CHEM 30A FALL 2004 Oct 28th

A 'HOW-TO' GUIDE FOR MIDTERM #1

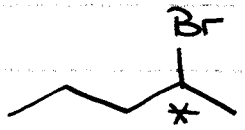
Q1 The best way to answer this question is to start by considering the carbon skeleton, and then adding in the Br atoms as we go along. We have 5 carbon atoms, NOT SIX, so what's the first choice...

Let's start with  →

So, where can we put the Br atoms:

There are THREE CHOICES

1 BROMOPENTANE



2 BROMOPENTANE

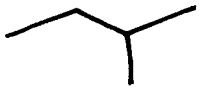
3 BROMOPENTANE

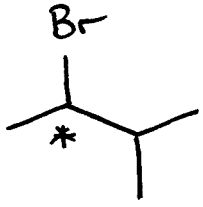
NOW, 1-BROMOPENTANE is going to be the least branched of any of the structures, so will have the highest boiling point, so this isomer boils at 130°C. In addition, note that 2-BROMOPENTANE contains a CHIRAL CENTER.

So, we've done PENTANES, what about BUTANES...

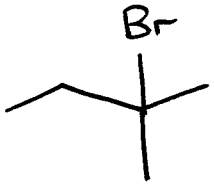
 ← so, this is butane,

and the only place to add a methyl group is to one of the two middle carbons, so we get:

 and now we have to add in a Br atom — how many places can we do this in?



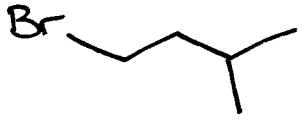
2-BROMO-3-METHYL BUTANE (CHIRAL)



2-BROMO-2-METHYL BUTANE

1-BROMO-2-METHYL BUTANE (CHIRAL)

NOTE If you add the Br to the other carbon atom, i.e., you get

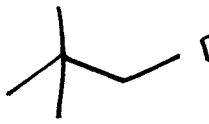


and this is the structure you were given

So,
We have 3 ISOMERIC BROMOPENTANES
and 3 ISOMERIC BROMOBUTANES,

and we only have one structure left →

a BROMOPROPANE

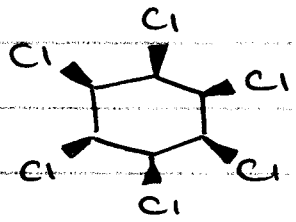


1-BROMO-2,2-DIMETHYLPROPANE

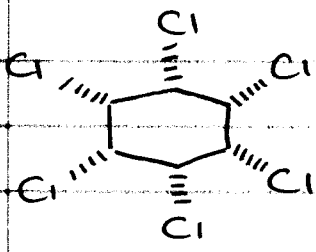
and this isomer is the one in which the carbon skeleton is branched the most, and so is the one with the lowest boiling point, so this is the 105°C.

So, there is a systematic way of approaching this question – JUST MAKE SURE THAT ALL THE STRUCTURES YOU DRAW HAVE THE CORRECT FORMULA – $C_5H_{11}Br$

Q2 Again, there is a systematic approach to this question, start with ALL Cls up



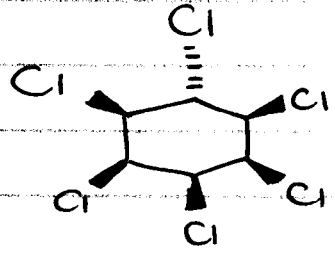
and realise that this is the SAME as the one in which the Cls are all DOWN



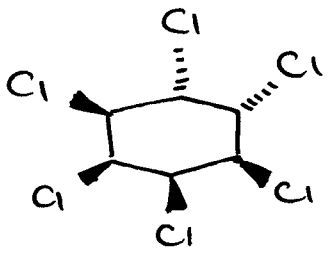
If you turn either of these molecules upside-down, you get the other.

