

Name \_\_\_\_\_ **KEY** \_\_\_\_\_

You may use model kits but no other material with chemical information without instructor approval. Tables of possibly useful data are included on the last page.

Please do not use any electronic gadgets (calculators, music players, phones, etc.).

**IUPAC Periodic Table of the Elements**

1 <b>H</b> hydrogen 1.008 (1.0078, 1.0082)																	2 <b>He</b> helium 4.0026
3 <b>Li</b> lithium 6.94 (6.938, 6.997)	4 <b>Be</b> beryllium 9.0122											13 <b>B</b> boron 10.81 (10.806, 10.821)	14 <b>C</b> carbon 12.01 (12.009, 12.012)	15 <b>N</b> nitrogen 14.007 (14.006, 14.008)	16 <b>O</b> oxygen 15.999 (15.998, 16.000)	17 <b>F</b> fluorine 18.998	18 <b>Ne</b> neon 20.180
11 <b>Na</b> sodium 22.990 (24.304, 24.307)	12 <b>Mg</b> magnesium 24.304 (24.304, 24.307)											13 <b>Al</b> aluminum 26.982 (26.981, 26.983)	14 <b>Si</b> silicon 28.086 (28.084, 28.088)	15 <b>P</b> phosphorus 30.974	16 <b>S</b> sulfur 32.06 (32.059, 32.076)	17 <b>Cl</b> chlorine 35.45 (35.446, 35.457)	18 <b>Ar</b> argon 39.948
19 <b>K</b> potassium 39.098	20 <b>Ca</b> calcium 40.078(4)	21 <b>Sc</b> scandium 44.956	22 <b>Ti</b> titanium 47.867	23 <b>V</b> vanadium 50.942	24 <b>Cr</b> chromium 51.996	25 <b>Mn</b> manganese 54.938	26 <b>Fe</b> iron 55.845(2)	27 <b>Co</b> cobalt 58.933	28 <b>Ni</b> nickel 58.693	29 <b>Cu</b> copper 63.546(3)	30 <b>Zn</b> zinc 65.38(2)	31 <b>Ga</b> gallium 69.723	32 <b>Ge</b> germanium 72.630(8)	33 <b>As</b> arsenic 74.922	34 <b>Se</b> selenium 78.971(8)	35 <b>Br</b> bromine 79.904 (79.901, 79.907)	36 <b>Kr</b> krypton 83.796(2)
37 <b>Rb</b> rubidium 85.468	38 <b>Sr</b> strontium 87.62	39 <b>Y</b> yttrium 88.906	40 <b>Zr</b> zirconium 91.224(2)	41 <b>Nb</b> niobium 92.906	42 <b>Mo</b> molybdenum 95.95	43 <b>Tc</b> technetium 98	44 <b>Ru</b> ruthenium 101.07(2)	45 <b>Rh</b> rhodium 102.91	46 <b>Pd</b> palladium 106.42	47 <b>Ag</b> silver 107.87	48 <b>Cd</b> cadmium 112.41	49 <b>In</b> indium 114.82	50 <b>Sn</b> tin 118.71	51 <b>Sb</b> antimony 121.76	52 <b>Te</b> tellurium 127.60(3)	53 <b>I</b> iodine 126.90	54 <b>Xe</b> xenon 131.29
55 <b>Cs</b> caesium 132.91	56 <b>Ba</b> barium 137.33	57-71 lanthanoids	72 <b>Hf</b> hafnium 178.49(2)	73 <b>Ta</b> tantalum 180.95	74 <b>W</b> tungsten 183.84	75 <b>Re</b> rhenium 186.21	76 <b>Os</b> osmium 190.23(3)	77 <b>Ir</b> iridium 192.22	78 <b>Pt</b> platinum 195.08	79 <b>Au</b> gold 196.97	80 <b>Hg</b> mercury 200.59	81 <b>Tl</b> thallium 204.38 (204.38, 204.39)	82 <b>Pb</b> lead 207.2	83 <b>Bi</b> bismuth 208.98	84 <b>Po</b> polonium 209	85 <b>At</b> astatine 210	86 <b>Rn</b> radon 222
87 <b>Fr</b> francium 223	88 <b>Ra</b> radium 226	89-103 actinoids	104 <b>Rf</b> rutherfordium 261	105 <b>Db</b> dubnium 262	106 <b>Sg</b> seaborgium 263	107 <b>Bh</b> bohrium 264	108 <b>Hs</b> hassium 265	109 <b>Mt</b> meitnerium 266	110 <b>Ds</b> darmstadtium 267	111 <b>Rg</b> roentgenium 268	112 <b>Cn</b> copernicium 269	113 <b>Nh</b> nihonium 270	114 <b>Fl</b> flerovium 271	115 <b>Mc</b> moscovium 272	116 <b>Lv</b> livermorium 273	117 <b>Ts</b> tennessine 274	118 <b>Og</b> oganesson 277



