Organic Chemistry Mechanistic Patterns (Canadian) 1st edition Ogilvie Solutions Manual

SKU: 9780176500269-SOLUTIONS

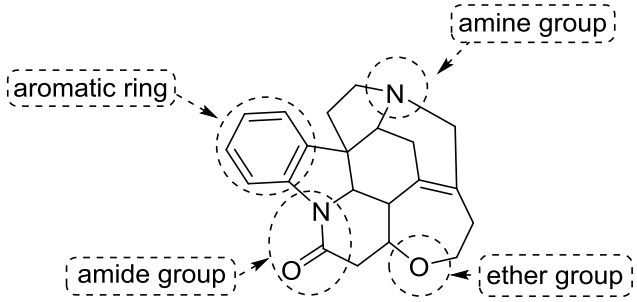
Chapter 2
Anatomy of an Organic Molecule

CHECKPOINT PROBLEMS

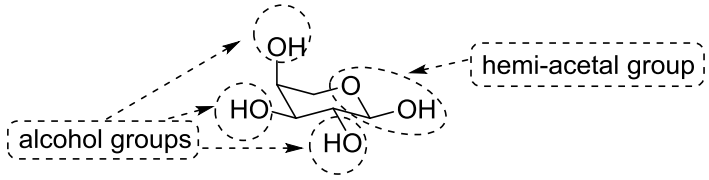
Practice Problem 2.1

Functional groups are shown in the following molecules.

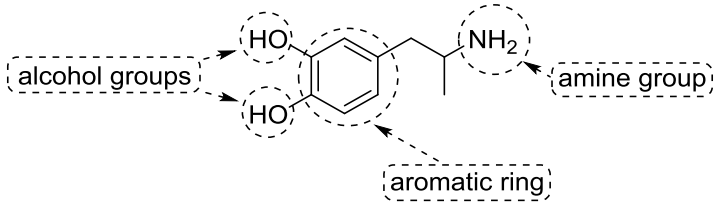
a)



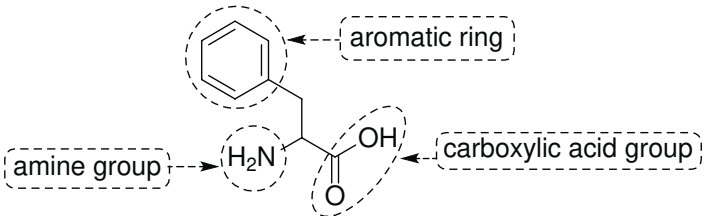
b)



c)



d)



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Integrate the Skill 2.2

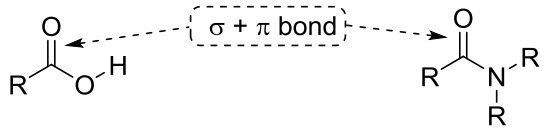
There are two groups based on the type of bonds involved (σ or π) in each of the functional groups in the molecules above. The following groups are all formed using only σ bonds:

alcohol group amine group ether group hemi-acetal group



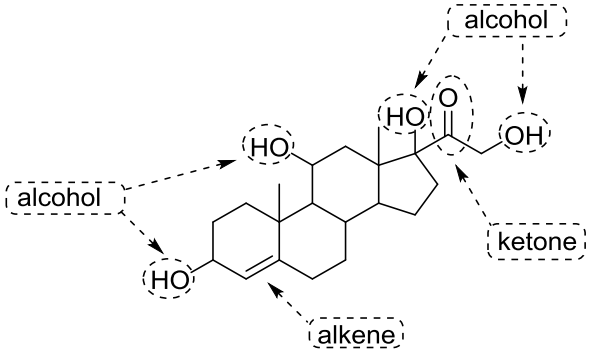
The following groups have both σ and π bonds. The π bonds are noted; all the rest are σ bonds.

carboxylic acid group amide group

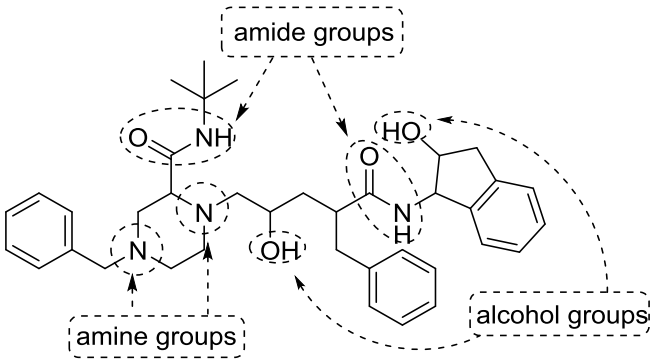


Practice Problem 2.3

a) The molecule has four alcohol groups. These can act as hydrogen bond donors and hydrogen bond acceptors. The oxygen in the ketone group can also act as a hydrogen bond acceptor.



b) The molecule has three types of functional groups. The amine groups with no attached hydrogen atoms can act as hydrogen bond acceptors. The alcohol groups will be hydrogen bond donors and hydrogen bonds acceptors. The amide groups will act as hydrogen bond donors and hydrogen bond acceptors.

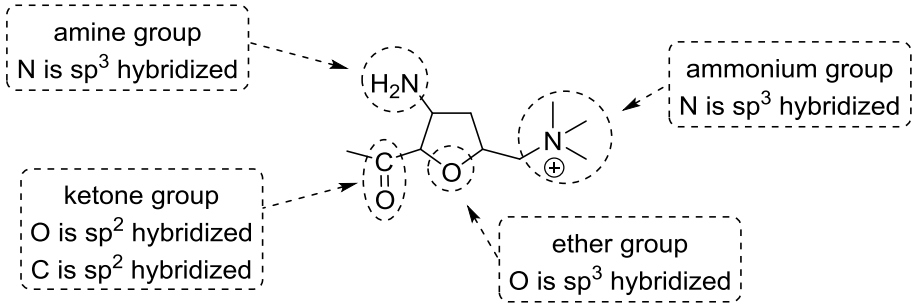


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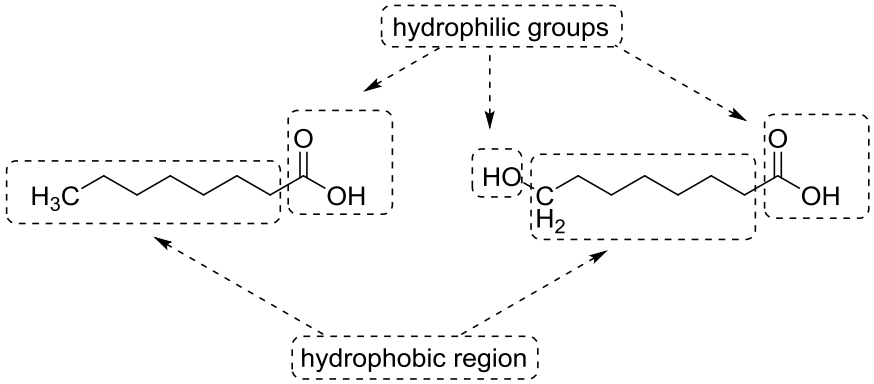
Integrate the Skill 2.4

Functional groups and hybridizations for atoms in each group are shown.