IMPORTANTLY, YOU MUST DRAW IN THE CHLORINE ATOMS, OTHERWISE IT IS A COMPLETELY DIFFERENT MOLECULE

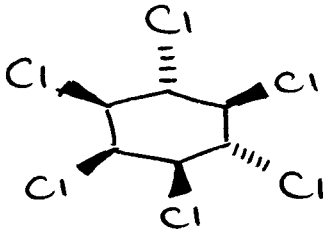
So next, let's put ONE Cl down

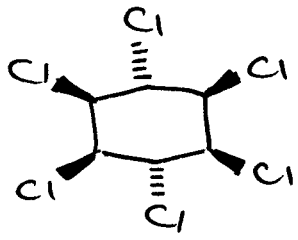


and next, let's put two Cls down:



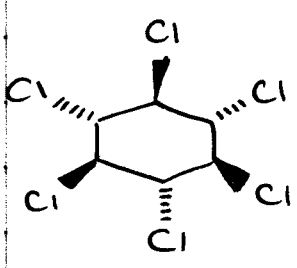
However, there are TWO other options here:

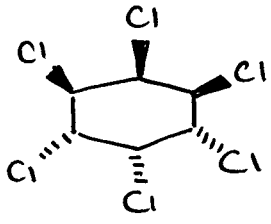


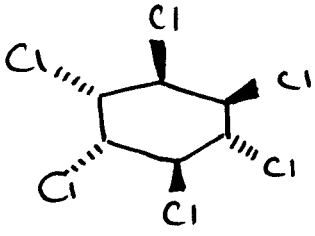


We have 1,2 down, 1,3 down and 1,4 down

NEXT, let's put THREE Cls DOWN → there are three options



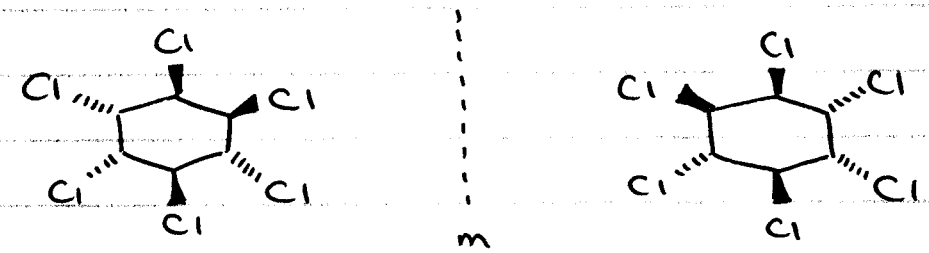




and with three Cls, we have:
1,3,5 down, 1,2,3 down, and 1,2,4 down

SO, these are the EIGHT diastereoisomeric 1,2,3,4,5,6- hexachlorocyclohexanes.

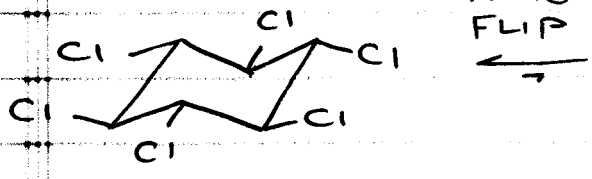
Seven of the eight are ACHIRAL, seven of them have planes of symmetry, only one of them DOES NOT, and that's the 1,2,4 down one:



NON SUPERIMPOSABLE MIRROR IMAGES

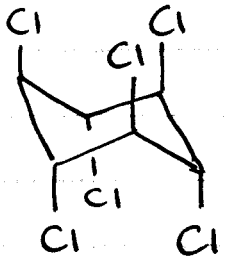
i.e. ENANTIOMERS

So, which is the most STABLE isomer? It's the one in which all of the Cl atoms are in the equatorial position, which is:



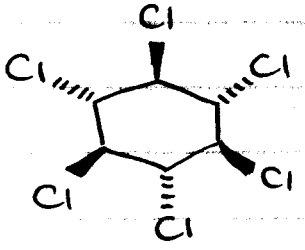
most stable

RING FLIP ⟷



least stable

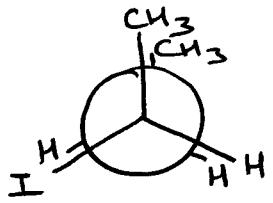
So, in flat form, it is



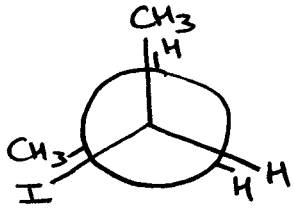
In ANY of these drawings, the Cls are UP-DOWN-UP-DOWN etc

Q3/ So, just what is the most UNSTABLE eclipsed conformer —

is it :

(A) 

or



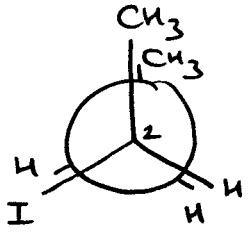
(B)

This all comes down to whether the CH_3–CH_3 eclipsed interaction is bigger or smaller than the CH_3–I eclipsed interaction

→ AND GUESS WHY I GAVE YOU THE A VALUES...

The fact that a methyl group (CH_3) has a larger A value than an iodine atom (I), means that the CH_3–CH_3 eclipsing interaction is a bigger repulsive interaction than a CH_3–I interaction.

So, the most unstable conformer is (A)

