

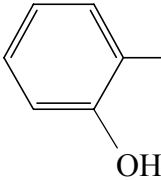
CHAPTER 19

ORGANIC CHEMISTRY II: FUNCTIONAL GROUPS

19.1 (a) RNH_2 , R_2NH , R_3N (b) ROH (c) RCOOH (d) RCHO

19.3 (a) ether; (b) ketone; (c) amine; (d) ester

19.5 (a) 2-iodo-2-butene; (b) 2,4-dichloro-4-methylhexane; (c) 1,1,1-triiodoethane; (d) dichloromethane

19.7 (a)  $\text{ClC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH}$, phenol;

(b) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$, secondary alcohol; (c)

$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$, primary alcohol;

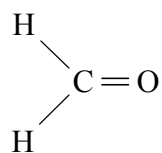
(d) $\text{CH}_3\text{C}(\text{CH}_3)(\text{OH})\text{CH}_2\text{CH}_3$, tertiary alcohol

19.9 (a) $\text{CH}_3\text{CH}_2\text{OCH}_3$; (b) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$; (c) CH_3OCH_3

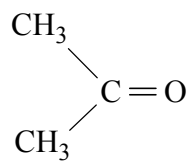
19.11 (a) butyl propyl ether; (b) methyl phenyl ether; (c) pentyl propyl ether

19.13 (a) aldehyde, ethanal; (b) ketone, propanone; (c) ketone, 3-pentanone

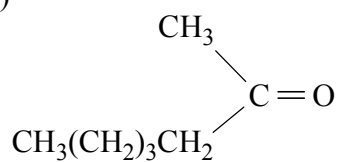
19.15 (a)



(b)

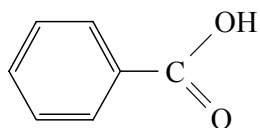


(c)

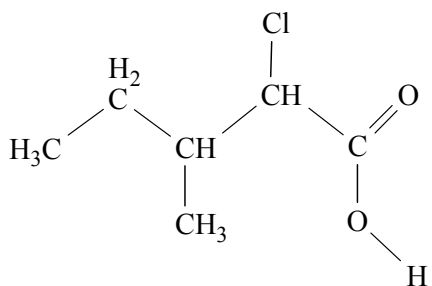


19.17 (a) ethanoic acid; (b) butanoic acid; (c) 2-aminoethanoic acid

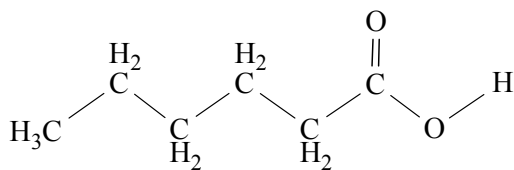
19.19 (a)



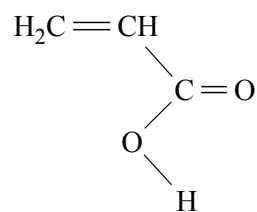
(b)



(c)



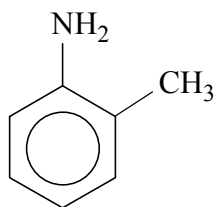
(d)



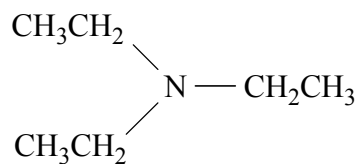
19.21 (a) methylamine; (b) diethylamine; (c) *o*-methylaniline or 2-methylaniline or *o*-methylphenylamine

19.23

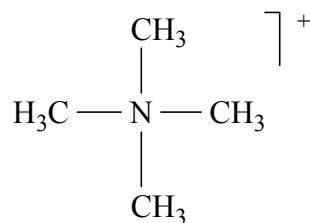
(a)



(b)



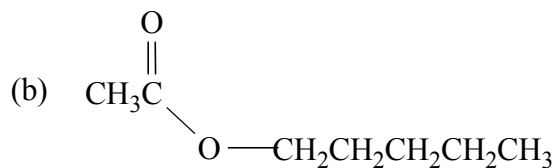
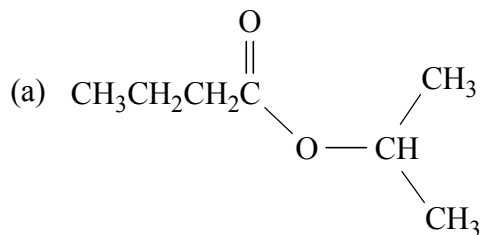
(c)

