

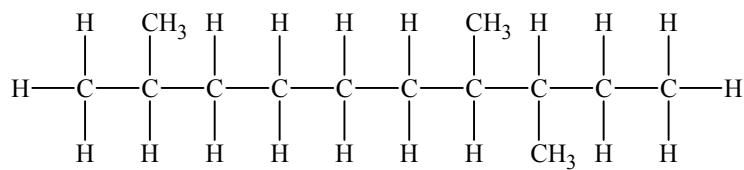
CHAPTER 18

ORGANIC CHEMISTRY I: THE HYDROCARBONS

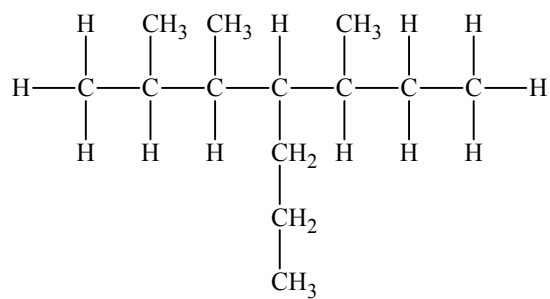
- 18.2** (a) C_6H_{12} , alkane; (b) C_5H_8 , alkene; (d) C_3H_4 , alkene; (d) C_8H_{18} , alkane
- 18.4** (a) $CH_3CH_2CH(CH_3)_2$ or C_5H_{12} , alkane; (b) $C_{10}H_8$, aromatic hydrocarbon (c) C_8H_{18} , alkene; (d) C_4H_4 , alkene and alkyne
- 18.6** (a) C_9H_{16} , alkene; (b) C_6H_{10} , alkyne; (c) C_9H_{16} , alkane; (d) $C_{10}H_8$, aromatic hydrocarbon
- 18.8** (a) nonane; (b) pentane; (c) hexane; (d) octane
- 18.10** (a) decyl; (b) ethyl; (c) butyl; (d) octyl
- 18.12** (a) hexane; (b) 2, 2, 3-trimethylpentane; (c) 2, 2, 4-trimethylpentane; (d) 2, 2-dimethylbutane
- 18.14** (a) 3-phenyl-1-octene; (b) 3-chloro-4, 5-dimethyl-1-hexyne
- 18.16** (a) $CH_3CH(CH_3)CH_2CH(CH_2CH_3)CH_2CH_3$
or $(CH_3)_2CHCH_2CH(CH_2CH_3)_2$
(b) $CH_2=CHC(CH_3)_2CH_2CH_3$
(c) *cis*- $CH_3CH=CHCH(CH_3)CH_2CH_3$

(d) *trans*-CH₃CH=CHCH₃

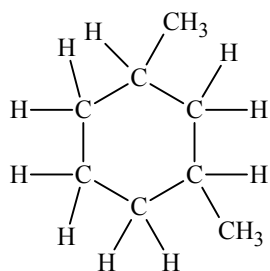
18.18 (a)



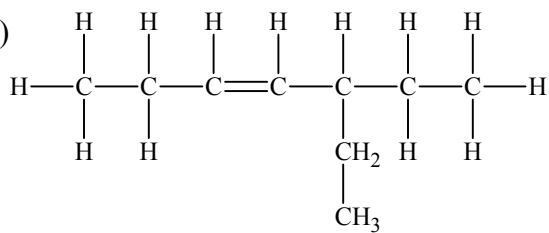
(b)



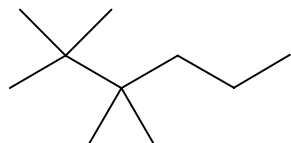
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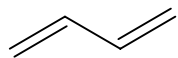
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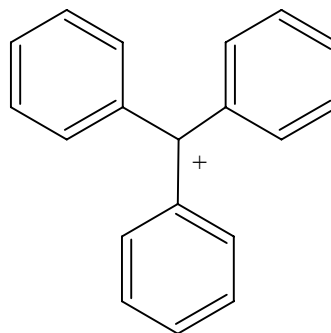
18.20 (a)