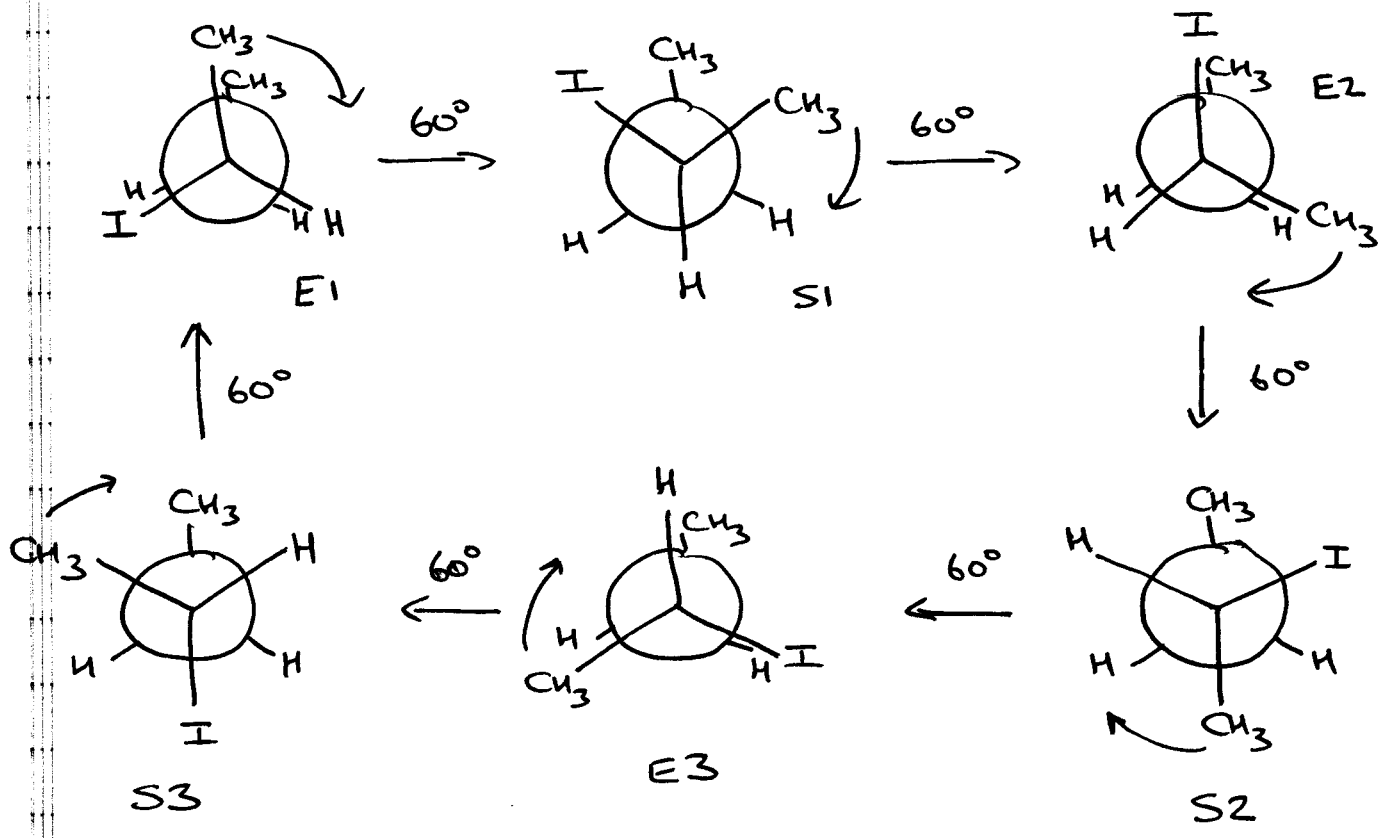


Now, follow the instructions, and it should be drawn as shown on the left, with C2 in the front.

Many people drew the enantiomer, with the I on the right, this is WRONG

... and make sure you rotate CLOCKWISE

So/



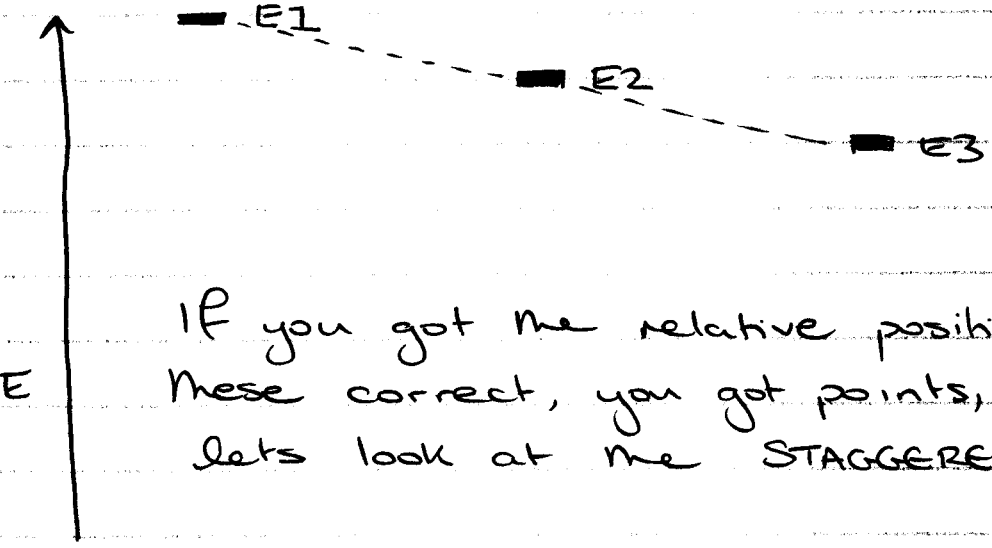
So, the energies of all of these species are different → LET'S compare the ECLIPSED ones:

E1	CH_3-CH_3	/ H-H / H-I	ECLIPSED
E2	CH_3-I	/ CH_3-H / H-H	ECLIPSED
E3	CH_3-~~H~~	/ CH_3-H / H-I	ECLIPSED

So, in E3, all 'big' groups are eclipsed with an H, so is the lowest energy of all the eclipsed ones, and E2 lies in energy

between E1 and E3, as two big groups (CH_3 e I) are eclipsed, but is not as bad as in E1, in which the two largest groups are eclipsed.