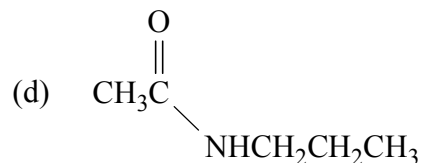
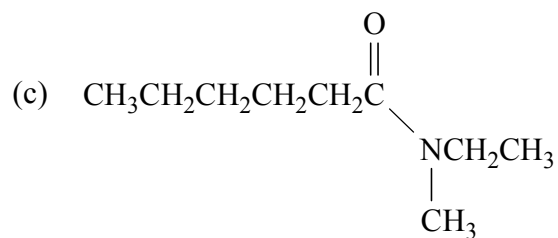


19.25 Only (a) and (c) may function as nucleophiles, because they have lone pairs of electrons that will be attracted to a positively charged carbon center. CO_2 and SiH_4 have no lone pairs and cannot function as nucleophiles.

19.27 (a) ethanol; (b) 2-octanol; (c) 5-methyl-1-octanol. These reactions can be accomplished with an oxidizing agent such as acidified sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7$.

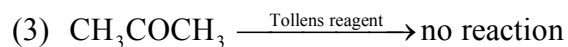
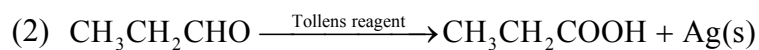
19.29





19.31 The following procedures can be used:

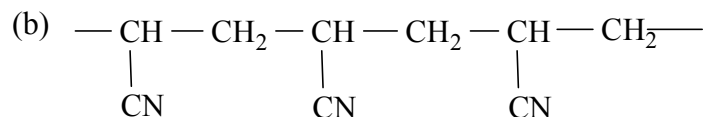
(1) Dissolve the compounds in water and use an acid-base indicator to look for a color change.

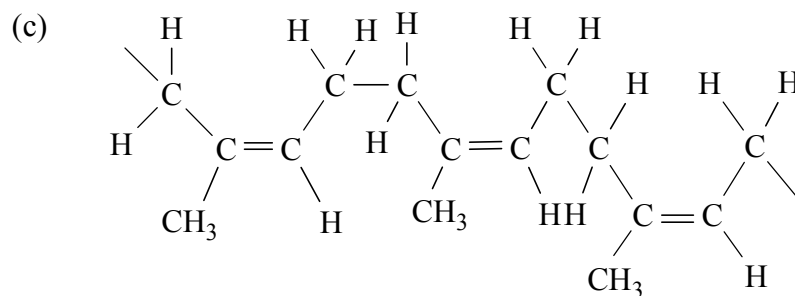


Procedure (1) will distinguish ethanoic acid; (2) and (3) will distinguish propanal from 2-propanone.

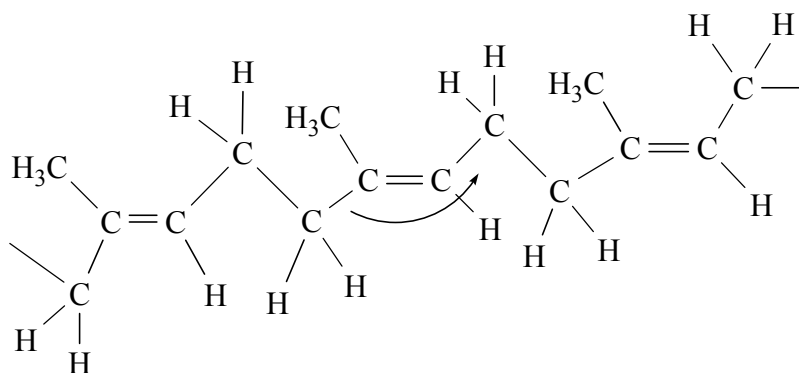


The greater the electronegativities of the groups attached to the carboxyl group, the stronger the acid (see Chapter 10).





cis version



trans version

19.37 (a) $\text{CHCl}=\text{CH}_2$; (b) $\text{CFCl}=\text{CF}_2$

19.39 (a) $-\text{OCCONH}(\text{CH}_2)_4\text{NHCOCONH}(\text{CH}_2)_4\text{NH}-$;

(b) $-\text{OC}-\text{CH}(\text{CH}_3)-\text{NH}-\text{OC}-\text{CH}(\text{CH}_3)-\text{NH}-$

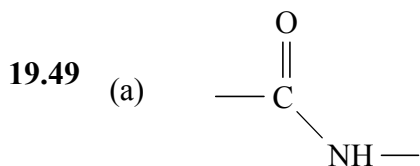
19.41 An isotactic polymer is a polymer in which the substituents are all on the same side of the chain. A syndiotactic polymer is a polymer in which the substituent groups alternate, from one side of the chain to the other. An atactic polymer is a polymer in which the groups are randomly attached, one side or the other, along the chain.