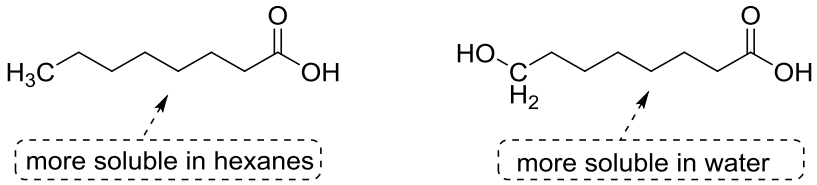


Practice Problem 2.5

The two molecules are drawn below, with hydrophobic and hydrophilic regions indicated.

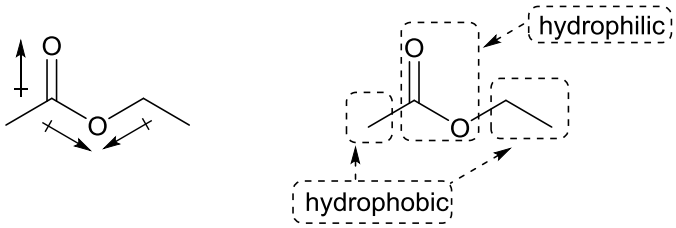


The alcohol-containing molecule would be more soluble in water, since it has an extra hydrogen bond site (donor and acceptor). The long hydrocarbon chain in the other molecule would interact favourably with long-chain hydrocarbon solvents like hexanes and make it more soluble in hexanes.



Integrate the Skill 2.6

Lewis structure of ethyl acetate—$CH_3CO_2CH_2CH_3$—with bond dipoles and hydrophobic and hydrophilic regions indicated:



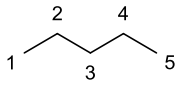
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Practice Problem 2.7

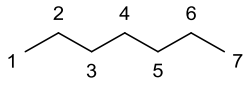
a) Five-carbon main chain:

$CH_3CH_2CH_2CH_2CH_3$



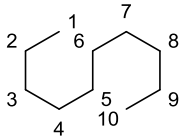
pentane

b) Seven-carbon main chain:



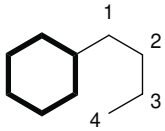
heptane

c) Ten-carbon main chain:



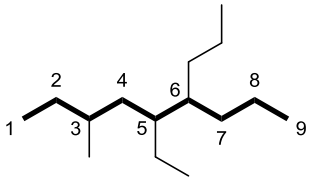
decane

d) The largest group of carbons are in the six-membered ring (in bold) with a four-carbon substituent.



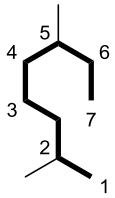
butylcyclohexane

e) The main chain has nine carbons (in bold) with three sidechains. The sidechains are given in alphabetical order and the main chain is numbered to minimize the numbers on the substituents.



5-ethyl-3-methyl-6-propylnonane

f) The main chain has seven carbons (in bold) with two methyl sidechains.

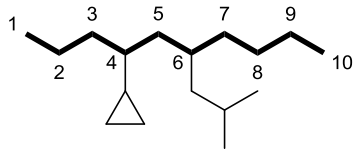


2,5-dimethylheptane

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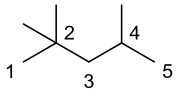
g)



4-cyclopropyl-6-(2-methylprop-1-yl)decane

Integrate the Skill 2.8

a) The IUPAC name for this compound is *isooctane*.

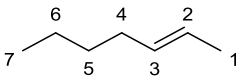


2,2,4-trimethylpentane

b) Octane is a straight-chain molecule. It can efficiently pack with other octane molecules to establish dispersion attractions. Isooctane is a branched molecule and, therefore, has a shorter carbon chain to effectively interact with other isooctane molecules. The branches will also inhibit effective packing of the molecule. So, octane will have greater dispersion attractions and a higher boiling point.

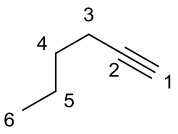
Practice Problem 2.9

a)



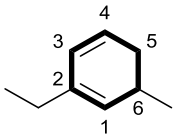
2-heptene

b)



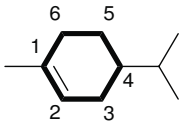
1-hexyne

c) The double bonds are in the ring, so it is named as a *cyclohexadiene*, shown in bold.



2-ethyl-6-methylcyclohexa-1,3-diene

d) The molecule is a redrawn in a planar projection for clarity.



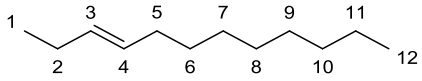
1-methyl-4-(1-methylethyl)cyclohex-1-ene

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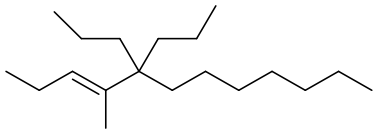
Integrate the Skill 2.10

First, draw the main chain, numbering the atoms in the chain. This helps with substituents.



dodec-3-ene

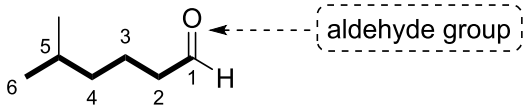
Now, add the substituents.