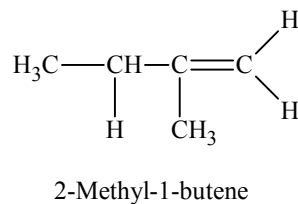
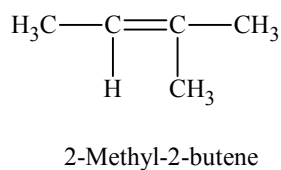
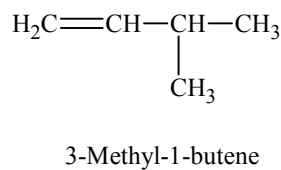
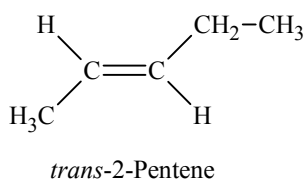
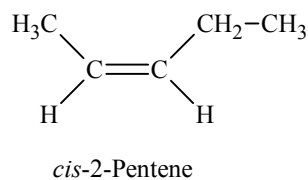
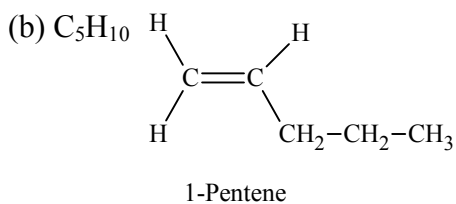
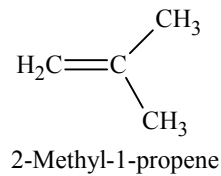
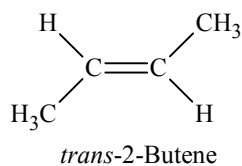
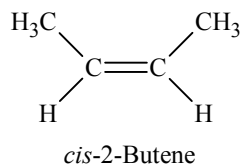
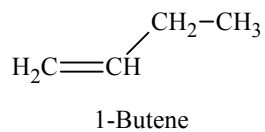
(c)



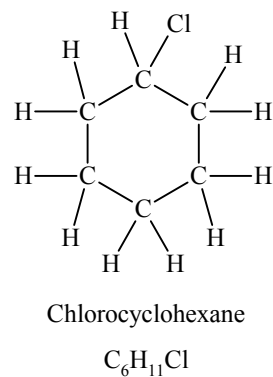
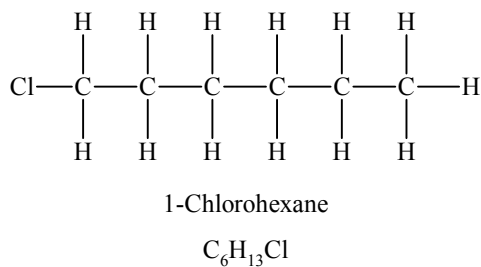
(b)



18.22 (a) C₄H₈



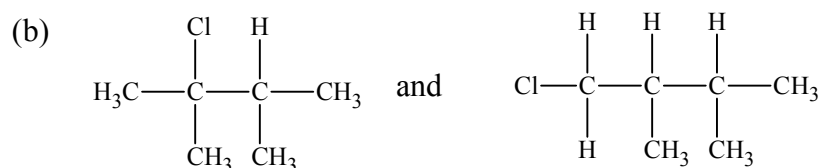
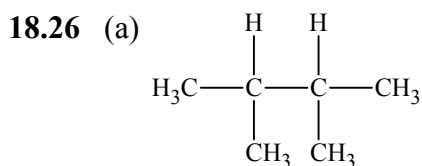
18.24 (a)



Different formula, not isomers.

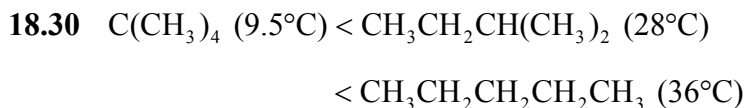
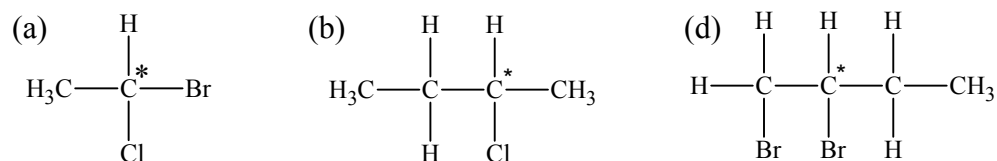
(b) Same formula, C_4H_8 , but different bonding arrangements: structural isomers.

(c) Same formula, $C_2H_2Cl_2$, same bonding arrangement, but different geometry: geometrical isomers.



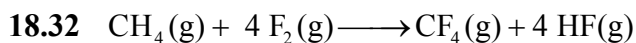
Note: Both H's and all four methyl groups are equivalent in the hydrocarbon.

18.28 (a), (b), and (d) display optical activity.



Because the molecular formulas are all identical, the compounds will have the same molar mass. The difference in boiling points can then be attributed to the degree of branching; the more highly branched compounds have the lower boiling points.

