7	1

EMPERICAL FORMULA IS C_4H_7O - THIS GIVES M = 71 AND OBSERVED m/e = 142

$\therefore$ MOLECULAR FORMULA IS $C_8H_{14}O_2$

 FAILS THE FORMULA (IT'S $C_8H_6O_2$) $\therefore$ ELIMINATE

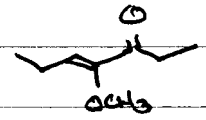
OTHERS ARE STILL POSSIBLE

ON TO <u>IR</u>

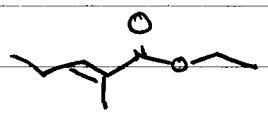
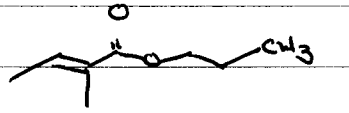
2980 cm^{-1} C-H STRETCH OF sp^3 C-H

1710 cm^{-1} C=O STRETCH EITHER OF KETONE, ALDEHYDE, ACID, OR A CONJUGATED ESTER - LOOKING AT THE POSSIBILITIES, IT MUST BE THE CONJUGATED ESTER.

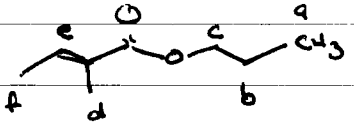
1660 cm^{-1} C=C STRETCH

So  FAILS, SINCE CONJUGATED KETONE WOULD GIVE $\nu_{C=O} \approx 1680\ cm^{-1}$

AND  FAILS, SINCE THIS ESTER IS NOT CONJUGATED, SO $\nu_{C=O}$ WOULD BE 1735–1740 cm^{-1}

∴  AND  ARE STILL POSSIBLE

ON TO THE ^1H NMR SPECTRUM.

LET'S TRY 

a PREDICT $\delta = 0.8$, t, A = 3 ACCEPTABLE MATCH $\bar{w}$ $\delta = 1.05$, A = 3, t

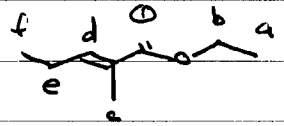
b PREDICT $\delta = 1.6$, tq (OR MULTIPLET, m), A = 2 WELL, THE A = 2, m, $\delta = 2.0$ ISN'T IMPOSSIBLE, BUT NOT V. CLOSE

c PREDICT $\delta = 4.1$, t, A = 2 NOPE; THE $\delta = 4.15$ RESONANCE IS AN A = 2, ~~q~~

d PREDICT $\delta = 1.6 + 0.3 = 1.9$, s, A = 3 ACCEPTABLE MATCH $\bar{w}$ A = 3, s, $\delta = 2.4$ (SINCE WE'RE ADDING 2' SHIFTS, WE GIVE THE MATCH MODE LEEWAY)

e. PREDICT $\delta = 6.9$, q, A = 1 NOPE; THE $\delta = 6.7$ RESONANCE IS A = 1, t

THAT'S TWO FAILS – THIS COMPOUND FAILS

SO LET'S TRY 

a PREDICT $\delta = 1.3$, t, A = 3 GOOD MATCH $\bar{w}$ A = 3, t, $\delta = 1.25$

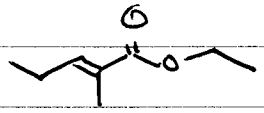
b PREDICT $\delta = 4.1$, q, A = 2 GOOD MATCH $\bar{w}$ A = 2, q, $\delta = 4.15$

c PREDICT $\delta = 1.6 + 0.3 = 1.9$, s, A = 3 ACCEPTABLE MATCH $\bar{w}$ A = 3, s, $\delta = 2.4$

d PREDICT $\delta = 6.9$, t, A = 1 GOOD MATCH $\bar{w}$ A = 1, t, $\delta = 6.7$

e PREDICT $\delta = \cancel{1.55}\ 2.0$, dq, A = 2 ~~ADEQUATE~~ GOOD MATCH $\bar{w}$ A = 2, m, $\delta = 2.0$

f PREDICT $\delta = 1.0$, t, A = 3 GOOD MATCH $\bar{w}$ A = 3, t, $\delta = 1.05$

THIS MATCHES WELL; IT'S  !