4-methyl-5,5-dipropyldodec-3-ene

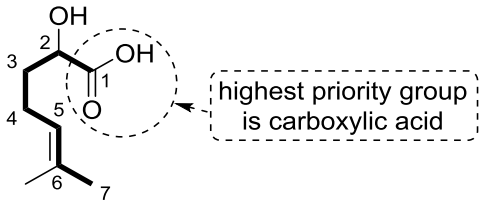
Practice Problem 2.11

a) The only functional group is an aldehyde, so the suffix is *-al*. Numbering is from the functional group end.



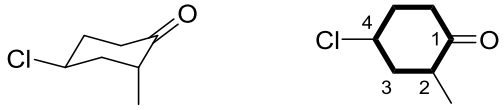
5-methylhexanal

b) The highest priority group is the carboxylic acid, with seven carbons in the longest chain. The alcohol group is named as a substituent, as it is not the highest priority functional group.



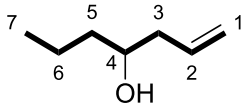
2-hydroxyhept-5-enoic acid

c) The ketone is the highest priority group. The substituents are named alphabetically.



4-chloro-2-methylcyclohexanone

d) The highest priority group is the alcohol. The locations of the double bond and the alcohol must be specified.



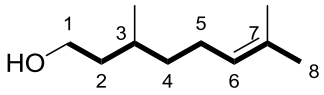
hept-1-en-4-ol

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Integrate the Skill 2.12

The systematic name of the molecule is based on an eight-carbon main chain (in bold). The highest priority functional group is the alcohol. Numbering starts at the alcohol end and leads to the following name.

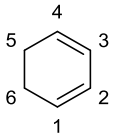


3,7-dimethyloct-6-en-1-ol

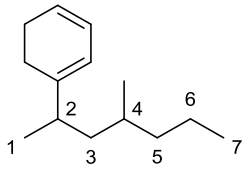
There are many possible results from searches. Wikipedia is one location with a large amount of chemical information that is generally properly referenced. Searching for "3,7-dimethyloct-6-en-1-ol" leads to the following page: https://en.wikipedia.org/wiki/Citronellol. The common name of this molecule is *citronellol*, reminiscent of *citronella oil*, of which citronellol is a component. It is often used to ward off biting insects like mosquitos and blackflies.

Practice Problem 2.13

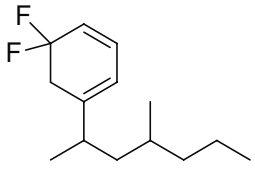
The root is cyclohexa-1,3-diene, so the framework upon which to build the molecule is



1-(4-methylheptan-2-yl) is a seven-carbon group attached by the second carbon in the chain. This group also has a methyl attached on the fourth carbon. This is connected to carbon 1 in the ring.



"5,5-difluoro" refers to two fluorine atoms, which are both attached to carbon 5 in the ring.



5,5-difluoro-1-(1,4-dimethylhexanyl)cyclohexa-1,3-diene

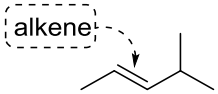
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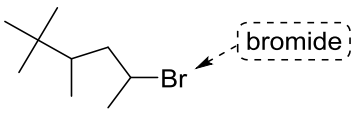
PROBLEMS

2.14

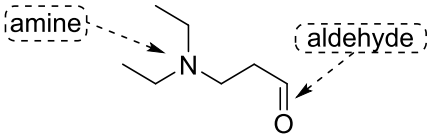
a)



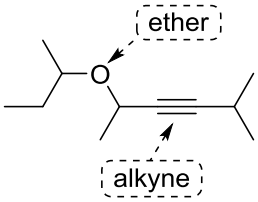
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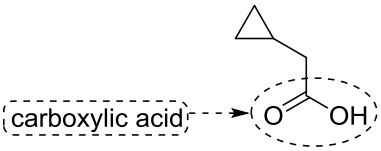
c)



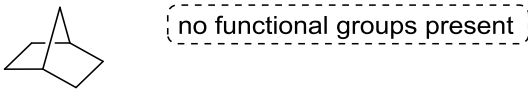
d)



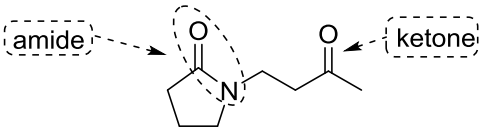
e)



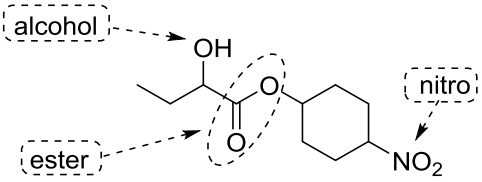
f)



g)

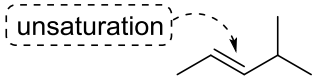


h)

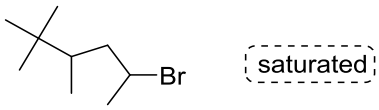


2.15 For unsaturated molecules, the site of unsaturation is indicated in the structures shown.

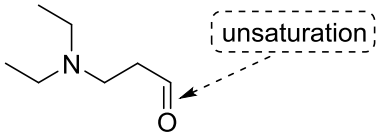
a)



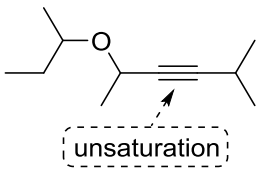
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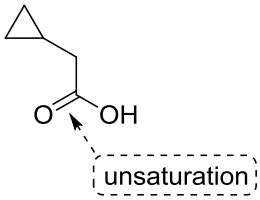
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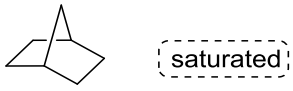
d)



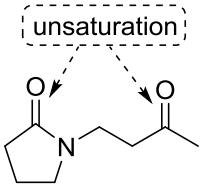
e)



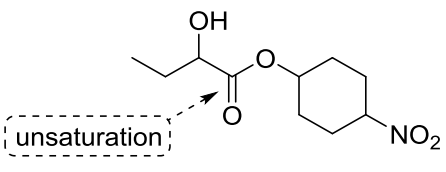
f)



g)



h)

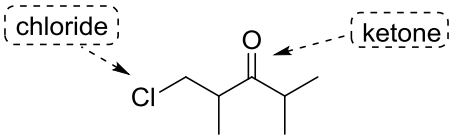


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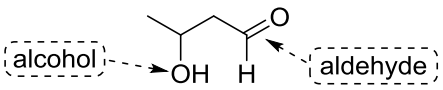
2.16 Line structures and functional groups are shown.