57 <b>La</b> lanthanum 138.91	58 <b>Ce</b> cerium 140.12	59 <b>Pr</b> praseodymium 140.91	60 <b>Nd</b> neodymium 144.24	61 <b>Pm</b> promethium 145	62 <b>Sm</b> samarium 150.36(2)	63 <b>Eu</b> europium 151.96	64 <b>Gd</b> gadolinium 157.25(3)	65 <b>Tb</b> terbium 158.93	66 <b>Dy</b> dysprosium 162.50	67 <b>Ho</b> holmium 164.93	68 <b>Er</b> erbium 167.26	69 <b>Tm</b> thulium 168.93	70 <b>Yb</b> ytterbium 173.05	71 <b>Lu</b> lutetium 174.97
89 <b>Ac</b> actinium 227	90 <b>Th</b> thorium 232.04	91 <b>Pa</b> protactinium 231.04	92 <b>U</b> uranium 238.03	93 <b>Np</b> neptunium 237	94 <b>Pu</b> plutonium 244	95 <b>Am</b> americium 243	96 <b>Cm</b> curium 247	97 <b>Bk</b> berkelium 247	98 <b>Cf</b> californium 251	99 <b>Es</b> einsteinium 252	100 <b>Fm</b> fermium 257	101 <b>Md</b> mendelevium 258	102 <b>No</b> nobelium 259	103 <b>Lr</b> lawrencium 260

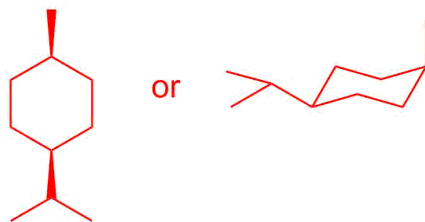
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1. (15 points) Draw correct structures for the following compounds.

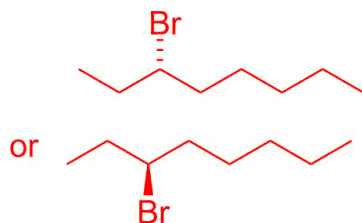
a. *trans*-1,3-dichlorocyclopentane



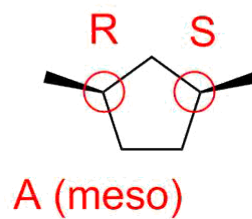
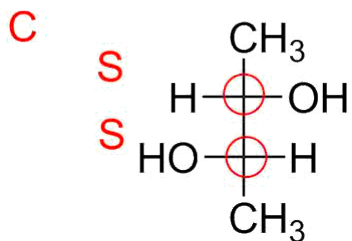
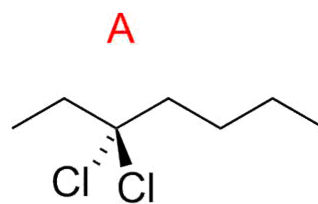
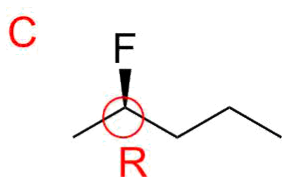
b. *cis*-4-methyl-*iso*-propylcyclohexane



c. *S*-3-bromooctane

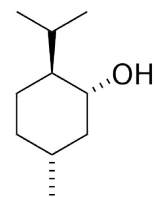


2. (20 points) Identify each molecule shown below as chiral (C) or achiral (A). Circle every stereocenter and assign the configuration as R or S.



3. (20 points) Menthol, the major flavoring component in peppermint, has the following structure (right). The specific rotation,  $[\alpha]_D = -50.2^\circ$ .

A. The enantiomer of (-)-menthol (we call it (+)-menthol) can be prepared synthetically. State what specific rotation it should show, and explain your reasoning.