So

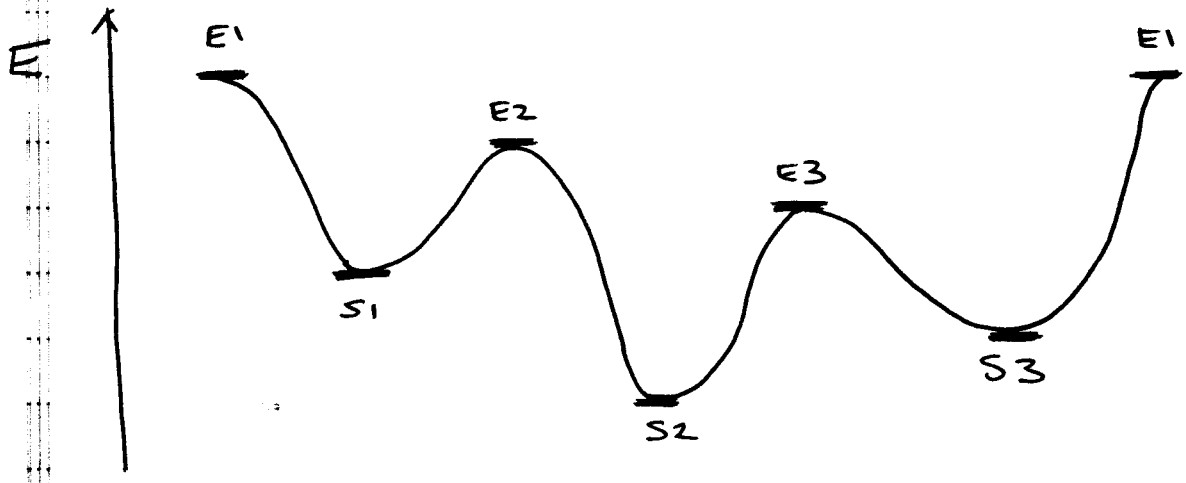


If you got the relative positions of these correct, you got points, now, lets look at the STAGGERED ones...

S1 CH_3-CH_3 gauche, CH_3-I gauche
S2 CH_3-I gauche
S3 CH_3-CH_3 gauche

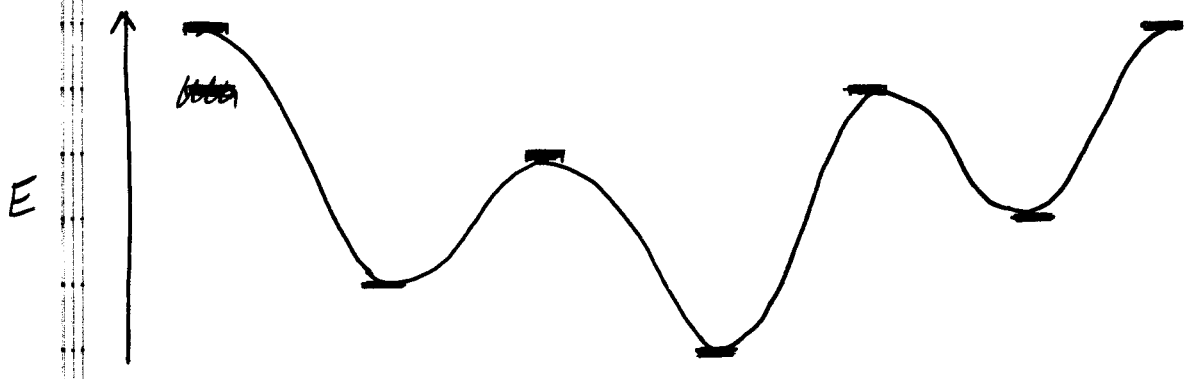
So, S1 is the least STABLE of the staggered conformers, and because a CH_3-CH_3 gauche interaction is worse than a CH_3-I gauche interaction, S2 is a more stable staggered conformer than S3...

