

(1)

"WHY MY SCORE SHOULD HAVE BEEN BETTER ON THAT CRAZY MIDTERM"

OR

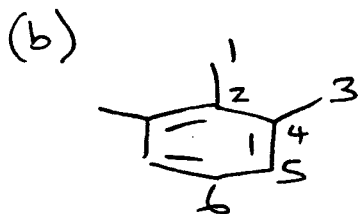
THE ANNOTATED ANSWER KEY

QUESTION 1

You saw something v. similar to this as a handout in class, and this question was generally answered well.

(a) 1 SIGNAL

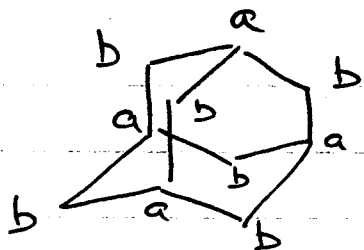
Lots of people wrote "3", but just because a molecule is drawn in one way on a two-dimensional piece of paper, that's not what it really looks like. You MUST THINK ABOUT MOLECULES IN 3D SPACE. This molecule is just CYCLODECANE, all of the C atoms are the same.



6 SIGNALS → NO excuses for getting this wrong, it was on the handout I gave out in class

2

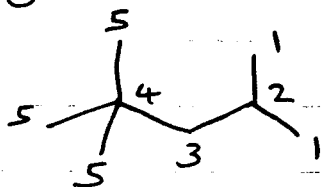
(c) OK, this was a genuinely tough question, but the answer is simply 2 SIGNALS



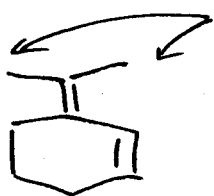
All CH₂s are the same and all CHs are the same

THIS MOLECULE IS CALLED:
ADAMANTANE

(d) This one may have been on the handout as well, or something very similar: the answer is 5 SIGNALS

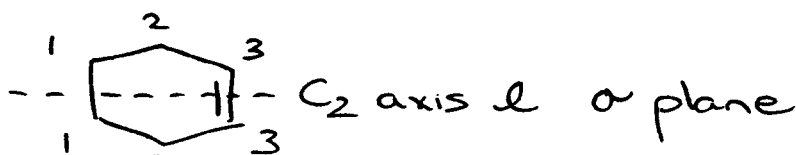


(e) THERE IS NO SYMMETRY → they are all different, hence 9 SIGNALS



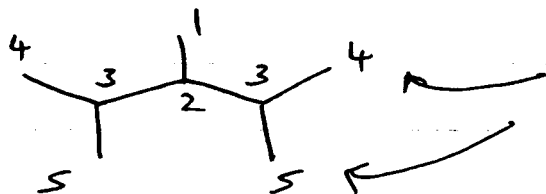
these are different, there is no rotation about a C=C bond, each C atom is unique

(f) 3 SIGNALS

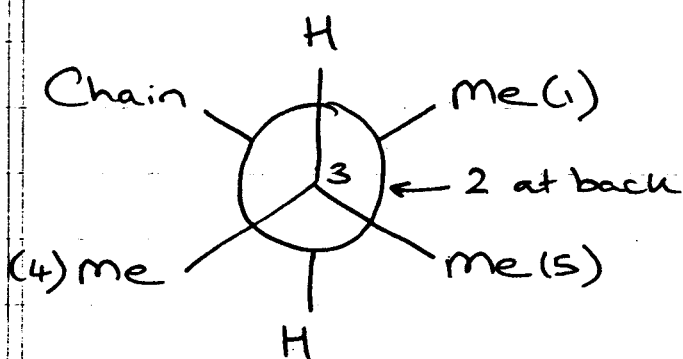


(3)

(g) AGAIN, no excuses, this was on the handout I gave out in class. The answer is 5 SIGNALS.



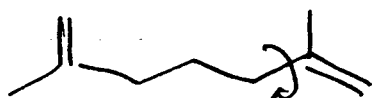
These ARE different, see me Newman projection



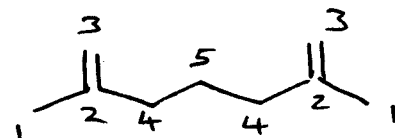
NO ROTATION or symmetry operation will exchange 4 and 5, they are different

IF YOU DON'T UNDERSTAND THIS CONCEPT, COME AND SEE ME.