* Indicates the chiral carbon atoms. (c) is optically inactive.



break 4 C–H bonds $4(+412 \text{ kJ} \cdot \text{mol}^{-1})$

break 4 F–F bonds $4(+158 \text{ kJ} \cdot \text{mol}^{-1})$

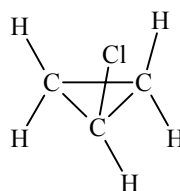
form 4 C–F bonds $4(-484 \text{ kJ} \cdot \text{mol}^{-1})$

form 4 H–F bonds $4(-565 \text{ kJ} \cdot \text{mol}^{-1})$

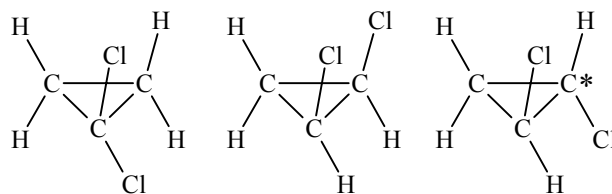
Total $-1916 \text{ kJ} \cdot \text{mol}^{-1}$

The corresponding reaction with chlorine is much less exothermic for two reasons. First, it requires much less energy to break the F-F bond, and second, the bonds formed between F and C or H are also stronger than the corresponding bonds to Cl. For this reason, direct fluorinations of hydrocarbons are extremely hazardous and may lead to fires and explosions. Chlorinations are also hazardous but are more easily done than fluorinations.

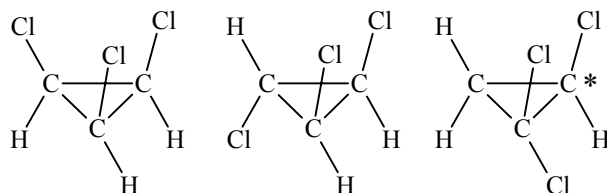
18.34 One monochlorocyclopropane:



Three dichlorocyclopropanes:

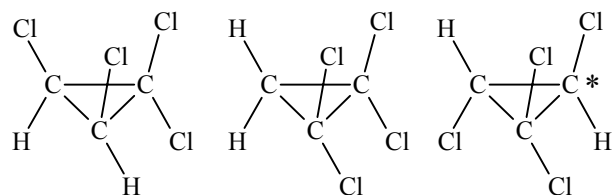


Three trichlorocyclopropanes:

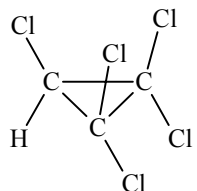


*Indicates a structure with a nonsuperimposable mirror image.

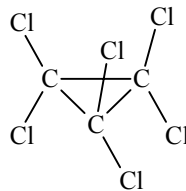
Three tetrachlorocyclopropanes:



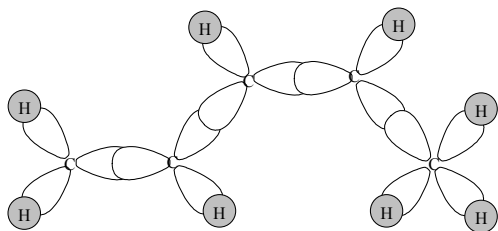
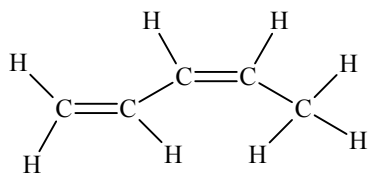
One pentachlorocyclopropane:



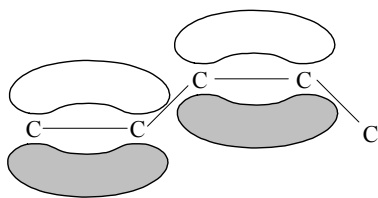
One hexachlorocyclopropane:



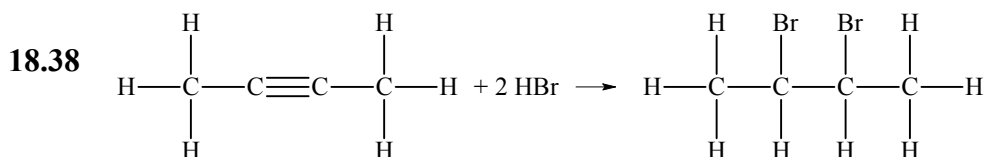
18.36



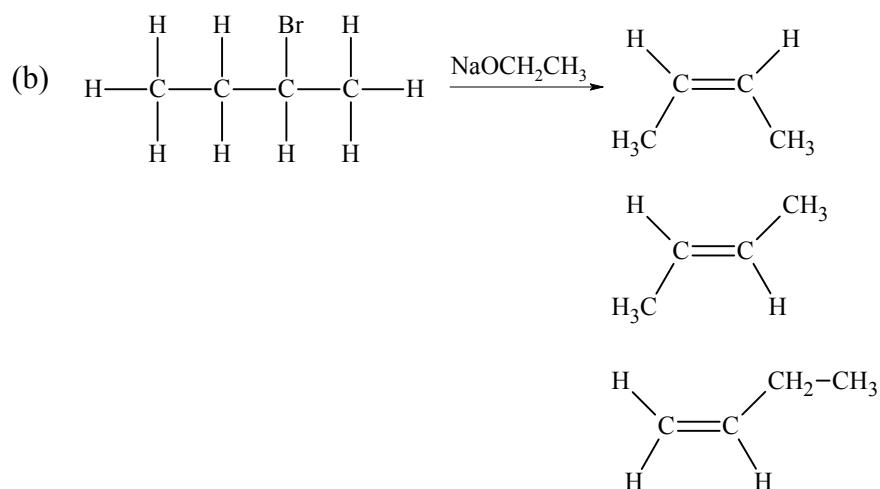
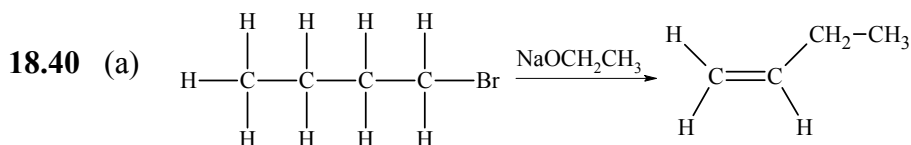
All carbon atoms are sp^2 hybridized except for the carbon on the far right side of the molecule, which is bonded to three hydrogen atoms and is sp^3 hybridized.



Pi bonds form the second bond in the $C=C$ double bonds.



Addition reaction



We will break one H–X bond and form one C–H bond and one C–X bond.

Using bond enthalpies:

Halogen	Cl	Br	I
H–X bond breakage ($\text{kJ} \cdot \text{mol}^{-1}$)	+ 431	+ 366	+ 299
C–H bond formation ($\text{kJ} \cdot \text{mol}^{-1}$)	– 412	– 412	– 412
C–X bond formation ($\text{kJ} \cdot \text{mol}^{-1}$)	– 338	– 276	– 238
Total ($\text{kJ} \cdot \text{mol}^{-1}$)	– 319	– 322	– 351

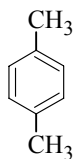
A general trend in the exothermicity of these reactions is not as obvious as in Exercise 18.41. There are two opposing factors involved. Although it

requires less energy to break an H—X bond as one descends the periodic table, there is also less energy released from the formation of a C—X bond.

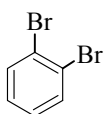
18.44 (a) 2-ethyl-4-methyl-1-propylbenzene

(b) 1-ethyl-4-propylbenzene

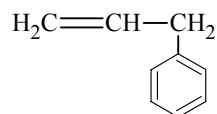
18.46 (a)



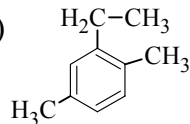
(b)



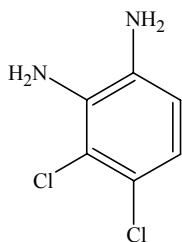
(c)



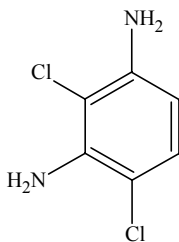
(d)



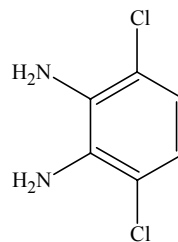
18.48 (a), (b)



