# CHAPTER 22: ALKENES, ALKYNES AND AROMATICS

## Organic and Biochemistry Supplement to Enhanced Introductory College Chemistry

by Gregory Anderson; Jen Booth; Caryn Fahey; Adrienne Richards; Samantha Sullivan Sauer; and David Wegman

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## In this chapter, you will learn about:

- Naming and drawing unsaturated hydrocarbons
- Identifying cis-trans isomers
- Formation and use of unsaturated hydrocarbons

## To better support your learning, you should be familiar with the following concepts before starting this chapter:

- Alkene, alkyne and aromatic functional groups (Chapter 22 Alkenes, Alkynes and Aromatics)
- Alkane naming and drawing (Chapter 19 Alkanes and Alkyl Halides)
- General reactions of carbon (Chapter 19.6 General Reactions of Carbon)
- Advanced bonding of carbon (Chapter 21 Advanced theories of Covalent Bonding)

Our modern society is based to a large degree on the chemicals we discuss in this chapter. Most are made from petroleum. Alkanes—saturated hydrocarbons—have relatively few important chemical properties other than that they undergo combustion and react with halogens. Unsaturated hydrocarbons—hydrocarbons with double or triple bonds—on the other hand, are quite reactive. In fact, they serve as building blocks for many familiar plastics—polyethylene, vinyl plastics, acrylics—and other important synthetic materials (e.g., alcohols, antifreeze, and detergents). Aromatic hydrocarbons have formulas that can be drawn as cyclic alkenes, making them appear unsaturated, but their structure and properties are generally quite different, so they are not considered to be alkenes. Aromatic compounds serve as the basis for many drugs, antiseptics, explosives, solvents, and plastics (e.g., polyesters and polystyrene).

**Figure 22.0a.** Tomatoes
(Credit: Tomato by Softeis, CC
BY-SA 3.0)

Alkenes also occur widely in nature. Ripening fruits and vegetables give off ethylene, which triggers further ripening. Fruit processors artificially introduce ethylene to hasten the ripening process; exposure to as little as 0.1 mg of ethylene for 24 h can ripen 1 kg of tomatoes as in Figure 22.0a. Unfortunately, this process does not exactly duplicate the ripening process, and tomatoes picked green and treated this way don't taste much like vine-ripened tomatoes fresh from the garden. The bright red colour of tomatoes is due to lycopene—a polyene (Figure 22.0b.).
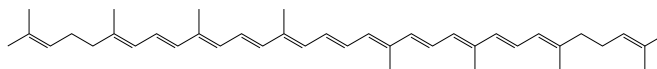


**Figure 22.0b:** The bright red colour of tomatoes is due to lycopene – a polyene. (credit: Image by Jeff Dahl, PDM).

Other alkenes that occur in nature include 1-octene, a constituent of lemon oil, and octadecene ($C_{18}H_{36}$) found in fish liver. Dienes (two double bonds) and polyenes (three or more double bonds) are also common. Butadiene ($CH_2=CHCH=CH_2$) is found in coffee. Lycopene and the carotenes are isomeric polyenes ($C_{40}H_{56}$) that give the attractive red, orange, and yellow colours to watermelons, tomatoes, carrots, and other fruits and vegetables. Vitamin A, essential to good vision, is derived from a carotene. The world would be a much less colourful place without alkenes. Infographic 22.0a. discusses if tomatoes should be stored in the fridge.

# THE CHEMISTRY OF TOMATOES

## SHOULD TOMATOES BE STORED IN THE FRIDGE?

**(Z)-3-HEXENAL**
Significant volatile compound in tomatoes

Chilling damages cell membranes in tomatoes, and inhibits enzyme activity, which can lead to a drastic loss of volatile compounds. Some of these, such as the C6 (six carbon) volatiles, do not contribute significantly to flavour, but others, such as geranial, have a noted impact on factors such as sweetness.
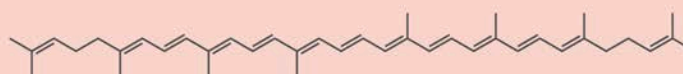
Taking tomatoes out of the fridge for 24 hours can lead to some recovery of volatile compounds, however, though only within a week of fridge storage. It's also worth noting that storing ripe tomatoes in the fridge can obviously be beneficial, to stop them from going off!
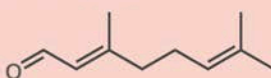
**GERANIAL**
Contributor to sweetness of tomatoes

## WHAT CAUSES THE COLOUR OF TOMATOES?

**LYCOPENE**
Absorbs all but the longest wavelengths of visible light

Green tomatoes are so coloured because of the presence of chlorophyll. As they ripen, the pigment lycopene develops; this compound absorbs light across most of the visible light spectrum, except the red portion, causing the tomato to appear red. It absorbs most visible light as a result of its highly conjugated structure - that is to say, it has lots of alternating double and single bonds.