19.43 block copolymer

19.45 Larger average molar mass corresponds to longer average chain length.

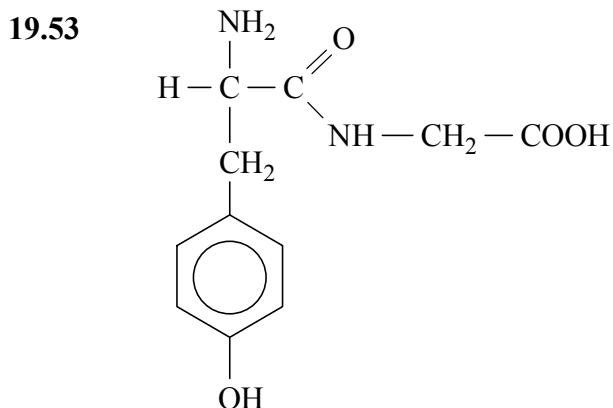
Longer chain length allows for greater intertwining of the chains, making them more difficult to pull apart. This twining results in (a) higher softening points, (b) greater viscosity, and (c) greater mechanical strength.

19.47 Highly linear, unbranched chains allow for maximum interaction between chains. The greater the intermolecular contact between chains, the stronger the forces between them, and the greater the strength of the material.

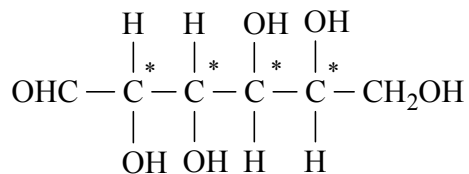


(b) amide; (c) condensation

19.51 Side groups that contain hydroxyl, carbonyl, amino, and sulfide groups are all potentially capable of participating in hydrogen bonding that could contribute to the tertiary structure of the protein. Thus, serine, threonine, tyrosine, aspartic acid, glutamic acid, lysine, arginine, histidine, asparagine, and glutamine satisfy the criteria. Proline and tryptophan generally do not contribute through hydrogen bonding, because they are typically found in hydrophobic regions of proteins.



19.55 The functional groups are alcohols and aldehydes. The chiral carbon atoms are marked with asterisks (*).



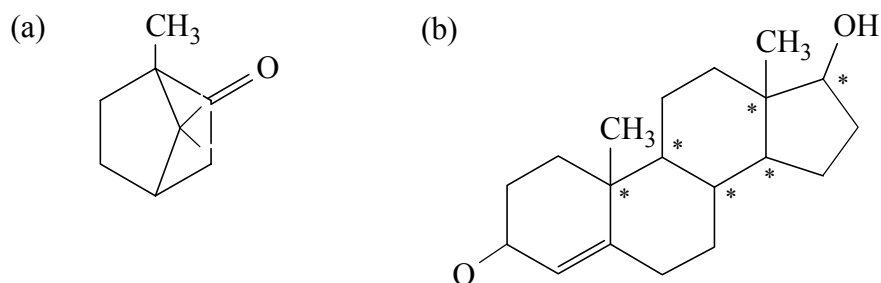
19.57 (a) GTACTCAAT; (b) ACTTAACGT

19.59 (a) $\text{C}_5\text{H}_5\text{N}_5\text{O}$ (b) $\text{C}_6\text{H}_{12}\text{O}_6$ (c) $\text{C}_3\text{H}_7\text{NO}_2$

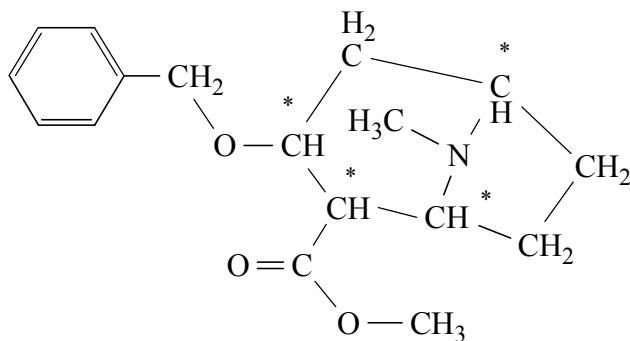
19.61 (a) alcohol, ether, aldehyde; (b) ketone, alkene; (c) amine, amide

19.63 (a) carboxylic acid, ester; (b) ether, ketone, phenol, alkene; (c) aromatic amine, tertiary amine; (d) ketone, alcohol, alkene