(h) Again, think about molecules in 3D.

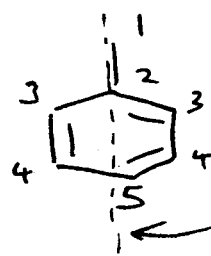


is the SAME AS



Just rotate about the C-C bond shown above, so the answer is 5 SIGNALS

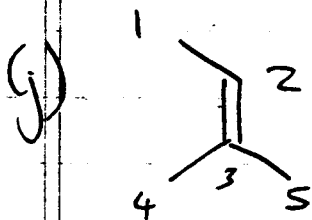
(i) NO excuses, it was on the handout in class



5 SIGNALS

C₂ axis of plane

(4)



5 SIGNALS, they are all different.

C4 and C5 are not the same, C4 is closer to C1 than is C5.

QUESTION 2

IR spectrum:

- Peak at $\sim 2200\text{cm}^{-1}$ = a triple bond, either $\text{C}\equiv\text{N}$ or $\text{C}\equiv\text{C}$

Mass Spec:

- $[\text{M}^+]$ is at $m/z = 133$
- It is ODD, there must be an odd number of Nitrogen atoms
- THIS MAY BE CONSISTENT WITH THE PRESENCE OF A $\text{C}\equiv\text{N}$.
- $\text{M}+2$ peak is about the same intensity as the M^+ peak, the compound must contain Br

(5)

- The intensity of $M+1$ vs M^+ is 2:49, which means the $M+1$ peak has a relative intensity of $\sim 4\%$

$$\frac{4}{1.1} = 3.636363636363636$$

hence molecule contains
3 carbon atoms

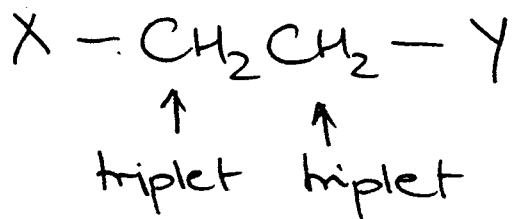
- So, $M^+ = 133$

$$133 - (\underbrace{79}_{\text{Br}} + \underbrace{3 \times 12}_{3\text{C}} + \underbrace{14}_{\text{N}}) = 4$$

(a) so the formula is $\text{C}_3\text{H}_4\text{BrN}$

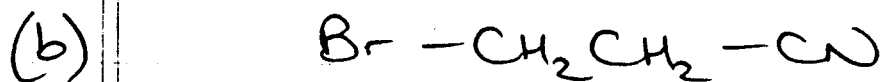
- $^1\text{H NMR}$

We have two equal intensity triplets, and as we only have 4 H atoms, it must be CH_2 and CH_2 , and as they are triplets, the CH_2 groups must be right next to each other



6

So now if we take on the other functional groups, we get



as the correct structure \Rightarrow this correlates well with the ^{13}C NMR data, i.e., 3 different C signals, 2 between 0 and 50, and 1 over 100 ppm

- The fragments at 93 and 95 obviously contain Br. Two equal intensity peaks separated by two mass units.

(c) The one at 93 is $^{79}\text{Br}-\text{CH}_2^+$

+
(d) and the one at 95 is $^{81}\text{Br}-\text{CH}_2^+$

each fragment corresponds to the loss of CH_2CN from the molecular ion.

(e) This fragment contains no Br, it has no significant $M+2$ peak. Subtract 79 from 133, and you get 54, hence this corresponds to the loss of Br from M^+ , leaving $\text{CH}_2\text{CH}_2\text{C}\equiv\text{N}^+$

7

Question 3

- IR spectrum

We have sp^3 CHs, and something at ~ 1750 that looks like some kind of C=O bond. There is a large strong peak at ~ 1200 , this may suggest a C-O bond.