a)



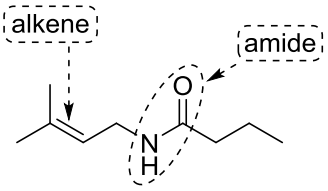
$ClCH_2CH(CH_3)COCH(CH_3)_2$

b)



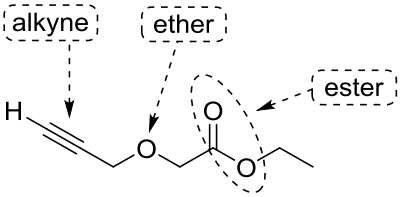
$CH_3CH(OH)CH_2CHO$

c)



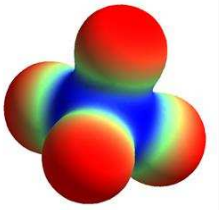
$(CH_3)_2C{=}CHCH_2NHCO(CH_2)_2CH_3$

d)



$HCCCH_2OCH_2COOC_2H_5$

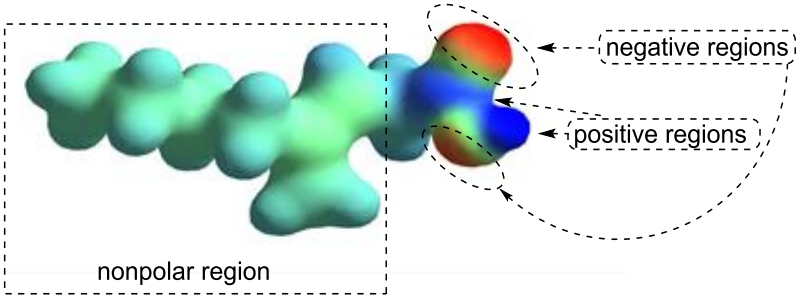
2.17



CF_4

The electron density is concentrated on the fluorine atoms (outer regions; red in the textbook) since fluorine is highly electronegative and attracts electron density away from the carbon atom (central region; blue in the textbook). In methane, the charge density is evenly distributed, since carbon and hydrogen have similar electronegativities.

2.18



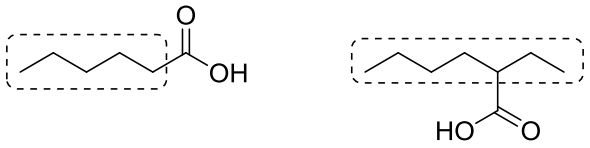
The non-polar region of the molecule is the long chain on the left. In the electrostatic potential map in the textbook, it is a light blue-green. The negative parts of the molecule are red in the electrostatic potential map in the textbook. The positive regions are dark blue in the electrostatic potential map in the textbook.

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2.19

The intermolecular forces would involve hydrogen bonding from the carboxylic acid groups. This would be similar for both molecules. The only difference would be in the dispersion forces between the hydrocarbon chains. Line drawings of both would look like:

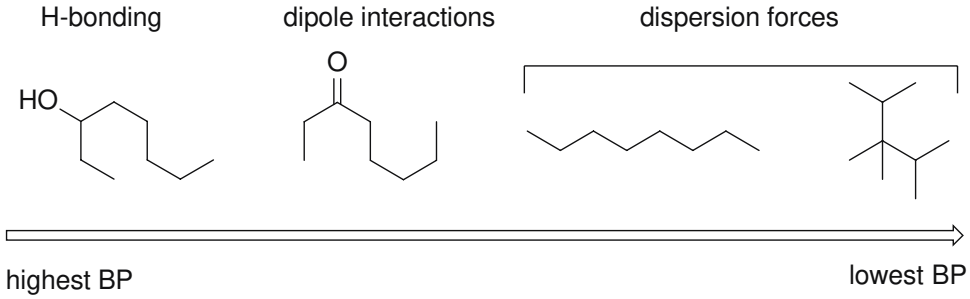


The alkane region in 2-ethylhexanoic acid is seven carbons long, while it is only five in hexanoic acid. This would result in more attractions in 2-ethylhexanoic acid and, therefore, 2-ethylhexanoic acid should have a higher boiling point.

2.20

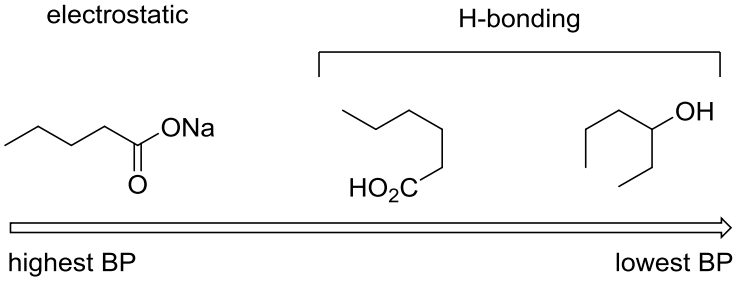
Molecules ranked in decreasing order of their *expected* boiling points.

a)



Since all the molecules are of similar size, the types of forces determine the order of expected boiling points. H-bonding is the strongest (highest BP), followed by dipole interactions, with dispersion forces being the weakest (lowest BP). The straight-chain alkane will have a higher boiling point, since the chains have more effective contact with neighbouring molecules and a higher net force of attraction.

b)

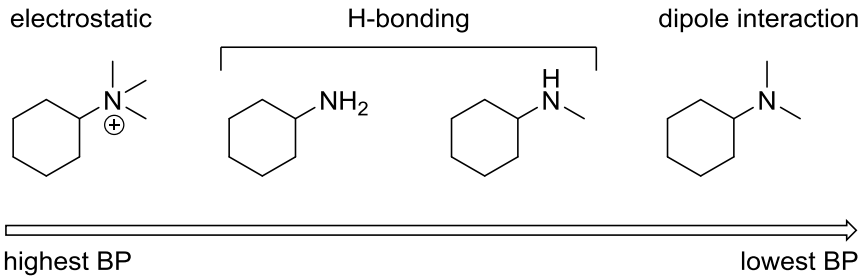


The highest BP would be for the sodium salt, since there are full charges and electrostatic forces of attraction. The carboxylic acid group is more polar than the alcohol, so the H-bonding would be stronger in the acid.