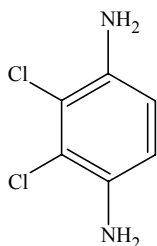
1,2-Diamino-3,4-dichlorobenzene



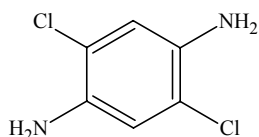
1,3-Diamino-2,4-dichlorobenzene



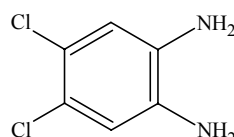
2,3-Diamino-1,4-dichlorobenzene



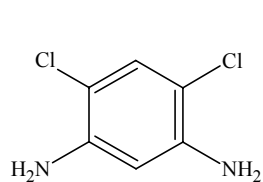
1,4-Diamino-2,3-dichlorobenzene



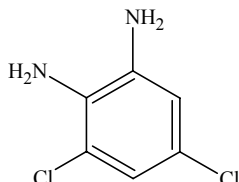
1,4-Diamino-2,5-dichlorobenzene



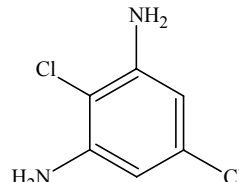
1,2-Diamino-4,5-dichlorobenzene



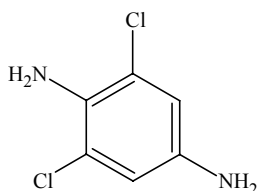
1,5-Diamino-2,4-dichlorobenzene



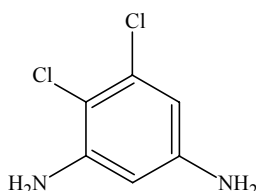
1,2-Diamino-3,5-dichlorobenzene



1,3-Diamino-2,5-dichlorobenzene



2,5-Diamino-1,3-dichlorobenzene



1,5-Diamino-2,3-dichlorobenzene

All these molecules will be at least slightly polar except for the 1,4-diamino-2,4-dichlorobenzene, which will be nonpolar.



The two reactions will give different product distributions because the directing influence of the groups attached to the ring are different. A nitro group is a metadirecting substituent; a bromo group would be ortho- and para-directing. Thus, the dominant products in the nitration reaction would be a mixture of 1-bromo-2-nitrobenzene and 1-bromo-4-nitrobenzene, whereas for the bromination reaction, the product would be primarily 1-bromo-3-nitrobenzene.

18.52 Like the nitro group, the aldehyde group is electron-withdrawing and forms resonance structures that place positive charge on the ortho and para positions. This group is, therefore, a meta-directing substituent.

18.54 Coal is not a pure substance and, as a result, does not burn cleanly. Some types of coal produce considerable amounts of sulfur and nitrogen oxides, which contribute to air pollution. The burning of high-sulfur coal contributed very much to the environmental damage in many of the eastern European nations, such as the former East Germany. This damage persists to this day. Coal is also not as easy to transport as gasoline because it is a solid rather than a liquid or gas. Liquids or gases can be placed in fuel tanks and pipelines.

18.56 Ethanol is a renewable fuel source, which may be produced from biomass (fermentation reactions). Currently, ethanol is more expensive to produce than normal components of gasoline, but a strong push for its use comes from the agricultural industry, which, of course, would benefit by the fermentation of biomass to produce automotive fuel. The requirement to

use ethanol in gasoline mixtures is a controversial issue in the United States, where there are strong lobbies both for and against its use.

18.58 (a) four tetrahedral sp^3 -hybrid orbitals with σ -bonds

(b) three trigonal planar sp^2 -hybrid orbitals with σ -bonds and one unhybridized p -orbital with a π -bond

(c) two linear sp -hybrid orbitals with σ -bonds and two unhybridized p -orbitals with two π -bonds

18.60 (a) $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3 + \text{H}_2 \xrightarrow{\text{Ni}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, addition reaction

(b) $\text{CH}_2=\text{CHCH}_3 + \text{HCl} \longrightarrow \text{CH}_3\text{CHClCH}_3$ and an isomer, $\text{CH}_2\text{ClCH}_2\text{CH}_3$, addition reaction

18.62 (a) The reaction is: $\text{C}_3\text{H}_6(\text{g})$ (propene) + $\text{H}_2(\text{g}) \rightarrow \text{C}_3\text{H}_8(\text{g})$ (propane).

To calculate the equilibrium constant, first calculate the free energy of reaction: $\Delta G_r = (-23.49 \text{ kJ} \cdot \text{mol}^{-1}) - (-32.82 \text{ kJ} \cdot \text{mol}^{-1}) = 9.33 \text{ kJ} \cdot \text{mol}^{-1}$.

The equilibrium constant is then:

$$K = e^{\frac{-\Delta G_r}{RT}} = e^{\frac{-9330 \text{ J} \cdot \text{mol}^{-1}}{(8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}} = 0.0232$$

(b) To determine how increasing the temperature will affect K , we must determine if the reaction is endothermic or exothermic:

$$\Delta H_r = (-103.85 \text{ kJ} \cdot \text{mol}^{-1}) - (-84.68 \text{ kJ} \cdot \text{mol}^{-1}) = -19.17 \text{ kJ} \cdot \text{mol}^{-1}.$$

The negative enthalpy of reaction indicates an exothermic reaction.

Applying Le Chatelier's principle, we would expect that increasing the reaction temperature would, therefore, favor reactants and decrease K .

18.64 (a) Because the double bond in *trans*-3-hexene should be planar, the torsion angle should be 0° . (b) The measured values from the Web site

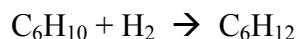
files are *trans*-3-hexene, 0°; cyclohexene, 8.8°; cyclohexane, 59.8°. The presence of the ring structure prevents the double bond in cyclohexene from being perfectly planar. There is a distortion of about 8.8° from planarity as a result of the geometrical constraints on the molecule.