19.65

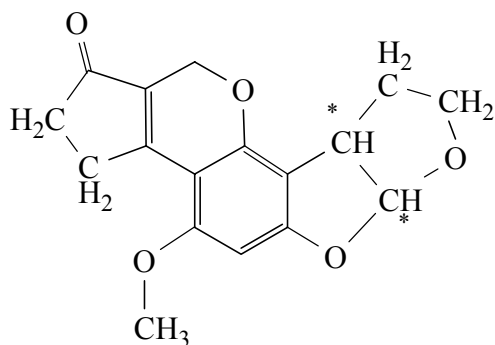


19.67 (a)

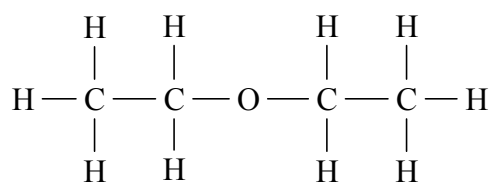


* An asterisk (*) denotes a chiral carbon atom.

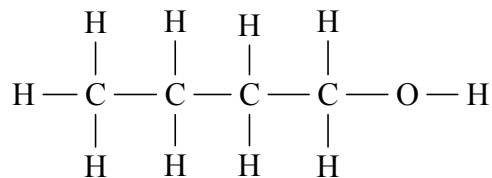
(b)



19.69 (a)



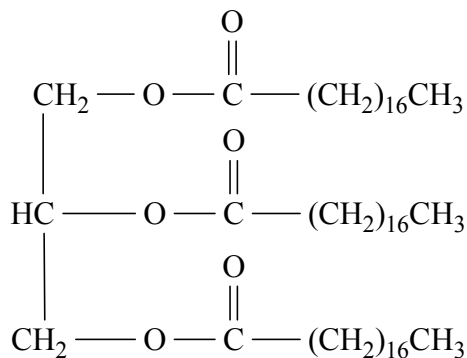
Diethyl ether



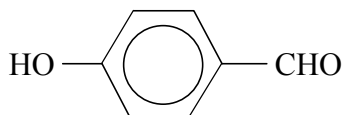
1-butanol

(b) 1-Butanol can hydrogen bond with itself but diethyl ether cannot, so 1-butanol molecules are held together more strongly in the liquid and therefore 1-butanol has the higher boiling point. Both compounds can form hydrogen bonds with water and therefore have similar solubilities.

19.71 (a)

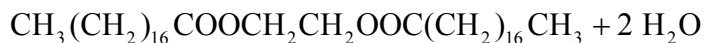


(b)



19.73 (a) addition; (b) condensation; (c) addition; (d) addition; (e) condensation

19.75 (a) $\text{HOCH}_2\text{CH}_2\text{OH} + 2 \text{CH}_3(\text{CH}_2)_{16}\text{COOH} \rightarrow$



(b)



(c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{COOH} \xrightarrow{\Delta}$



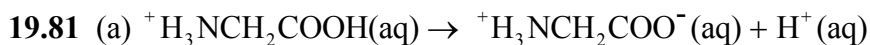
19.77 Polyalkenes < polyesters < polyamides, due to the increasing strength of intermolecular forces between the chains. The three types of polymer have about the same London forces if their chains are about the same length. However, polyesters also have dipole forces contributing to the strength of intermolecular forces, and polyamides form very strong hydrogen bonds between their chains.

19.79 (a) Primary structure is the sequence of amino acids along a protein chain.

Secondary structure is the conformation of the protein, or the manner in which the chain is coiled or layered, as a result of interactions between amide and carboxyl groups. Tertiary structure is the shape into which sections of the proteins twist and intertwine, as a result of interactions between side groups of the amino acids in the protein. If the protein consists of several polypeptide units, then the manner in which the units stick together is the quaternary structure.

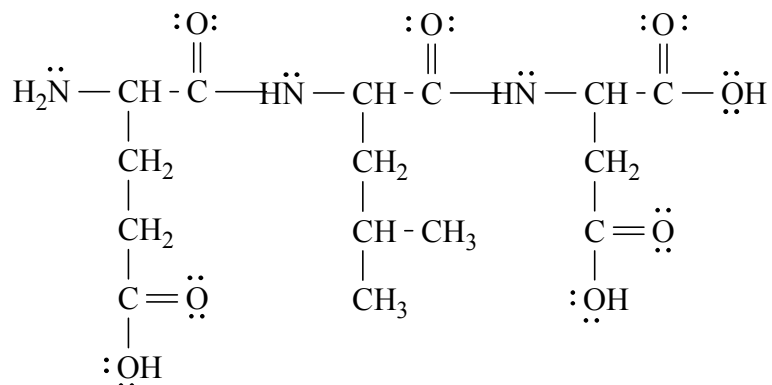
(b) The primary structure is held together by covalent bonds.