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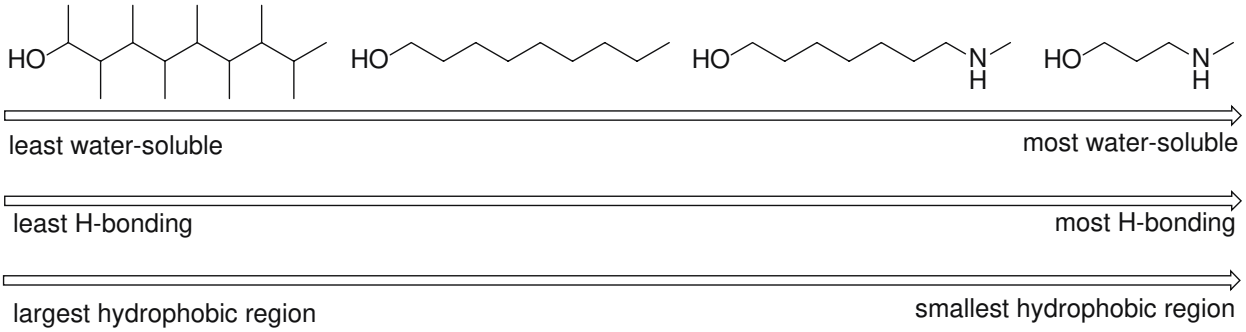
c)



The ammonium salt has isolated charges and electrostatic interactions. The molecules with hydrogen-substituted N atoms will have H-bonding. It will be stronger for the nitrogen with two attached hydrogens. The last molecule has no H-bond donors, so only dipole interactions are possible.

2.21

Molecules ranked in the expected order of increasing solubility in water:



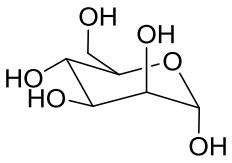
The two most soluble molecules have two hydrogen bonding groups on them. The smaller of the two will be most soluble, since it has a smaller hydrophobic region. The two least-soluble molecules have one hydrogen bonding group, but the least-soluble one has a much larger hydrophobic region due to the extra methyl substituents.

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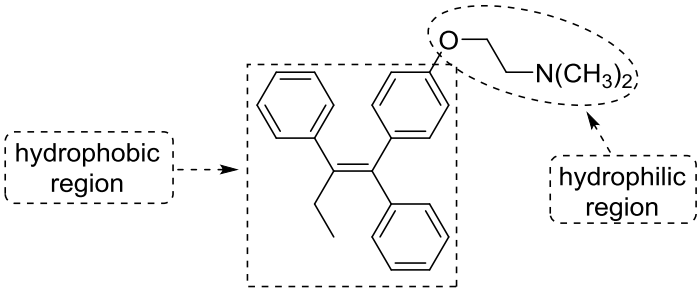
2.22

a)



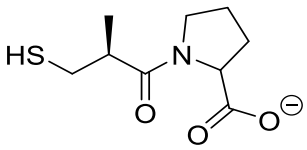
All of the –OH groups are hydrogen-bonding donors and acceptors. The ring carbons will be the hydrophobic region, but they are all close to polar groups. This will make this molecule very soluble in water and not very soluble in non-polar organic solvents.

b)



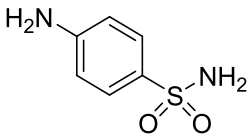
The majority of this molecule is hydrophobic and it should be soluble in organic solvents. The hydrophilic region is small in comparison, so only limited solubility in water would be expected.

c)



The amide and carboxylate groups are all hydrophilic. The carbon backbone is hydrophobic. This molecule has a formal charge (carboxylate group) and hydrogen bond acceptors (amide and carboxylate). So, it should have good solubility in water and polar organic solvents. It would have limited solubility in non-polar organic solvents.

d)



The amine ($–NH_2$) and $–SO_2NH_2$ groups are hydrophilic hydrogen bond donors and acceptors. The aromatic ring would be the hydrophobic region. It should have good solubility in water and polar organic solvents. It would have limited solubility in non-polar organic solvents.

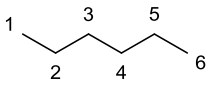
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2.23

Carbons in the main chain are numbered in some diagrams to assist in naming.

a)

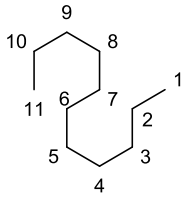


hexane

b) $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

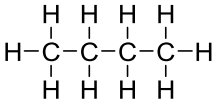
octane

c)



undecane

d)

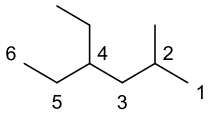


butane

2.24

Carbons in the main chain are numbered in some diagrams to assist in naming.

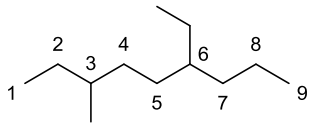
a)



4-ethyl-2-methylhexane

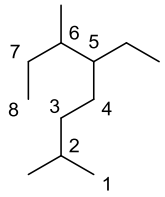
b) Line structure makes naming easier.

$CH_3CH_2CCH_3CH_2CH_2CH(CH_2CH_3)CH_2CH_2CH_3$



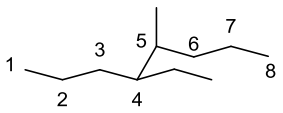
6-ethyl-3-methylnonane

c)



5-ethyl-2,6-dimethyloctane

d)



4-ethyl-5-methyloctane

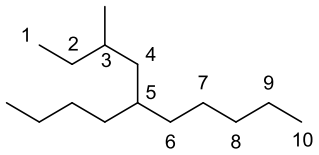
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2.25

Carbons in the main chain are numbered in some diagrams to assist in naming.

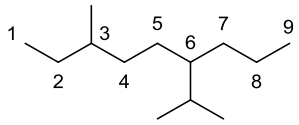
a) This might also be referred to as "4-(*n*-butyl)-3-methyldecane."



4-(1-butyl)-3-methyldecane

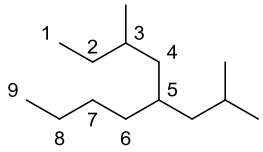
b) Converting condensed structure to a line structure makes naming easier.