**Infographic 22.0a.** Read more about "The Chemistry (https://www.compoundchem.com/2014/10/02/tomatoes/)of Tomatoes" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 22.0a [New tab].

# Attribution & References

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- "13.4: Properties of Alkenes and Alkynes" In *Map: Fundamentals of General Organic and Biological Chemistry (McMurry et al.)*, CC BY-NC-SA 3.0 . / A derivative of *Basics of GOB (Ball et al.)*, CC BY-NC-SA 4.0 a LibreTexts version of *Introduction to Chemistry: GOB (v. 1.0)*, CC BY-NC 3.0
- 1st paragraph is adapted from "13.0: Prelude to Unsaturated and Aromatic Hydrocarbons" In *Basics of General, Organic, and Biological Chemistry (Ball et al.)* by David W. Ball, John W. Hill, and Rhonda J. Scott via LibreTexts, licensed under CC BY-NC-SA 4.0. / A derivative of *Introduction to Chemistry: GOB (v. 1.0)*, CC BY-NC 3.0

# 22.1 ALKENES AND ALKYNES - STRUCTURE AND NAMING

As noted before, **alkenes** are hydrocarbons with carbon-to-carbon double bonds ($R_2C=CR_2$) and **alkynes** are hydrocarbons with carbon-to-carbon triple bonds ($R-C\equiv C-R$). Collectively, they are called unsaturated hydrocarbons because they have fewer hydrogen atoms than does an alkane with the same number of carbon atoms, as is indicated in the following general formulas in Figure 22.1a.
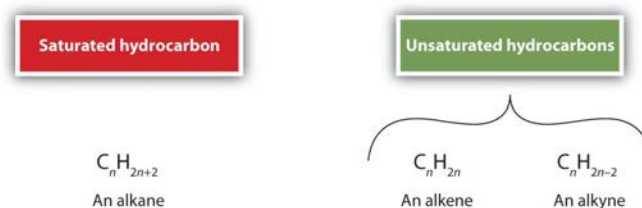


**Figure 22.1a.** The general formulas of alkanes, alkenes and alkynes (credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

You have likely heard of unsaturated fats. These are complex organic molecules with long chains of carbon atoms, which contain at least one double bond between carbon atoms. Double and triple bonds give rise to a different geometry around the carbon atom that participates in them, leading to important differences in molecular shape and properties. The differing geometries are responsible for the different properties of unsaturated versus saturated fats.

# Alkenes

Ethene, $C_2H_4$, is the simplest alkene. Each carbon atom in ethene, commonly called ethylene, has a trigonal planar structure. The second member of the series is propene (propylene) (Figure 22.1b.); the butene isomers follow in the series. Four carbon atoms in the chain of butene allows for the formation of isomers based on the position of the double bond, as well as a new form of isomerism.
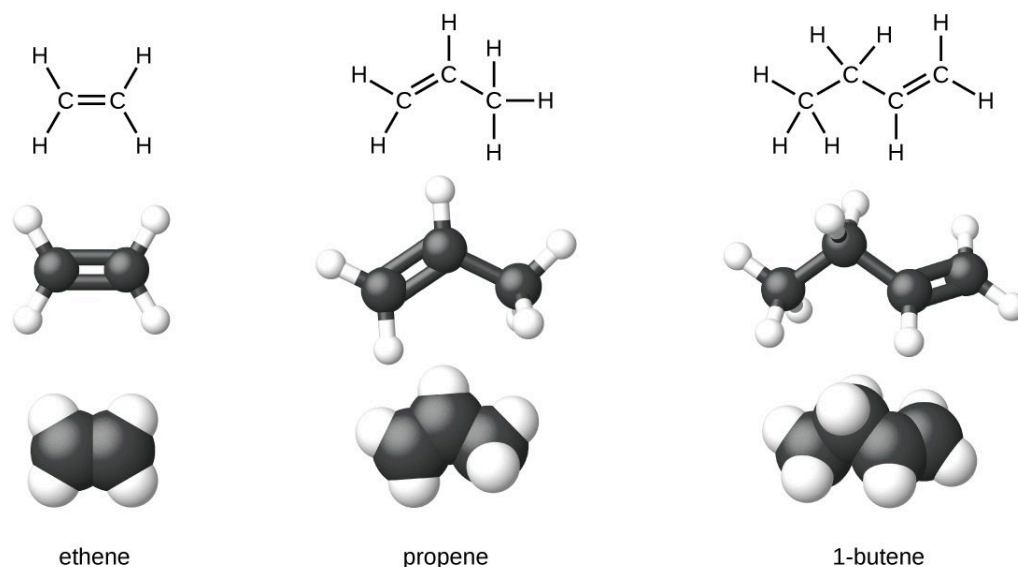