1c. C, 81.44 % ; H, 8.70 % ; O, 9.86 %

$\frac{81.44}{12.011} : \frac{8.70}{1.008} : \frac{9.86}{15.999}$

$= 6.78 : 8.63 : 0.616$

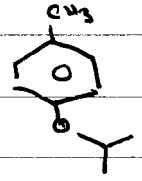
$\div 0.616 \quad \div 0.616 \quad \div 0.616$

$= 11 : 14 : 1$

∴ Emperical Formula is $C_{11}H_{14}O$, would Give M= 162

Mass Spectral m/e is 162

∴ Molecular Formula is $C_{11}H_{14}O$

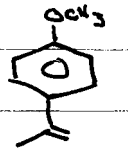


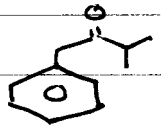
Doesn't match, as it's $C_{10}H_{14}O$ ∴ Eliminate

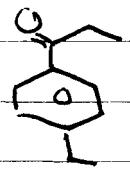
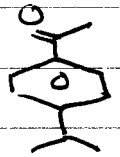
The Rest are Still possible

IR Spectrum

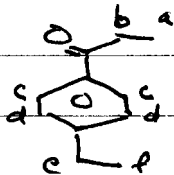
3005 cm^{-1}	C-H	sp^2 C-H
2987 cm^{-1}	C-H	sp^3 C-H
1681 cm^{-1}	C=O	Either Amide, or Ketone / Aldehyde / Acid that is Conjugate - Looking at the Possibles, it's Clearly the Conjugated Ketone

This Eliminates  which has no carbonyl at all

And  which has a ketone that is not conjugated, so we'd expect $\nu_{C=O} \approx 1710 cm^{-1}$

∴  and  are still in the running

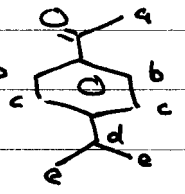
On to the ^1H nmr Spectrum

Let's Consider  First

a PREDICT A=3, t, δ= 1.1 NOTHING TO MATCH THIS; THE δ=1.1 RESONANCE IS AN A=6, d.

b PREDICT A=2, q, δ=2.3 (I'D ALSO ACCEPT 2.3+0.4=2.7) NOTHING MATCHING THAT ANYWHERE

THIS STRUCTURE FAILS ... TWO BIG FAILURES AT NMR MATCHING

SO LET'S TRY 

a, PREDICT A=3, s, δ= 2.1 (I'D ALSO ACCEPT δ=2.1+0.4=2.5)

GOOD MATCH W/ A=3, s, δ=2.5

b, PREDICT A=2, δ= 6.7-8.2 ... FOR MULTIPLICITY, THE SIMPLEST POSSIBILITY WOULD BE A d (DOUBLET).

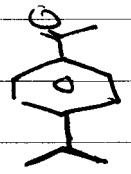
GOOD MATCH W/ δ=6.8, A=2, d.

c, PREDICT A=2, δ= 6.7-8.2 .... SAME STATEMENT ON MULTIPLICITY

GOOD MATCH W/ δ=7.4, A=2, d.

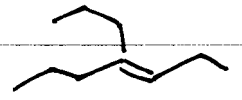
d, PREDICT A=1, septet, δ=2.8 GOOD MATCH W/ A=1, m, δ=2.9

e, PREDICT A=6, d, δ=1.2 GOOD MATCH W/ A=6, d, δ=1.2.

GOOD MATCHING OVERALL, SO IT IS 

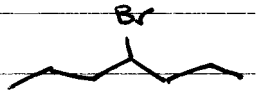
2. 

EtOH, Δ



- NO BASE → FAVOURS E1
- POLAR SOLVENT → FAVOURS CARBOCATION; ∴ E1
- 3° SUBSTRATE → FAVOURS CARBOCATION; ∴ E1

∴ ESSENTIALLY ALL E1 CHARACTER.



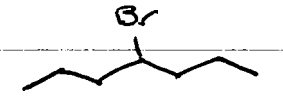
KO^{t}Bu
^{t}BuOH

PRETTY POLAR SOLVENT ... MORE TOWARDS E1

- 2° SUBSTRATE → LESS E1 THAN ABOVE CASE, BUT COULD BE E1 OR E2
- BASE - V. STRONG ∴ E2 FAVOURED
- NEXT PG. FOR CONCLUSION

∴ MAY MORE E2 THAN ABOVE CASE, BUT WE'LL SEE THE NEXT TWO ARE EVEN MORE E2 FAVOURING.