- MASS SPEC

M^+ is at $m/z = 88$ NOT 43

43 is the base peak, I even refer to it as a fragment in part (c) of the question.

So, we know we have at least one Oxygen atom (maybe two) from the IR, so,

$$88 - 16 = 72$$

(There are no N atoms — or at least not just ONE, as m/z of M^+ is even)

So, what could 72 be made up of?

8

72 could be $6 \times C$, but that would give a formula of C_6O

so, how about 5 C atoms?

$5 \times 12 = 60$, leaving room for 12 Hs. That would give me formula

$C_5H_{12}O$ ← this is reasonable (so far)

How about 4 C atoms

$4 \times 12 = 48$, leaving 24 Hs — that's not possible, so how about if we use another oxygen? That gives me formula

$C_4H_8O_2$ ← also reasonable

Now, let's look at the ^{13}C NMR.

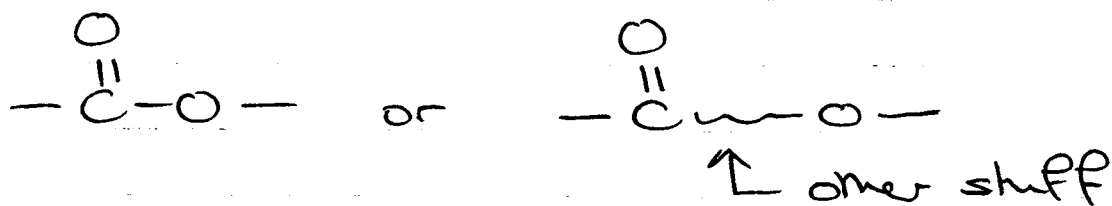
We see 4 peaks. The one at ~ 170 is very suggestive of $C=O$. The one at ~ 60 is also suggestive of $C-O$, which again, hints at there being 2 oxygens in our formula.

So for now, let's rule out $C_5H_{12}O$, and see if we can reconcile $C_4H_8O_2$ with the 1H NMR?

9

What could $C_4H_8O_2$ be?

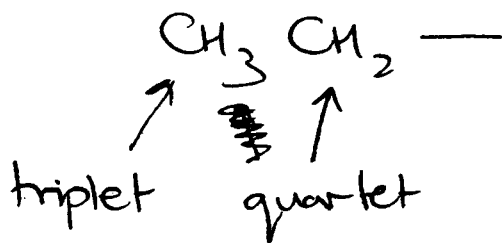
Well, we're pretty sure it has a $C=O$, and from the IR, we can tell that there is no OH group, so the second oxygen either goes with the $C=O$ to make an ester, or it is an ether somewhere else in the molecule, i.e.,



so, we are left with C_3H_8 .

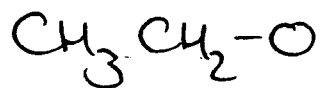
Now - let's look at the 1H NMR.

We have a quartet over four ppm, and a triplet just over one ppm - this is very diagnostic for an ethyl (CH_3CH_2-) group.

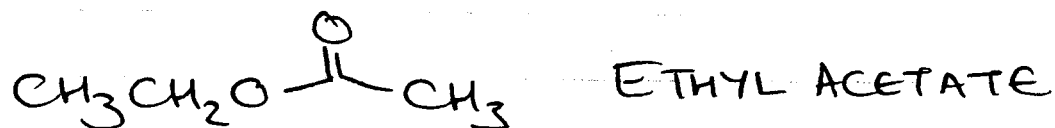


(10)

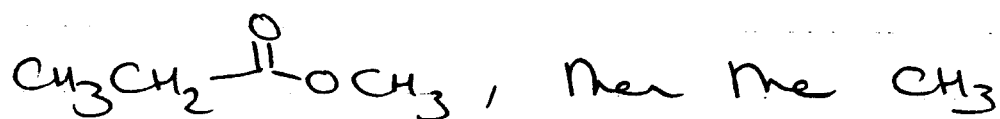
The fact that the CH_2 is over four, also suggest that it is bonded directly to an oxygen atom, suggesting



That leaves us with a C=O and a CH_3 group (which would account for a 3H singlet in the NMR), so we get



If we pieced it together another way, and got:



singlet would be at around 4 ppm, and the CH_2 quartet would be at ~ 2 ppm, so we can rule this one out. So, ETHYL ACETATE is the correct answer.