ethene                    propene                    1-butene

**Figure 22.1b.** Expanded structures, ball-and-stick structures, and space-filling models for the alkenes ethene, propene, and 1-butene are shown. (credit: *Chemistry (OpenStax)*, CC BY 4.0)

Some representative alkenes—their names, structures, and physical properties—are given in Table 22.1a. In general, as the chain length increases, the melting and boiling points increase. In comparison to alkanes, alkenes have higher melting points but lower boiling points. For instance, looking at propane versus propene, propane has a melting point of -190°C and a boiling point of -42°C, whereas propene has a melting point of -185°C and a boiling point of -47°C. When comparing alkenes to alkanes, refer to Table 20.1b Properties of Some Alkanes.

**Table 22.1a. Physical Properties of Some Selected Alkenes**

| IUPAC Name | Molecular Formula | Condensed Structural Formula | Melting Point (°C) | Boiling Point (°C) |
|---|---|---|---|---|
| ethene | $C_2H_4$ | $CH_2=CH_2$ | −169 | −104 |
| propene | $C_3H_6$ | $CH_2=CHCH_3$ | −185 | −47 |
| 1-butene | $C_4H_8$ | $CH_2=CHCH_2CH_3$ | −185 | −6 |
| 1-pentene | $C_5H_{10}$ | $CH_2=CH(CH_2)_2CH_3$ | −138 | 30 |
| 1-hexene | $C_6H_{12}$ | $CH_2=CH(CH_2)_3CH_3$ | −140 | 63 |
| 1-heptene | $C_7H_{14}$ | $CH_2=CH(CH_2)_4CH_3$ | −119 | 94 |
| 1-octene | $C_8H_{16}$ | $CH_2=CH(CH_2)_5CH_3$ | −102 | 121 |

**Table source:** "13.1: Alkenes: Structures and Names" In *Basics of GOB Chemistry (Ball et al.)*, CC BY-NC-SA 4.0.

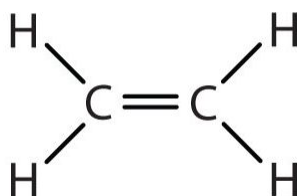We used only condensed structural formulas in Table 1. Thus, $CH_2=CH_2$ is illustrated in Figure 22.1c.



**Figure 22.1c.** The structural representation of $CH_2=CH_2$ (credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

The double bond is shared by the two carbons and does not involve the hydrogen atoms, although the condensed formula does not make this point obvious. Note that the molecular formula for ethene is $C_2H_4$, whereas that for ethane is $C_2H_6$.

The first two alkenes in Table 22.1a., ethene and propene, are most often called by their common names—ethylene and propylene, respectively (Figure 22.1d.). Ethylene is a major commercial chemical. The US chemical industry produces about 25 billion kilograms of ethylene annually, more than any other synthetic organic chemical. More than half of this ethylene goes into the manufacture of polyethylene, one of the most familiar plastics. Propylene is also an important industrial chemical. It is converted to plastics, isopropyl alcohol, and a variety of other products.
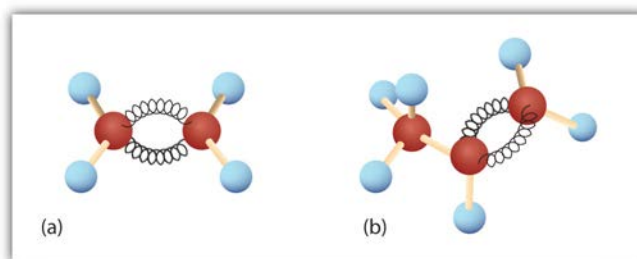
**Figure 22.1d.** Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles. (credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

# Naming Alkenes

Alkenes are named using a series of rules similar to those for alkanes, with the suffix *-ene* used instead of *-ane* to identify the functional group. There are three steps to this process.