So, assuming all staggered conformers are more stable than eclipsed ones, we get:



So, I'm not bothered by absolutes, but if you get the relative energy levels in the same positions as above, that was full credit - but only if you draw in the curve - THAT'S WHAT I ASKED IN THE QUESTION.

For part (c), I wanted you not to waste too much time, and draw the energy profile you would expect for the enantomer or MIRROR IMAGE compound, which is (S)-2-IODOBUTANE - and simply, the graph would be the MIRROR IMAGE...



For part (d), the S1 and S3 conformers for 2-iodobutane are simply:

CONFORMATIONAL DIASTEREOISOMERS

They are non-superimposable non mirror images

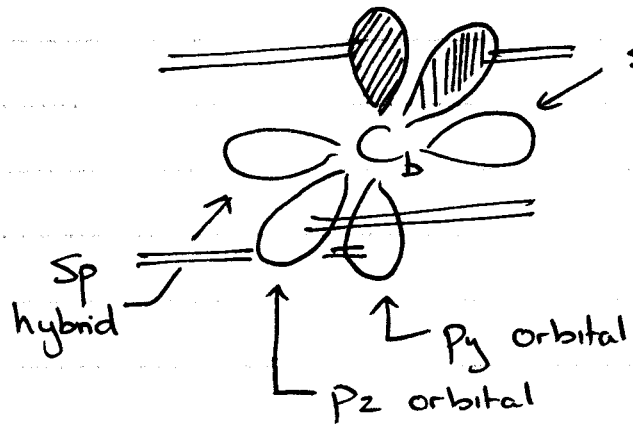
Q4 – This question is all about ALLENE

$$\underset{a}{CH_2}=\underset{b}{C}=\underset{c}{CH_2}$$

a) C atoms a and c each have three things around them, and so are sp^2 hybridized.

b) C atom b has two things attached, and so is sp hybridized.

c) The key to this problem is to realize that the p orbitals that C_b uses to form π bonds are at 90° to each other:



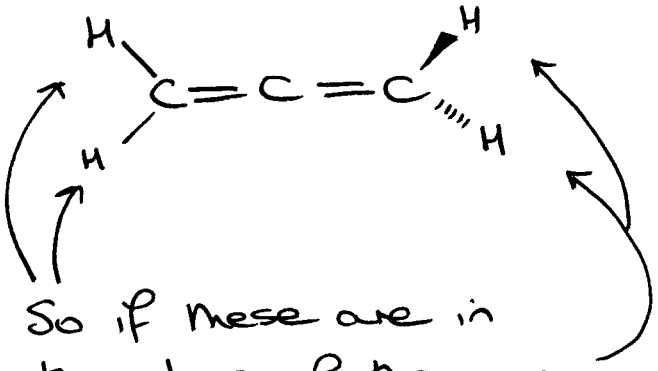
So, the π bonds will be at 90° to each other.

d) So the DIHEDRAL angle between

$H-C_a-C_b$ and C_b-C_c-H

is <u>90°</u>

e) So a better representation of allene is:

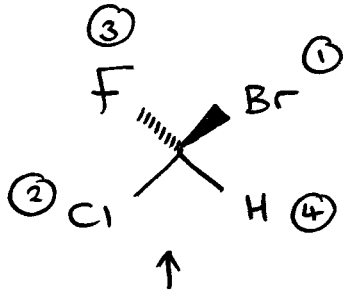


So if these are in the plane of the page,

these two go in and out of the plane of the paper (i.e. DASH & WEDGE)

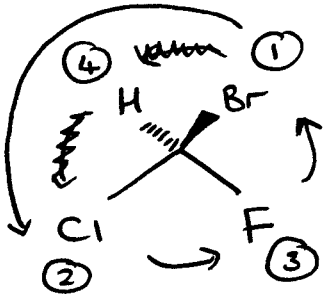
Q5

a)