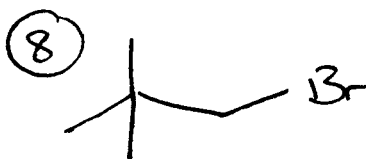
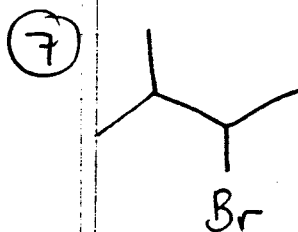
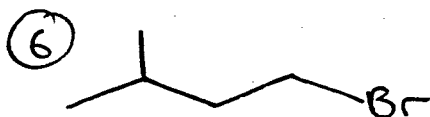
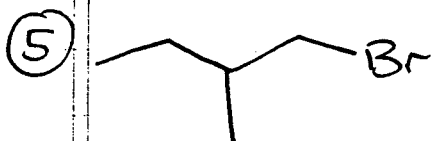
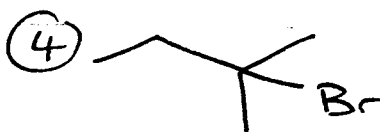
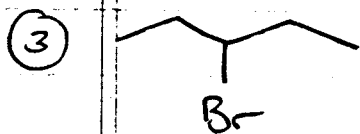
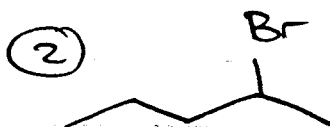
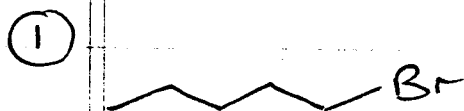
If you try to match $\text{C}_5\text{H}_{12}\text{O}$ structures with the ^1H NMR data, that would not be possible.

(11)

QUESTION 4

The trick to this question, was to read it. The formula $C_5H_{11}Br$ has ZERO DBE, and can only have a small number of isomers. You just have to match the correct isomer with each spectrum - you don't even really need to worry about chemical shift values.

POSSIBLE ISOMERS OF $C_5H_{11}Br$



(12)

Unless I missed one, there are 8 - you should have been drawing isomers in HIGH school → maybe you didn't, but it's something you should know by the time you get to 30B.

So, just match the structures with the NMRs.

C has two different CH_2 s, one type of CH_3 and one type of CH

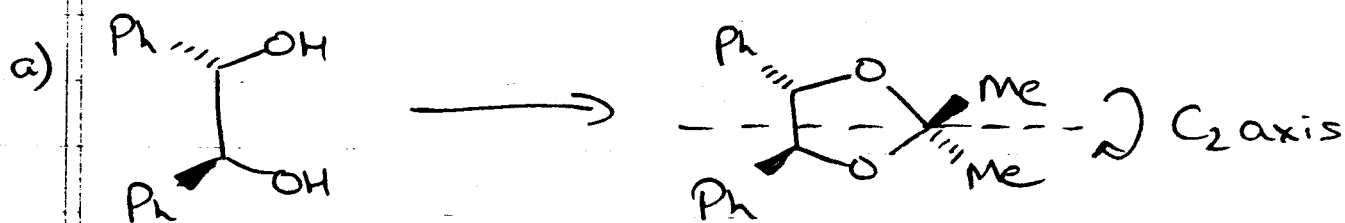
The only one that fits the bill is (6)

D has only one type of CH_2 , two different types of CH_3 , no CH s, and one quaternary C. So, it must be (8) or (4), and as (8) has only one kind of CH_3 , the answer is (4)