$CH_3CH_2CCH_3CH_2CH_2CH(CH(CH_3)_2)CH_2CH_2CH_3$



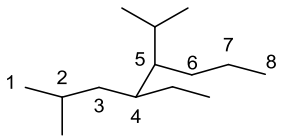
3-methyl-6-(2-propyl)nonane

c)



3-methyl-5-(2-methylpropyl)nonane
or
3-methyl-5-isobutylnonane

d)



4-ethyl-2-methyl-5-(2-propyl)octane

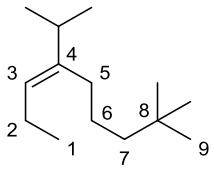
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2.26

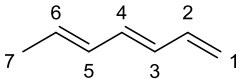
Carbons in the main chain are numbered in some diagrams to assist in naming.

a)



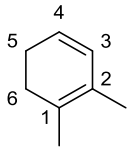
8,8-dimethyl-4-(2-propyl)non-3-ene

b)



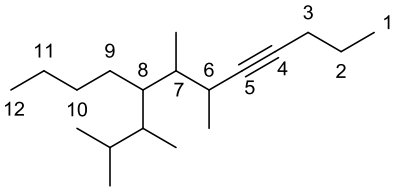
1,3,5-heptatriene

c)



1,2-dimethylcyclohexa-1,4-diene

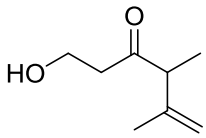
d)



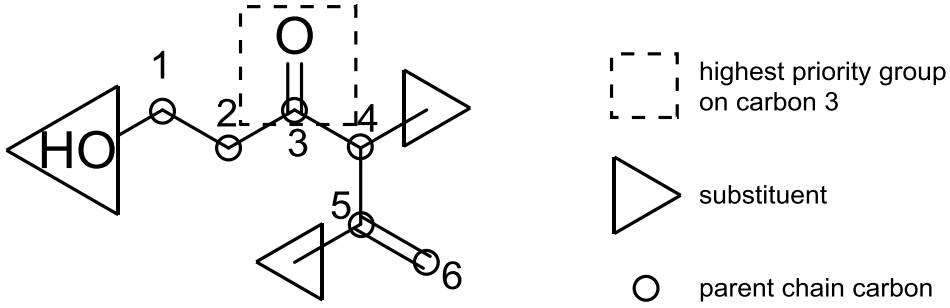
8-(3-methylbut-2-yl)-6,7-dimethyldodec-4-yne

2.27

Parts (a) through (h) refer to this molecule.



Answers to (a), (b), (c), and (e) appear in the diagram below.



d) Root name: hex-5-en-3-one

f) Substituents: C1 hydroxy, C4 methyl, C5 methyl

g) 1-hydroxy-4,5-dimethyl

h) 1-hydroxy-4,5-dimethylhex-5-en-3-one

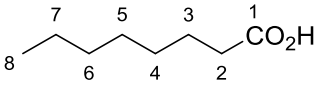
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2.28

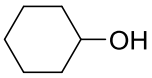
Carbons in the main chain are numbered in some diagrams to assist in naming.

a)



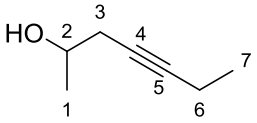
octanoic acid

b)



cyclohexanol

c)

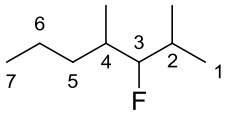


hept-4-yne-2-ol

2.29

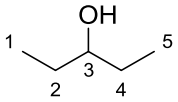
Carbons in the main chain are numbered in some diagrams to assist in naming.

a)



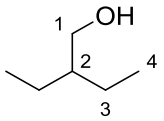
3-fluoro-2,4-dimethylheptane

b)



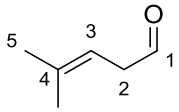
3-pentanol

c)



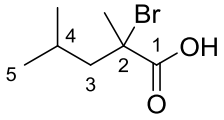
2-ethyl-1-butanol

d)



4-methylpent-3-enal

e)



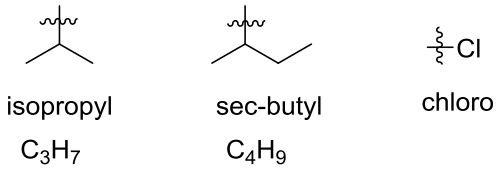
2-bromo-2,4-dimethylpentanoic acid

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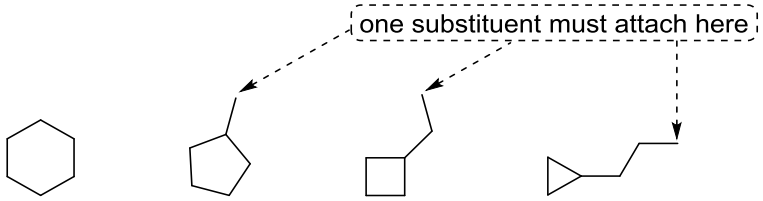
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2.30

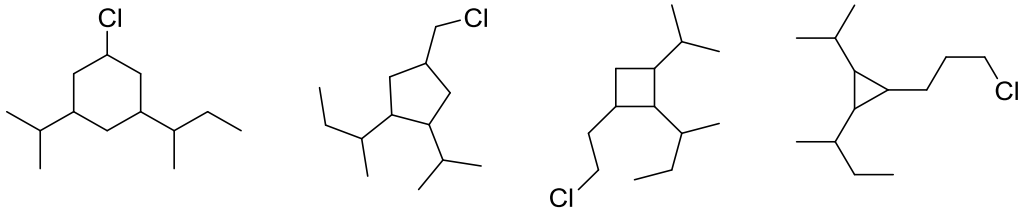
a) First, account for the atoms needed for substituents. The three groups would require seven carbon atoms, sixteen hydrogen atoms, and the chlorine atom.



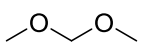
This leaves C_6H_9 for the ring. This could be a cyclohexane ring, a cyclopentane ring with a $–CH_2–$ sidechain, a cyclobutane with a $–(CH_2)_2–$ sidechain, or a cyclopropane with a $–(CH_2)_3–$ sidechain. One of the substituents needs to be on the sidechain of the smaller rings to meet the criteria presented. Other substituents must be on the ring in all four cases.