(c) The cyclohexane ring allows the molecule to adopt normal bond angles (109.5°) for all the sp^3 -hybridized carbon atoms. While the sp^2 -hybridized carbon atoms in the double bond of cyclohexene show a slight distortion from the ideal bond angles (about 121–122°), so do the sp^3 -hybridized carbon atoms immediately adjacent to the double bond (angles are about 112°).

- 18.66** (a) 1-pentene; (b) *cis*-3-methyl-2-pentene, *trans*-3-methyl-2-pentene; (c) 2,4-dimethyl-2-pentene; (d) 5-methyl-2-heptyne; (e) 5-methyl-3-heptyne

- 18.68** (a) 2-methylpropane; (2) 2-methylbutane; (c) *iso*- is added as a prefix to denote the isomer of a straight chain hydrocarbon in which the end CH_3 group has been moved from the end of the chain to a position one carbon unit inward. The systematic name for isohexane will thus be 2-methylpentane.

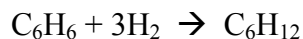
- 18.70** (a) 1 mol of hexene will react with 1 mol of H_2 to form one mole of hexane:



The volume of one mole of H_2 at 298 K and 1.00 atm is:

$$V = \frac{n \cdot R \cdot T}{P} = \frac{(1 \text{ mol})(0.082057 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}{1 \text{ atm}} = 22.5 \text{ L}$$

Three moles of H_2 are required to completely react with one mole of benzene:



Therefore, the volume of H_2 needed is three times that needed to react with one mole of hexene or 67.5 L

(b) For the reaction of hexene with H_2 :

Break 1 C=C bond:	+612 kJ·mol ⁻¹
Break 1 H—H bond:	+436 kJ·mol ⁻¹
Form 1 C—C bond:	-348 kJ·mol ⁻¹
Form 2 C—H bonds:	2(-412 kJ·mol ⁻¹)
Total:	-124 kJ·mol ⁻¹

For the reaction of benzene with H_2 :

Break 6 C=C bonds:	6(+518 kJ·mol ⁻¹)
Break 3 H—H bond:	3(+436 kJ·mol ⁻¹)
Form 6 C—C bonds:	6(-348 kJ·mol ⁻¹)
Form 6 C—H bonds:	6(-412 kJ·mol ⁻¹)
Total:	-144 kJ·mol ⁻¹

Hydrogenation of benzene is not three times more exothermic than the hydrogenation of hexene due to resonance stabilization of the C-C bonds in benzene. The resonance stabilization of benzene makes the carbon-carbon bonds more stable, reducing the overall amount of energy released during the reaction.

$$\begin{aligned} \text{18.72 amount (moles) of H} &= 6.75 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} \\ &= 0.749 \text{ mol H} \end{aligned}$$

amount (moles) of

$$\text{C} = 17.55 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} = 0.399 \text{ mol C}$$

$$\frac{0.749 \text{ mol H}}{0.399 \text{ mol C}} = 1.88 \frac{\text{mol H}}{\text{mol C}} \approx \frac{15 \text{ mol H}}{8 \text{ mol C}}$$

The empirical formula is C_8H_{15} . The molecular formula could be $\text{C}_{16}\text{H}_{30}$, which is of the type $\text{C}_n\text{H}_{2n-2}$, corresponding to an alkyne or a dialkene.

18.74 (a) Ethane can form no chiral products. (b) Propane can form no chiral products. (c) 2-Bromobutane is chiral. (d) 2-Bromopentane is chiral.

18.76 Assume a 100 g sample.

$$\text{amount (moles) of C} = 90 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 7.5 \text{ mol C}$$

$$\text{amount (moles) of H} = 10 \text{ g H} \times \frac{1 \text{ mol H}}{1.01 \text{ g H}} = 9.9 \text{ mol H}$$

$$\frac{9.9 \text{ mol H}}{7.5 \text{ mol C}} = \frac{1.3 \text{ mol H}}{1 \text{ mol C}} \approx \frac{4 \text{ mol H}}{3 \text{ mol C}}$$

The empirical formula is C_3H_4 , which has a molar mass of $40 \text{ g} \cdot \text{mol}^{-1}$.