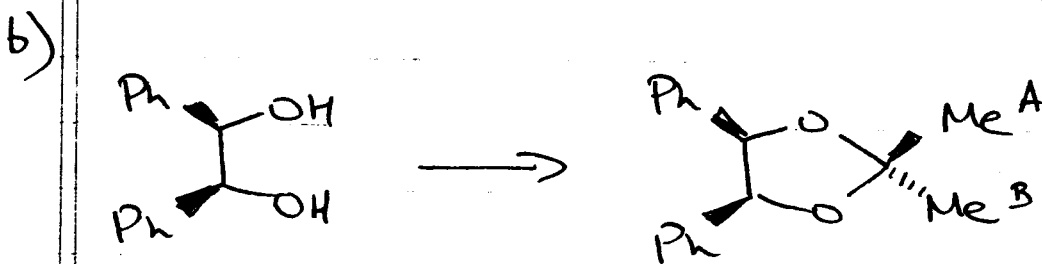
E has four different CH_2 s and one CH_3 - this one is easy, it is obviously (1)

QUESTION 5

You're making cyclic ketals, I tell you that in the question, and the exam was open book - no excuse for not getting the correct products!

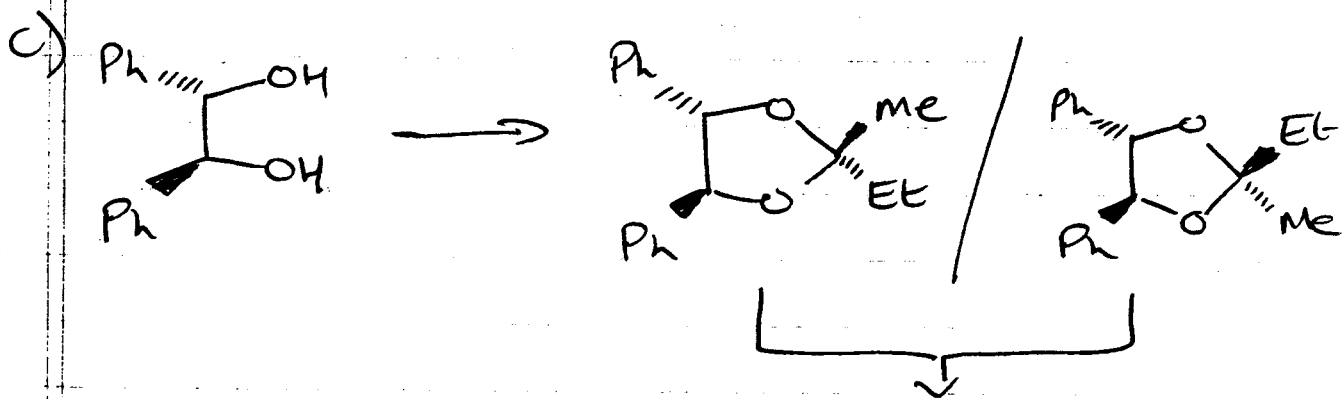


Methyl groups are exchanged by a C₂ axis, hence they are homotopic ⇒ 1 SIGNAL



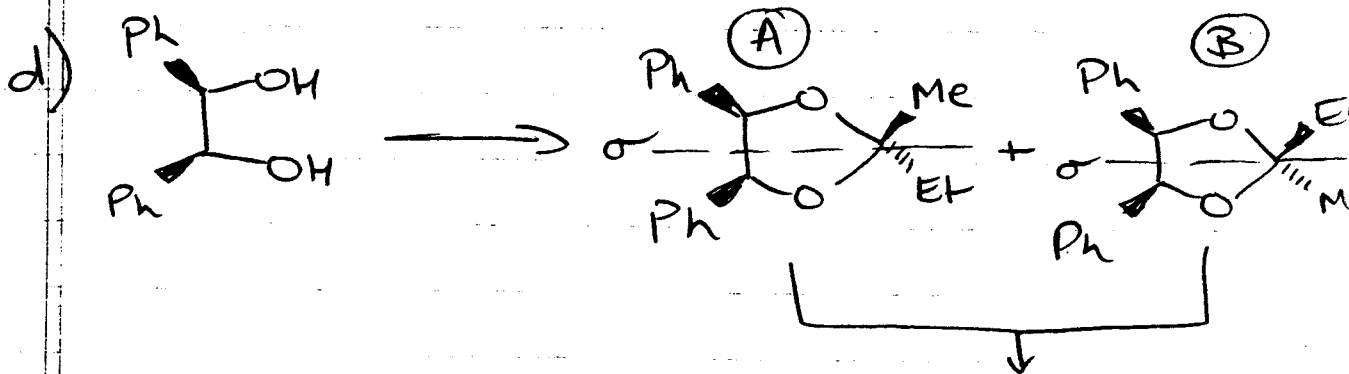
The methyl groups are different, they are not exchanged by any symmetry operation → THINK ABOUT IT.