There are many possible molecules, depending on where the substituents are attached. Some examples are shown below.



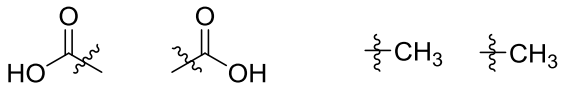
b) There are no unsaturations (rings or double bonds), based on the molecular formula. So, all bonds will have to be single bonds. The oxygen atoms will have lone pairs, which will provide the hydrogen bond acceptor property. Alcohols cannot be used, since that would make the molecule a hydrogen bond donor. So, the oxygen atoms need to be bonded to two carbon atoms, which leads to the only possible molecule: an acetal.



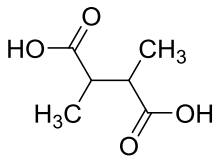
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c) The required groups will consume four C, eight H, and four O atoms.

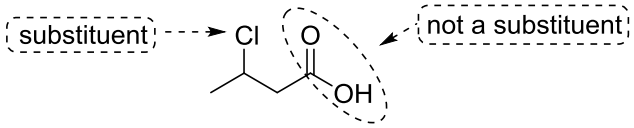


This leaves two C and two H for the backbone. There is more than one possible answer, depending on where the groups are attached to the two-carbon framework. One possible molecule is shown.



2.31

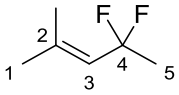
In order for a substituent to not be a functional group, it would have to be an alkyl group. An ethyl group would be an example of this. A functional group is not a substituent if it is the highest priority group in the molecule and, therefore, the basis for the name of the molecule. The carboxylic acid group in 3-chlorobutanoic acid would be an example of this.



2.32

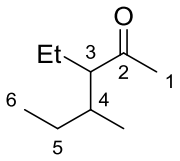
Carbons in the main chain are numbered in some diagrams to assist in naming.

a)



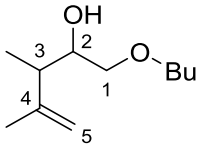
4,4-difluoropent-2-ene

b)



3-ethyl-4-methylhex-2-one

c)

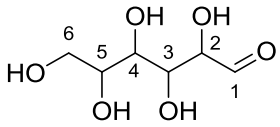


1-butoxy-3-methylpent-4-en-2-ol

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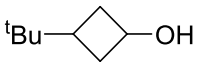
2.33



2,3,4,5,6-pentahydroxyhexanal

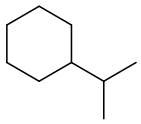
2.34

a)



3-(2-methylprop-2-yl)cyclobutanol

b)



isopropylcyclohexane

2.35

a) **i)** 2-methylpropan-1-al prefix: 2-methyl
root: propan suffix: 1-al

ii) 2,3-dichlorocyclopent-1-ene prefix:
2,3-dichloro
root: cyclopent
suffix: 1-ene

iii) heptan-3-ol prefix: none root: heptan
suffix: 3-ol

iv) 5,6-diethyl-7-hydroxyoct-1-yn-3-one
prefix: 5,6-diethyl-7-hydroxy
root: oct-1-yn
suffix: 3-one

b) **i)** aldehyde (-al)
ii) alkene (-ene)
iii) alcohol (-ol)
iv) ketone (-one)

c) **i)** prop = 3 carbon chain
C=O double bond at C1

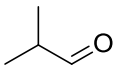
ii) pent = 5 carbon chain
C=C double bond at C1

iii) hept = 7 carbon chain
no multiple bonds

iv) oct = 8 carbon chain C≡C triple bond
at C1 C=O double bond at C3

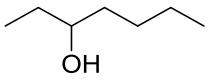
d) **i)** methyl group at C2
ii) chloro group at C2 chloro group at C3
iii) no substituents
iv) ethyl group at C5 ethyl group at C6
hydroxyl group at C7

e) **i)**



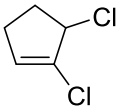
2-methylpropan-1-al

iii)



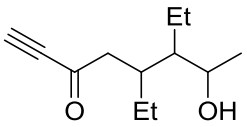
heptan-3-ol

ii)



2,3-dichlorocyclopent-1-ene

iv)

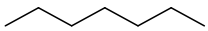


5,6-diethyl-7-hydroxyoct-1-yn-3-one

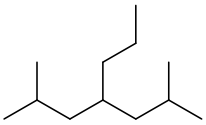
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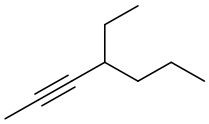
2.36

a) 

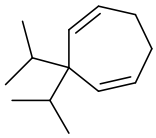
heptane

b) 

2,6-dimethyl-4-propylheptane

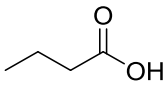
c) 

4-ethylhept-2-yne

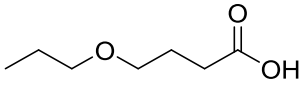
d) 

3,3-diisopropylcyclohepta-1,4-diene

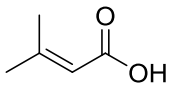
2.37

a) 

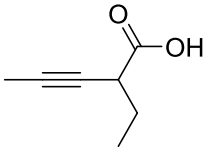
butanoic acid

b) 

4-propoxybutanoic acid

c) 

3-methylbut-2-enoic acid

d) 

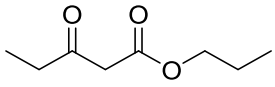
2-ethylpent-3-ynoic acid

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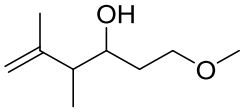
2.38

a)



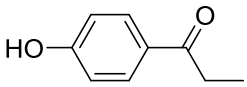
propyl 3-oxopentanoate

b)



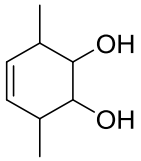
1-methoxy-4,5-dimethylhex-5-en-3-ol

c)



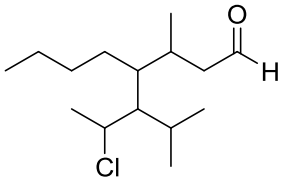
1-(4-hydroxyphenyl)propan-1-one

d)



3,6-dimethylcyclohex-4-ene-1,2-diol

e)

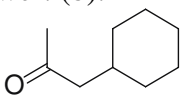


4-(2-chloro-4-methylpentan-3-yl)-3-methyloctanal

MCAT Style Problems

2.39

Answer: (b).