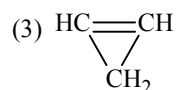
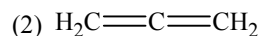
Because $40.06 \text{ g} \cdot \text{mol}^{-1}$ is the molar mass of the compound, the molecular formula is C_3H_4 as well. The compound could be a cyclic alkene, dialkene, or alkyne. See the structures of the possible isomers below.

$$\text{amount (moles) of } \text{C}_3\text{H}_4 = \frac{1.46 \text{ g}}{40.06 \text{ g} \cdot \text{mol}^{-1}} = 3.6 \times 10^{-2} \text{ mol}$$

$$\begin{aligned} \text{amount (moles) of } \text{H}_2 = n_{\text{H}_2} &= \frac{PV}{RT} = \frac{1.0 \text{ atm} \times 1.600 \text{ L}}{0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 273 \text{ K}} \\ &= 7.2 \times 10^{-2} \text{ mol} \end{aligned}$$

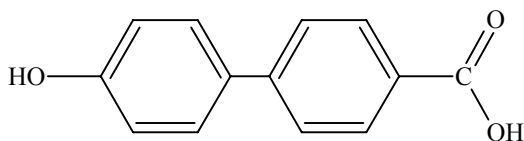
$$\text{Thus } \frac{n_{\text{H}_2}}{n_{\text{C}_3\text{H}_4}} = \frac{7.2 \times 10^{-2} \text{ mol}}{3.6 \times 10^{-2} \text{ mol}} = 2$$

There are two π -bonds across which H_2 can add. This is consistent with the compound's being an alkyne or a dialkene. No definite identification of the hydrocarbon can be made on the basis of the data provided. The three possible isomers consistent with the formula C_3H_4 are

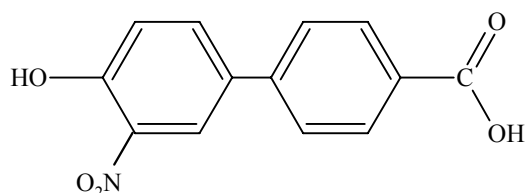


Structure (3) is inconsistent with the hydrogenation data.

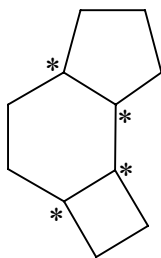
- 18.78** The question here is twofold: (1) Which ring will be nitrated? and (2) Which position of that ring will be the site of electrophilic substitution?



The OH group is an activating function because it donates electrons to the aromatic ring, whereas the COOH group is electron-withdrawing and, therefore, deactivating. We would thus expect the ring with the OH group attached to be the one that is substituted. Because OH is an ortho-, para-directing group, we would expect the substitution to occur at one of those sites. Because the para position is already substituted, this leaves only the position ortho to the OH group for the substitution. The expected product is, therefore,



- 18.80** (a) There are four carbon atoms in the molecule that each have four substituents attached. Each of these carbon atoms is labeled with an asterisk. Each of these carbons has two possible configurations.