Intermolecular forces provide the major stabilizing force of the secondary structure. The tertiary structure is maintained by a combination of London forces, hydrogen bonding, and sometimes ion-ion interactions. The same forces are responsible for the quaternary structure.

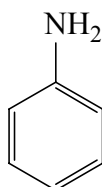


19.83 Condensation polymerization involves the loss of a small molecule, often water or HCl, when monomers are combined. Dacron is more linear than the polymer obtained from benzene-1,2-dicarboxylic acid and ethylene glycol, so Dacron can be more readily spun into yarn.

19.85



19.87 (a)



(b) sp^3 ; (c) sp^2 ; (d) each N atom carries one lone pair of electrons; (e) Yes, the N atoms help to carry the current because the unhybridized p orbital on each N atom is part of the extended π conjugation (delocalized π -bonds) that allows electrons to move freely along the polymer.

19.89 (a) reduced; (b) oxidized; O = 1- in the peroxide anion, O_2^{2-} , but O = 2- in water; C = $\frac{2}{3}+$ in ascorbic acid, but C = 1+ in dehydroxyascorbic acid.

19.91 Two peaks are observed with relative overall intensities 3 : 1. The larger peak is due to the three methyl protons and is split into two lines with equal intensities. The smaller peak is due to the proton on the carbonyl carbon atom and is split into four lines with relative intensities 1 : 3 : 3 : 1.

19.93 The peaks in the spectrum can be assigned on the basis of the intensities and the coupling to other peaks. The hydrogen atoms of the CH_3 unit of

the ethyl group will have an intensity of 3 and will be split into a triplet by the two protons on the CH_2 unit. This peak is found at $\delta \approx 1.2$. The CH_2 unit will have an intensity of 2 and will be split into a quartet by the three protons on the methyl group. This peak is found at $\delta = 4.1$. The CH_2 group that is part of the butyl function will have an intensity of two but will appear as a singlet because there are no protons on adjacent carbon atoms. This is the signal found at $\delta = 2.1$. The remaining CH_3 groups are equivalent and also will not show coupling. They can be attributed to the signal at $\delta = 1.0$. Notice that the peak that is most downfield is the one for the CH_2 group attached directly to the electronegative oxygen atom, and that the second most downfield peak is the one attached to the carbonyl group.

19.95 If one considers the reaction, the products should be those arising from substitution of hydrogen atoms on the propane by chlorine atoms. We would expect then to form a chloropropane or, perhaps a dichloropropane. Remember that in the halogenation of alkanes, substitution becomes more difficult as more halogen atoms are introduced. If we then consider the NMR spectrum, we see that there is one large peak that sees a single proton, because it is split into a doublet. There is also a weaker feature, corresponding most likely to one proton, which is split into a septet. This indicates that the proton sees six equivalent protons. The structure that is consistent with this spectrum is 2-chloropropane.

19.97 (a) ^{13}C ; (b) 1.11%; (c) No. The reason is that the probability of finding two ^{13}C nuclei next to each other is very low. A ^{12}C nucleus next to a ^{13}C nucleus will not interact with the ^{13}C nucleus because the ^{12}C nucleus has no spin. Because the natural abundance of ^{13}C is 1.11%, the probability of finding two ^{13}C nuclei next to each other in an organic molecule will be 0.0111×0.0111 or 1.23×10^{-4} . Although such coupling

is possible, it is generally not observed because the signal is so much weaker than the signal due to the molecules with a single ^{13}C nucleus. (d) Maybe. Because most of the carbon to which the protons are attached is ^{12}C , the bulk of the signal will not be split. The protons that are attached to the ^{13}C atoms will be split, but this amounts to only 1.11% of the sample, so the peaks are very small. Peaks that result from coupling to a small percentage of a magnetically-active isotope are referred to as satellites and may be observed if one has a very good spectrum. (e) Yes. Although the splitting of protons by ^{13}C may not be observed because the amount of ^{13}C present is low, the opposite situation is not true. If a ^{13}C is attached to H atoms, the large majority of those H atoms will have a spin and so the ^{13}C will show fine structure due to splitting by the H atoms.

- 19.99** (a) 1; (b) 1; (c) 1; (d) Free rotation around the C-C and C-Cl bonds averages out the environments so that both CH_2 hydrogens are equivalent and all three CH_3 hydrogens are equivalent, resulting in just two different hydrogen signals.