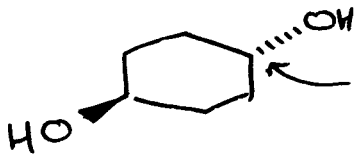
THIS IS (R)

so switch



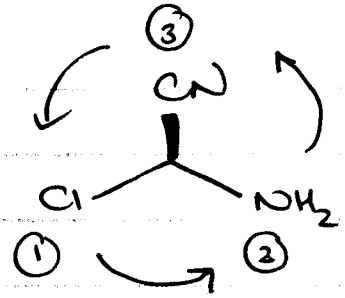
THIS IS (S)

b)



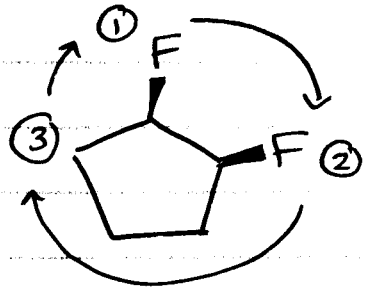
not a chiral center — only 3 different things coming from it

c)



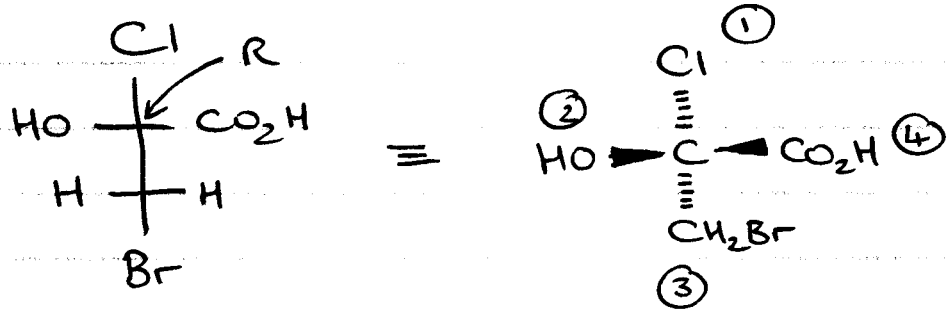
So, this is (S)

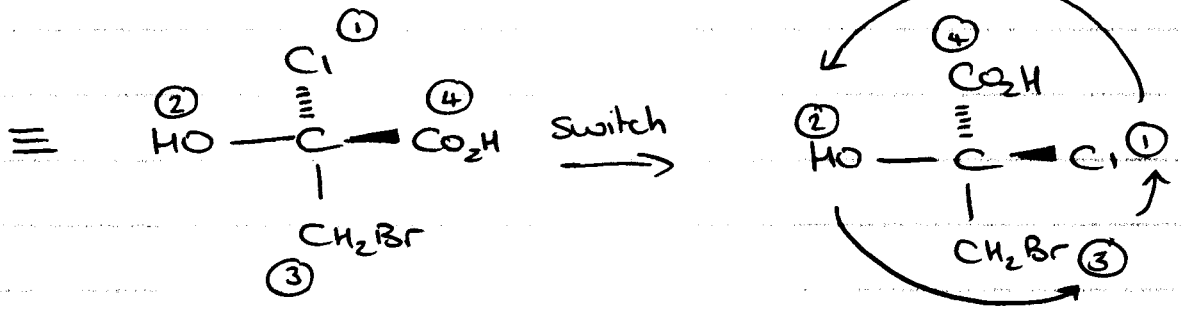
d)



So, this is (R)

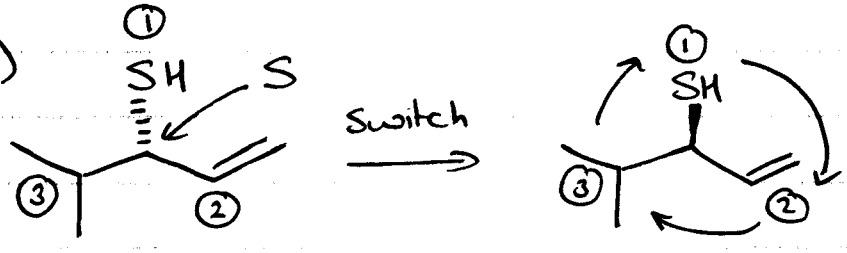
e)