∴ 2ND MOST E1 (EVEN THOUGH IT'S > 50% E2 CHARACTER. PROBABLY)

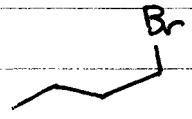


- SOLVENT (THF) : NOT V. POLAR ∴ NO SUPPORTING CATION
∴ MORE E2 (LESS E1) THAN CASES # 1 & 2

KO^tBu, THF

- SUBSTRATE 2° ; E1 OR E2 POSSIBLE
- BASE V. STRONG ; FAVOURING E2

∴ 2ND MOST E2 CHARACTER



- SOLVENT (THF) LOW POLARITY → E2 FAVOURED
- SUBSTRATE 1° ; E2 FAVOURED (E1'S CARBOCATION DISFAVOURED)

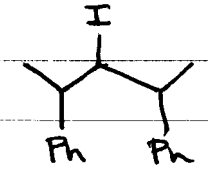
KO^tBu, THF

- BASE V. STRONG ∴ FAVOURS E2

∴ MOST E2 CHARACTER OF ALL

---

6).

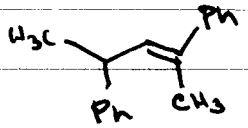


ALL ARE 2° HALIDES - COULD BE E1 OR E2

ALL ARE I LEAVING GROUPS - EXCELLENT, BUT WELL-KNOWN TO GIVE E1 OR E2

KO^tBu, ^tBuOH

- SAME SOLVENT - A BIT TOWARDS THE POLAR SIDE (MAYBE E1 FAVOURING A BIT)
- THIS ONE V. STRONG BASE ∴ TENDS TO E2, STRONGLY.
- ARYLS AT β-POSITION - ALSO TENDS TO E2



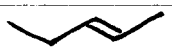
∴ MOST E2 CHARACTER OF ALL.

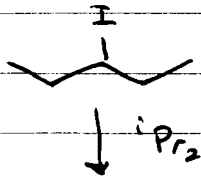
- SAME HALIDE ; ALSO 2° ∴ E1 OR E2

KO^tBu, ^tBuOH

- KO^tBu V. STRONG BASE ∴ FAVOURS E2
- NOT ANY β-ARYLS - LESS E2 THAN ABOVE CASE

∴ 2ND MOST E2 CHARACTER

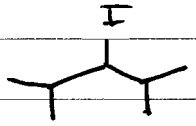




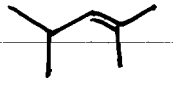
↓ $^iPr_2NEt$

- SAME HALIDE, AND STILL 2° ∴ E1 OR E2
- SAME SOLVENT
- NO β-ARYLS ∴ LESS E2 THAN CASE #1; THE SAME AS CASE #2 ABOVE
- $^iPr_2NEt$ IS A MUCH WEAKER BASE ∴ MORE E1, LESS E2 THAN CASES WITH KO^tBu.

∴ 3RD MOST E2 CHARACTER.



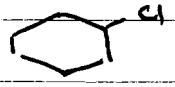
↓ $^iPr_2NEt$



- SAME HALIDE, STILL 2° ∴ E1 OR E2
- SAME SOLVENT
- $^iPr_2NEt$ IS WEAKER BASE THAN #1 & #2 ∴ MORE TOWARDS E1 END
- THERE IS β-ALKYL BRANCHING, WHICH DISFAVOURS E2 ∴ PUSHED TOWARDS E1 MORE

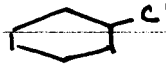
∴ LEAST E2 CHARACTER OF ALL.

C.