1-cyclohexylpropan-2-one

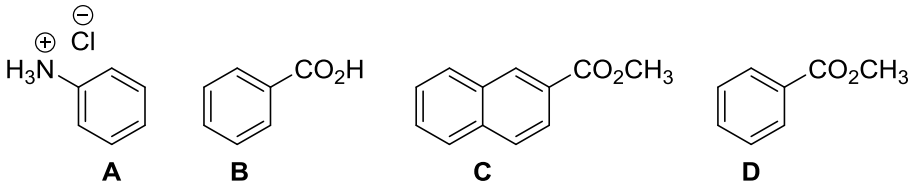
For (a), 2-oxo-propylbenzene, there is no aromatic ring. Answer (c), 1-cyclohexylacetaldehyde, is a ketone, not an aldehyde. For (d), 2-oxo-propylcyclohexane, the highest-priority group is the ketone, so the suffix should be *-one*.

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2.40

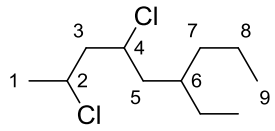
Place the following molecules in order of increasing solubility in water.



Answer: (d); **C** < **D** < **B** < **A**. The charged molecule (**A**) would be most soluble, due to electrostatic interactions with the water. **B** would be next most soluble, with the carboxylic acid being both a hydrogen bond donor and acceptor. **C** and **D** are only hydrogen bond acceptors and would be the least soluble. **C** would be less soluble than **D**, since it has a larger hydrophobic region.

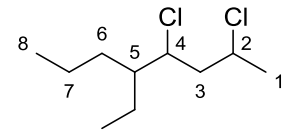
2.41

Answer: (d).



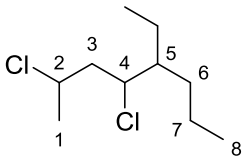
2,4-dichloro-5-ethylnonane

a)



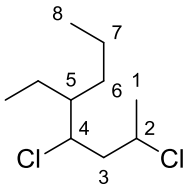
2,4-dichloro-5-ethyloctane

b)



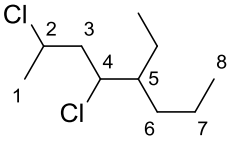
2,4-dichloro-5-ethyloctane

c)



2,4-dichloro-5-ethyloctane

e)



2,4-dichloro-5-ethyloctane

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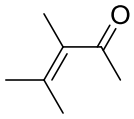
2.42

Answer: (d). The map has to have negatively polarized areas (red) for the fluorine and oxygen atoms. The maps in (a) and (d) are the only ones showing this. This rules out (b) and (c). The hydrogen attached to the oxygen atom would be positively polarized (dark blue). Map (d) is the only one with this feature, so (d) is the correct map.

Challenge Problems

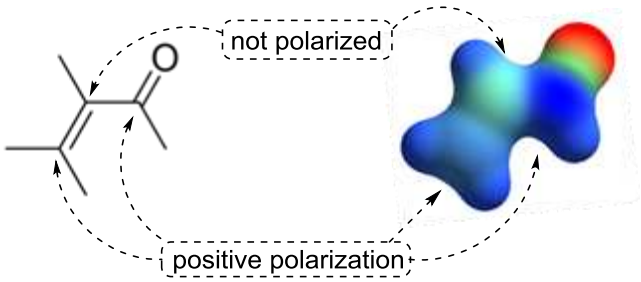
2.43

a)

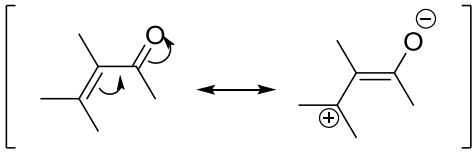


3,4-dimethylpent-3-en-2-one

b)



The electrostatic map shows that the carbon nearest the oxygen and the one on the double bond furthest from the oxygen are positively polarized, while the middle one is more neutral. The one closest to the oxygen is electron deficient, due to the electronegative oxygen drawing electron density away from it. The second resonance form (shown below) shows a formal charge on the other electron deficient carbon, explaining its lack of electron density.

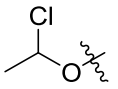


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2.44

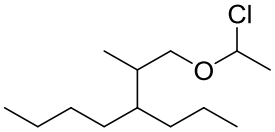
a)



(1-chloroethoxy)

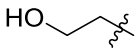


propan-2-yl

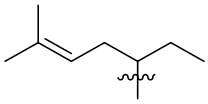


4-(1-(1-chloroethoxy)propan-2-yl)octane

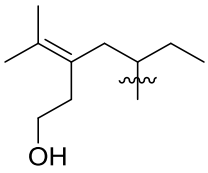
b)



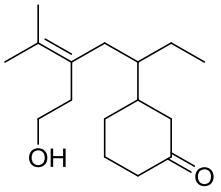
2-hydroxyethyl



6-methylhept-5-en-3-yl



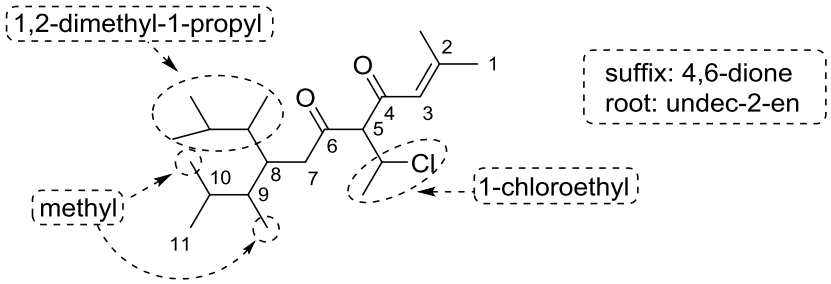
5-(2-hydroxyethyl)-6-methylhept-5-en-3-yl



3-(5-(2-hydroxyethyl)-6-methylhept-5-en-3-yl)cyclohexan-1-one

2.45

The main chain is numbered and the various substituents are identified in the figure below. The isopropyl groups need to be expanded into line-drawing form to correctly name the molecule.



The systematic name would then be: 5-(1-chloroethyl)-9,10-dimethyl-8-(1,2-dimethyl-1-propyl)undec-2-en-4,6-dione.

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