Name $\qquad$

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.).
 PURE AND APPLIED CHEMISTRY


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
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, $[\alpha]_{\mathrm{D}}=-20.8^{\circ}$.

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.)

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.
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.
C. How would placing an oxygen at atom 5 in the ring (in place of $\mathrm{CH}_{2}$ ) change the equilibrium between the two ring flip isomers? Explain (Hint: consider why one ring flip isomer is disfavored).
5. (20 points) Draw each product expected from monochlorination of 3-methylpentane using $\mathrm{Cl}_{2}$ and hv . Include all distinct stereoisomers.

If the following free radical intermediate could be generated selectively (a challenging task!), would its reaction with $\mathrm{Cl}_{2}$ generate a racemic or a nonracemic mixture of products? Explain.

?

Bond strengths (kcal/mol):

| $\mathrm{F}-\mathrm{F}$ | 38 |
| :--- | :--- |
| $\mathrm{Cl}-\mathrm{Cl}$ | 58 |

$\mathrm{Br}-\mathrm{Br} \quad 46$
I-I 36
H-F 136
$\mathrm{H}-\mathrm{Cl} \quad 103$
$\mathrm{H}-\mathrm{Br} \quad 87$
$\mathrm{H}-\mathrm{I} \quad 71$
$\mathrm{CH}_{3}$ - $\mathrm{H} \quad 105$
$\mathrm{CH}_{3} \mathrm{CH}_{2}-\mathrm{H} \quad 101$
$\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}-\mathrm{H} \quad 98.5$
$\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}-\mathrm{H} \quad 96.5$
$\mathrm{CH}_{3}-\mathrm{F} \quad 110$
$\mathrm{CH}_{3}-\mathrm{Cl} \quad 85$
$\mathrm{CH}_{3}-\mathrm{Br} \quad 70$
$\mathrm{CH}_{3}-\mathrm{I} \quad 57$
$\mathrm{CH}_{3} \mathrm{CH}_{2}-\mathrm{F} \quad 111$
$\mathrm{CH}_{3} \mathrm{CH}_{2}-\mathrm{Cl} \quad 84$
$\mathrm{CH}_{3} \mathrm{CH}_{2}-\mathrm{Br} \quad 70$
$\mathrm{CH}_{3} \mathrm{CH}_{2}$-I 56
$\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}-\mathrm{F} \quad 111$
$\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}-\mathrm{Cl} 84$
$\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}-\mathrm{Br} \quad 71$
$\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}-\mathrm{I} \quad 56$
$\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}-\mathrm{F} \quad 110$
$\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}-\mathrm{Cl} \quad 85$
$\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}-\mathrm{Br} \quad 71$
$\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}-\mathrm{I} \quad 55$

A values (kcal/mol)

| Substituent | $A$ |
| :--- | :--- |
| Me | 1.8 |
| Et | 1.8 |
| ${ }^{\mathrm{i} P r}$ | 2.1 |
| ${ }^{\mathrm{t}} \mathrm{Bu}$ | 4.5 |
| $\mathrm{O}-\mathrm{Me}$ | 0.75 |
| Cl | 0.52 |
| Br | 0.55 |
| I | 0.46 |

Methyl-Methyl 1,3
interaction 3.7