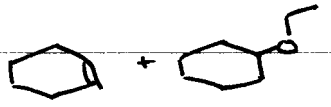


↓ KO^tBu, ^tBuOH

- BASE IS V. STRONG, AND QUITE BULKY ∴ A POOR NUCLEOPHILE
- ESSENTIALLY ALL (E2) ELIMINATION



↓ NaOEt, EtOH, Δ

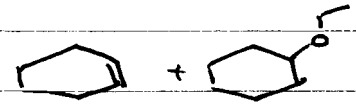


- BASE IS V. STRONG, BUT NOT STERICALLY HINDERED ∴ A GOOD NUCLEOPHILE TOO
- ELIMINATION (E2) AND SUBSTITUTION (S_N2) ARE BOTH QUITE POSSIBLE
- THE FACT THAT IT IS HEATED PUSHES RXN MORE TOWARDS ELIMINATION SIDE

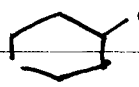
∴ 2ND MOST (E2) ELIMINATION PRODUCT

$EtO^- Na^+$
EtOH, RT

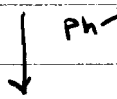
- ARGUMENTS ARE EXACTLY THE SAME AS ABOVE, EXCEPT...
- IT IS NOT HEATED, SO NOT THE ADDITIONAL IMPETUS PUSHING RXN TOWARDS ELIMINATION



∴ 2ND LEAST E2 CHARACTER

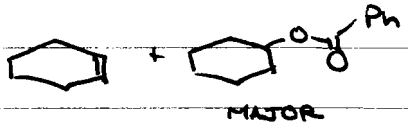


- BASE IS V. WEAK, STILL A DECENT NUCLEOPHILE (NOT STERICALLY HINDERED BASE)



$Ph-O^- Na^+$
EtOH

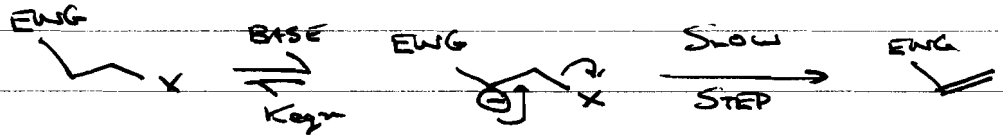
∴ MORE TOWARDS SUBSTITUTION (S_N2) THAN ELIMINATION



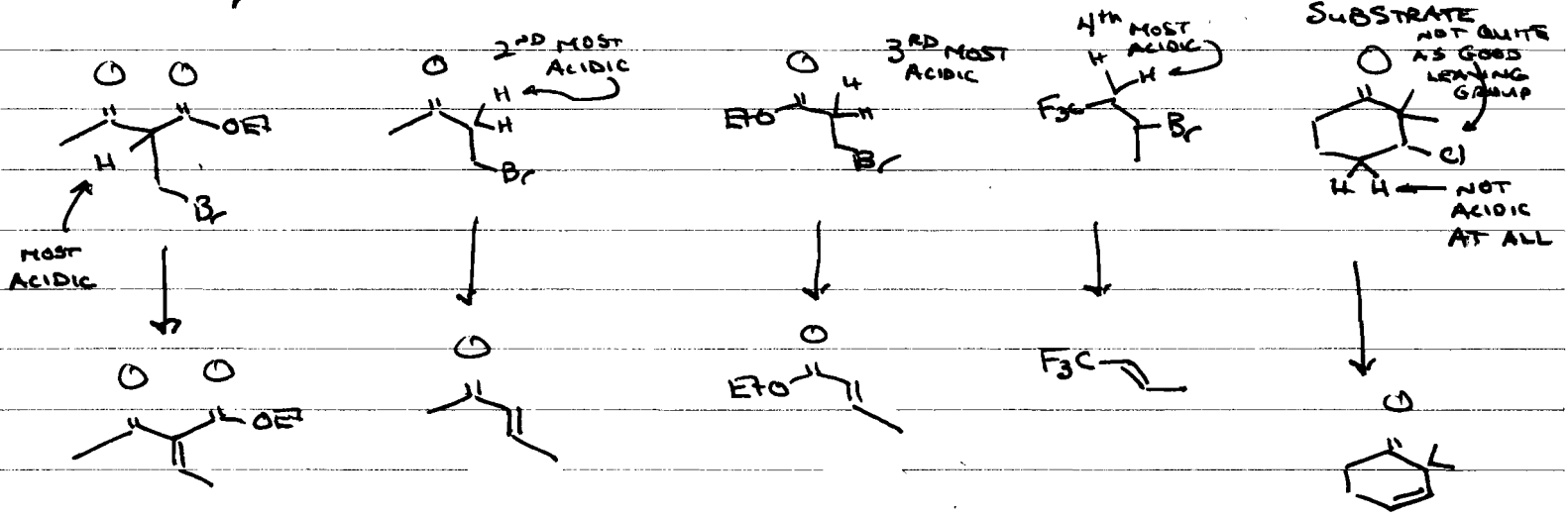
MAJOR

∴ MOST S_N2 CHARACTER (LEAST ELIMINATION)

d) KEYS FOR E1cb.