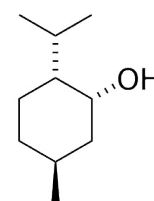


(-)-menthol

It will be  $+50.2^\circ$ . Enantiomers show equal but opposite rotations.

B. The synthesis of this enantiomer also results in a third compound, (-)-neomenthol, with the structure at the right. The amount produced varies with reaction conditions but is typically 2-15%. Its specific rotation,  $[\alpha]_D = -20.8^\circ$ .

Predict the approximate specific rotation that would be observed for the synthetic mixture of (+)-menthol and (-)-neomenthol. Explain your reasoning. (A quantitative calculation is not necessary.)



(-)-neomenthol

Since the rotation is opposite that of (+) menthol, the impurity would decrease the magnitude. Since the rotation would be dominated by the major isomer (there's more of it, and the specific rotation is larger), the sign would still be (+).

C. Which of the following mixtures could be separated by recrystallization (relying on different solubilities)?

- A 1:1 mixture of (+)-menthol and (-)-menthol
- A 1:1 mixture of (+)-menthol and (-)-neomenthol

Explain your choice(s) based on the nature of the stereochemical relationship between each pair of isomers.

A 1:1 mixture of (+)-menthol and (-)-menthol is a racemic mixture of enantiomers—they have the same solubilities and will be inseparable by recrystallization.

A 1:1 mixture of (+)-menthol and (-)-neomenthol is a mixture of two diastereomers. Their solubilities will differ, and at least one of these can be separated and purified by recrystallization from some solvent.

4. (25 points) This question deals with *cis*-1,3-dimethylcyclohexane.

A. Draw the two ring-flip isomers of the chair conformation of *cis*-1,3-dimethylcyclohexane.



B. Which of these is more stable, and by how much? Explain your reasoning.

The form on the right (diequatorial).

The energy cost of the diaxial form is  $2 \times 1.8$  kcal/mol (the cost of each methyl group going axial) PLUS the cost of the methyl-methyl steric interaction (3.7 kcal/mol) = 7.3 kcal/mol.

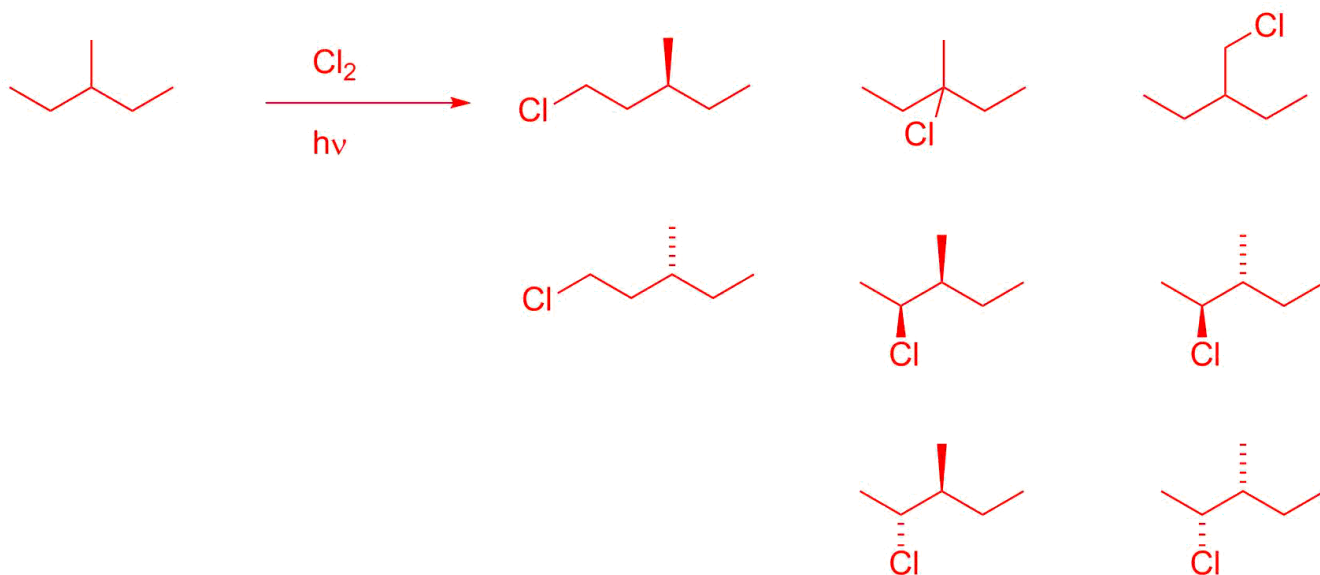
C. How would placing an oxygen at atom 5 in the ring (in place of  $\text{CH}_2$ ) change the equilibrium between the two ring flip isomers? Explain (Hint: consider why one ring flip isomer is disfavored).