Methyl A is, and always will be, closer to the Ph groups than Methyl B - they are diastereotopic, hence we see TWO METHYL SIGNALS



THESE ARE THE SAME

The Ph groups are not exchanged by any symmetry operation, they are **DIASTEREOTOPIC**



THESE ARE DIASTEREO-ISOMERS

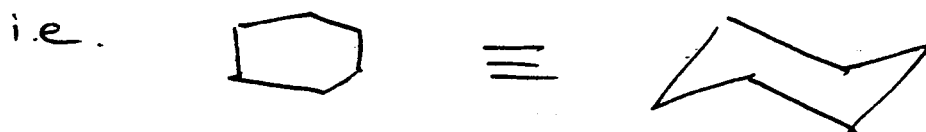
In (A), the methyl group is close to the Ph groups, whereas in (B), the ethyl group is the closest.

In each case, however, the Ph groups are **ENANTIOTOPIC** - they are exchanged by a plane of symmetry (σ)

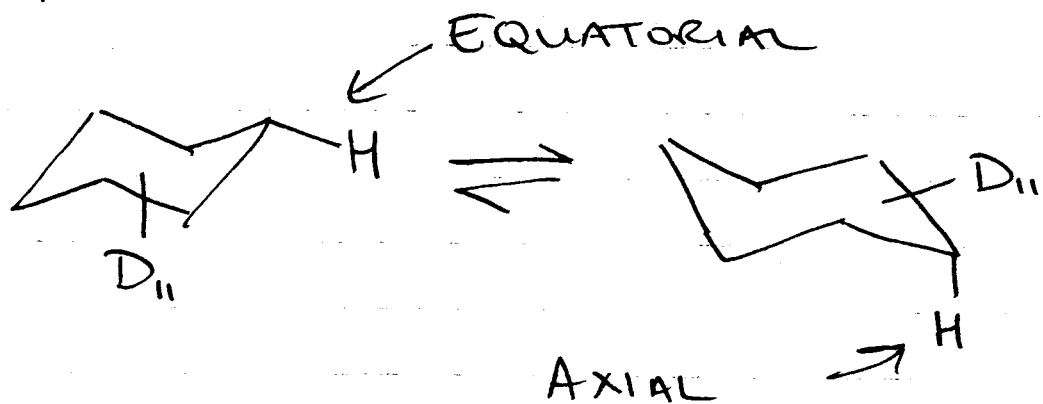
(15)

Bonus
Q6

First thing you think of when you see a six membered ring should be CHAIRS!



So, at low temp, we see two H signals, because of the following species

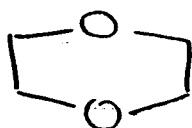


EQUATORIAL AND AXIAL are two different chemical environments, so at -100°C , we see a signal for the H in the AXIAL position, and a different signal for the H in the EQUATORIAL position. We see this because at -100°C , the ring-flip is relatively slow.

b) At room temperature, however, the ring flip is relatively fast, so the NMR does not "see" the H in the two different environments, it sees an AVERAGE, hence ONE SIGNAL.

7 If you were still awake / not completely crushed at this point, the answer was relatively easy.

There is 1 DBE for $C_4H_8O_2$, in this case it is a ring, and the structure is



JUST MAKE SURE WHEN I GIVE YOU A FORMULA AND ASK YOU TO WRITE YOU DRAW A STRUCTURE WITH THE CORRECT FORMULA - GET THAT WRONG AT THIS POINT IN YOUR CHEM CLASSES, AND THAT IS A BIG, BIG PROBLEM. - THIS IS A GENERAL COMMENT NOT JUST ABOUT Q7, BUT ALL QUESTIONS ON THIS MIDTERM.