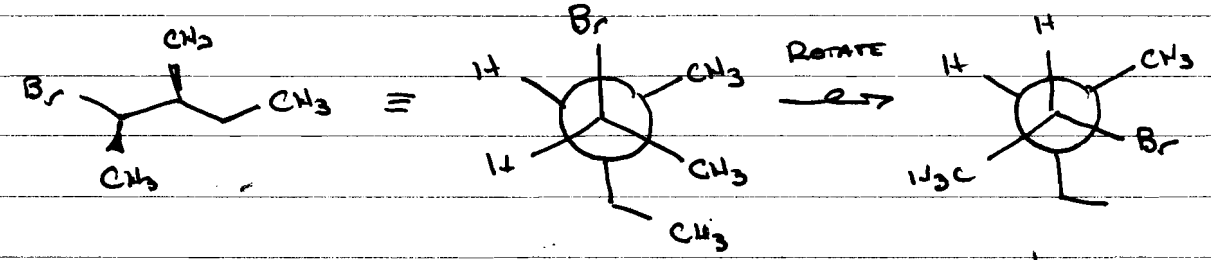


- RDS. (RATE DETERMINING STEP) SPED UP W/ BETTER LEAVING GROUP.
- K_{eqm} (EQUILIBRIUM CONST.) MORE FAVOURABLE FOR MORE ACIDIC

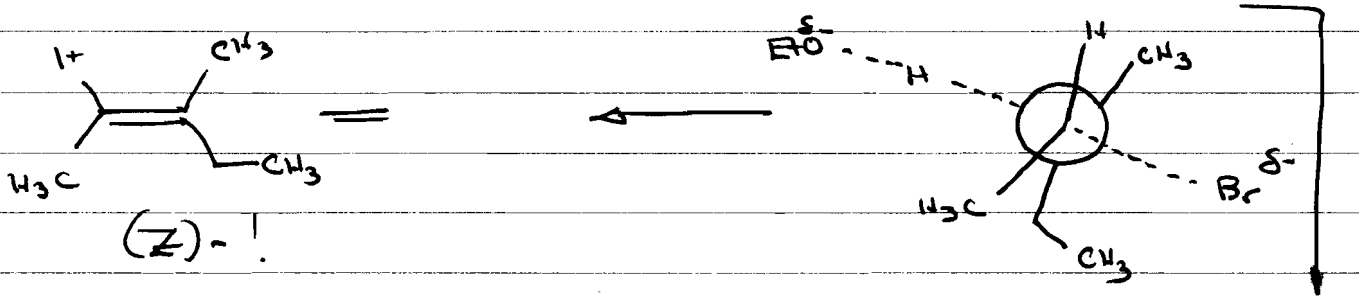


FASTEST E1cb | 2ND FASTEST | 3RD FASTEST | 4TH FASTEST | PROBABLY WON'T DO E1cb AT ALL (E2 LIKELY)

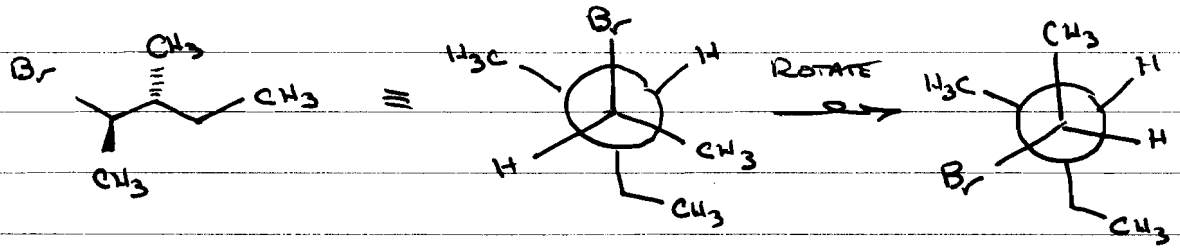
3. LEFT



NOW ELIMINATES



RIGHT



NOW ELIMINATES