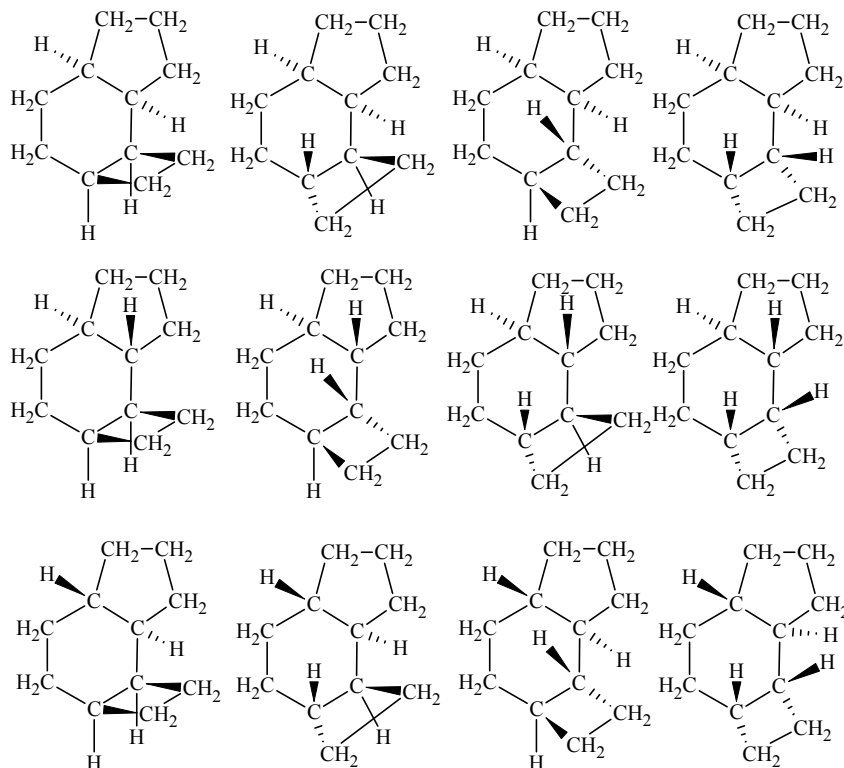


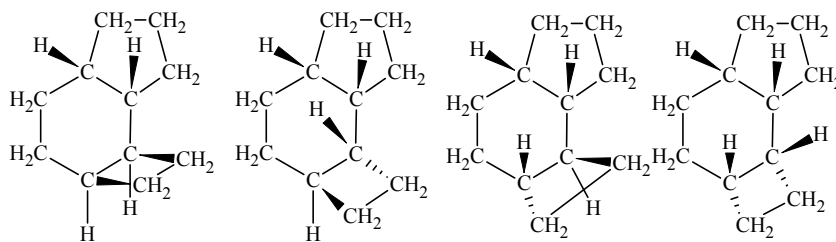
- (b) Because each chiral carbon atom has two possible configurations, there will be $2 \times 2 \times 2 \times 2 = 16$ different configurations. These are shown below. This can be seen readily if we label the configuration at each

carbon atom. In organic chemistry, conventions have been developed that use the symbols R and S to designate the two different configurations possible at a particular chiral carbon atom. It is not important here to understand the conventions associated with each configuration; they are simply provided as labels to show what the possible combinations are. Thus, if we label each chiral carbon atom as R or S, we have the following possible configurations:

RRRR	RRRS	RRSR	RSRR
RRSS	RSSR	RSRS	
RSSS			
SRRR	SRRS	SRSR	SSRR
SSRS	SSSR	SRSS	
SSSS			

(c) Yes. In fact, the 16 isomers can be divided into eight pairs of enantiomers. If we use the R,S designations, we find that isomers that are completely opposite in configuration are mirror images of each other. Thus, RRRR is the mirror image of SSSS, RSRS is the mirror image of SRSR, etc.





18.82 (a) 2,4,6-trinitrotoluene. (b) The methyl group on the toluene directs electrophilic aromatic substitution toward the meta and para positions (see section 18.9) because the methyl group is slightly electron-donating. A nitro group, however, is electron-withdrawing and will tend to cause electrophilic substitution meta to its position. The result is that, once a nitro group has substituted onto the ring, it reinforces the directing influence of the methyl group. For example, in 2-nitrotoluene (meta-nitrotoluene) the methyl group will cause preferential substitution at the 4 position. The position is also the meta position relative to the nitro group, so that group enhances substitution at this location as well.

18.84 Because D has twice the mass of H, the parent ion for D_2O will occur at $(2 \times 2 \text{ u}) + 16 \text{ u} = 20 \text{ u}$, rather than at 18 u. Although H_2O shows a peak at this mass, that peak is very small due to the natural probability of finding two D atoms or one ^{18}O atom in the water molecule. For D_2O , this peak will be the largest peak. A small peak at 22 u will be observed for $D_2^{18}O$, as will peaks at 18 u for $D^{16}O$ and at 16 u for ^{16}O . A peak for $D^{18}O$ would overlap with a peak for $D_2^{16}O$, but they will not be exactly the same; a high resolution mass spectrometer may be able to resolve them. Because D_2O easily absorbs water, one might also find signals associated with normal isotopic abundance H_2O .

18.86 This reaction is a classic electrophilic substitution reaction, so we would expect the product to be one of the possible chloromethylbenzenes. If we

calculate the parent ion mass expected for $\text{C}_6\text{H}_4\text{CH}_3\text{Cl}^+$, we find that Cl has two isotopes in a roughly 3:1 ratio (^{35}Cl , ^{37}Cl , respectively). The parent ion will thus show two peaks in roughly a 3:1 ratio. The masses of these peaks will be $(7 \times 12 \text{ u}) + (7 \times 1 \text{ u}) + 35 \text{ u} = 126 \text{ u}$ and $(7 \times 12 \text{ u}) + (7 \times 1 \text{ u}) + 37 \text{ u} = 128 \text{ u}$, the latter peak being about 1/3 the size of the former. The peaks at 113 u and 111 u represent the parent ion minus the methyl group (15 u). The formula of this fragment will be $\text{C}_6\text{H}_4\text{Cl}^+$. As with the parent ion, these two peaks will be roughly in a 3:1 ratio. The peak at 91 u represents the loss of the Cl atom from the parent ion with a formula of $\text{C}_6\text{H}_4\text{CH}_3^+$. Note that because this ion does not contain Cl, it does not have a companion peak with which to form a 3:1 intensity ratio.