THIS is (S), so...
original was (R)

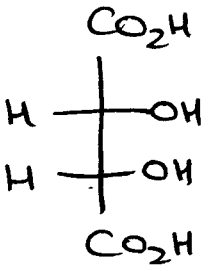
f)



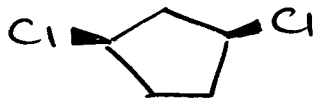
So, this is (R),
so
original was
(S)

g) ACHIRAL molecule with 2 stereocenters

So, draw a molecule that has 2 stereocenters and a plane of symmetry, such as:



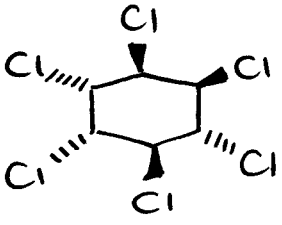
or



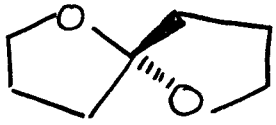
BOTH MESO

h) The only criteria for a molecule to be CHIRAL is that it is NON SUPERIMPOSABLE with it's mirror image, it has little to do with stereocenters, other than the fact that a molecule with stereocenters is usually CHIRAL, unless it is MESO.

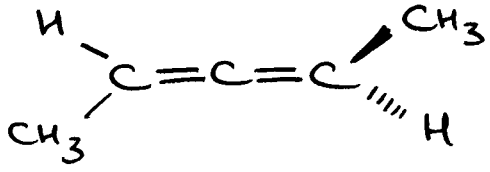
Anyway here are some examples of CHIRAL molecules with NO stereocenters



(from QZ!)

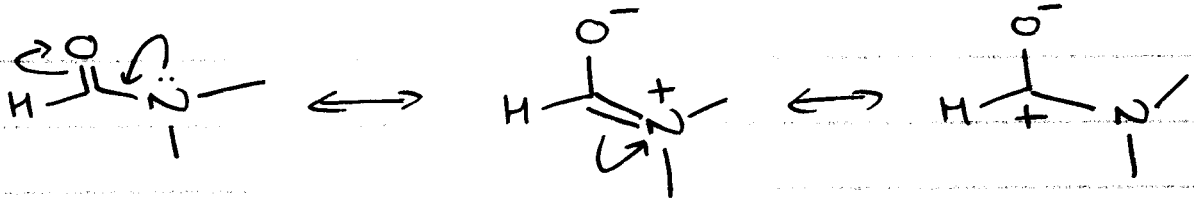


Spiro compounds



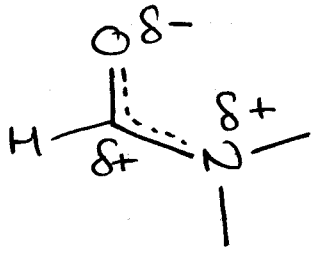
substituted alleres

Extra Credit (1)



The resonance hybrid contains charge wherever a resonance contributer contains charge, and partial bonds where a double bond appears in ONLY some contributors..

So



The rotation about the $C sp_2 - N$ bond is so slow, because it is not a single bond, it is actually a partial double bond, as there is a contributing structure that contains a C–N DOUBLE BOND

Extra Credit (2)

a) If there are two species in equilibrium, and there is more of one than the other, then that MUST BE the more stable species, ie. (B)

b) $\Delta G = -RT \ln K_{eq}$

$\Delta G = -2 \times 300 \times \ln e$

($\ln e = 1$, in fact $\log_x X = 1$)

<u>so</u> $\Delta G = -600$ cal/mol

which $= -0.6$ kcal/mol

WHY ON EARTH some of you chose to use 298 K as the temperature, I will NEVER know !!

The moral of the story, is

READ THE QUESTION!