This would have a minor impact, but it does remove one 1-3 transannular interaction with an axial hydrogen in the diaxial form:

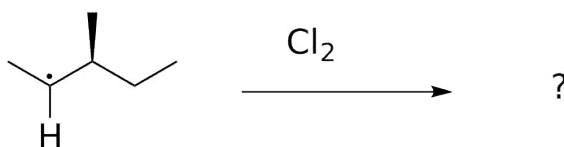


However, the transannular interaction of the methyls remains, so the cost is still  $> 3.7$  kcal/mol. While shifting the equilibrium a little bit toward the diaxial form, the difference would be small.

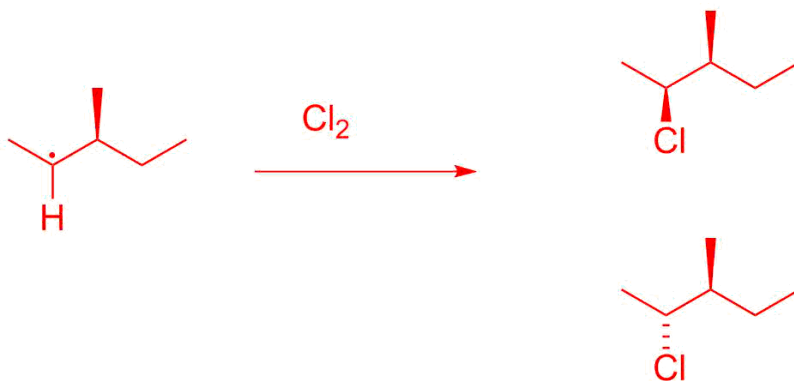
5. (20 points) Draw each product expected from monochlorination of 3-methylpentane using  $\text{Cl}_2$  and  $h\nu$ . Include all distinct stereoisomers.



If the following free radical intermediate could be generated selectively (a challenging task!), would its reaction with  $\text{Cl}_2$  generate a racemic or a nonracemic mixture of products? Explain.



The reaction would form two diastereomers: the stereocenter at C3 would be the same in both (and would be S), but formation of a new C-Cl bond can occur from either face and would create approximately equal amounts of the R and S configurations.



## Bond strengths (kcal/mol):

F-F	38
Cl-Cl	58
Br-Br	46
I-I	36
H-F	136
H-Cl	103
H-Br	87
H-I	71
CH <sub>3</sub> -H	105
CH <sub>3</sub> CH <sub>2</sub> -H	101
(CH <sub>3</sub> ) <sub>2</sub> CH-H	98.5
(CH <sub>3</sub> ) <sub>3</sub> C-H	96.5
CH <sub>3</sub> -F	110
CH <sub>3</sub> -Cl	85
CH <sub>3</sub> -Br	70
CH <sub>3</sub> -I	57
CH <sub>3</sub> CH <sub>2</sub> -F	111
CH <sub>3</sub> CH <sub>2</sub> -Cl	84
CH <sub>3</sub> CH <sub>2</sub> -Br	70
CH <sub>3</sub> CH <sub>2</sub> -I	56
(CH <sub>3</sub> ) <sub>2</sub> CH-F	111
(CH <sub>3</sub> ) <sub>2</sub> CH-Cl	84
(CH <sub>3</sub> ) <sub>2</sub> CH-Br	71
(CH <sub>3</sub> ) <sub>2</sub> CH-I	56
(CH <sub>3</sub> ) <sub>3</sub> C-F	110
(CH <sub>3</sub> ) <sub>3</sub> C-Cl	85
(CH <sub>3</sub> ) <sub>3</sub> C-Br	71
(CH <sub>3</sub> ) <sub>3</sub> C-I	55

## A values (kcal/mol)

<u>Substituent</u>	<u>A</u>
Me	1.8
Et	1.8
<sup>i</sup> Pr	2.1
<sup>t</sup> Bu	4.5
O-Me	0.75
Cl	0.52
Br	0.55
I	0.46
Methyl-Methyl 1,3 interaction	3.7