1. Name the parent hydrocarbon. Find the longest carbon chain containing the double bond, and name the compound accordingly, using the suffix *-ene* as in Figure 22.1e.
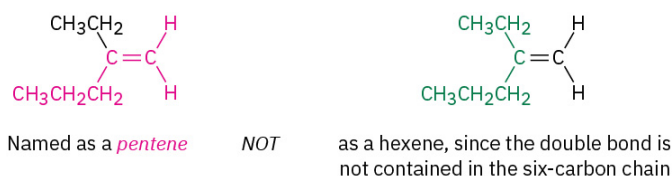


**Figure 22.1e.** Finding the longest chain in an alkene using pentene as the example. (credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0)

2. Number the carbon atoms in the chain. Begin at the end nearer the double bond or, if the double bond is equidistant from the two ends, begin at the end nearer the first branch point. This rule ensures that the double-bond carbons receive the lowest possible numbers such as those examples shown in Figure 22.1f.



**Figure 22.1f.** Numbering the carbon atoms in the chain to ensure the double-bond carbons receive the lowest possible numbers. (credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0)

3. Write the full name. Number the substituents according to their positions in the chain, and list them alphabetically. Indicate the position of the double bond by giving the number of the first alkene carbon and placing that number directly before the parent name. If more than one double bond is present, indicate the position of each and use one of the suffixes *-diene, -triene,* and so on.
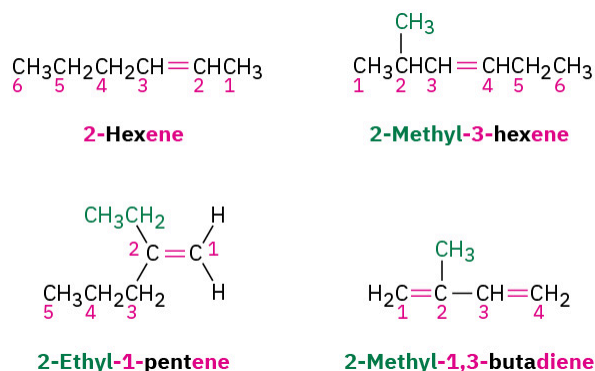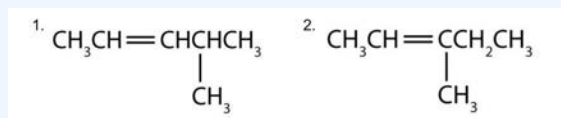
$$CH_3CH_2CH_2CH=CHCH_3$$
6 5 4 3 2 1

**2-Hexene**

$$CH_3 \atop | \atop CH_3CHCH=CHCH_2CH_3$$
1 2 3 4 5 6

**2-Methyl-3-hexene**

$$CH_3CH_2 \quad H \atop \diagdown \diagup \atop 2 C=C 1 \atop \diagup \diagdown \atop CH_3CH_2CH_2 \quad H$$
5 4 3

**2-Ethyl-1-pentene**

$$CH_3 \atop | \atop H_2C=C-CH=CH_2$$
1 2 3 4

**2-Methyl-1,3-butadiene**

**Figure 22.1g.** Examples when numbering substituents within an alkene chain or when you have more than one double-bond present. (credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0)

## Example 22.1a

Name each compound.

1. $CH_3CH=CHCHCH_3$
   $\quad\quad\quad\quad |$
   $\quad\quad\quad\quad CH_3$

2. $CH_3CH=CCH_2CH_3$
   $\quad\quad\quad\quad |$
   $\quad\quad\quad\quad CH_3$

(Credit: *Introduction to Chemistry: GOB (V. 1.0).*, CC BY-NC-SA 3.0.)

## Solution

1. The longest chain containing the double bond has five carbon atoms, so the compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the fourth carbon atom (rule 3), so the compound's name is 4-methyl-2-pentene.
2. The longest chain containing the double bond has five carbon atoms, so the parent compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the third carbon atom (rule 3), so the compound's name is 3-methyl-2-pentene.

## Example 22.1b

Name this compound.
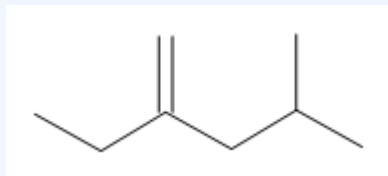


### Solution:

First, find the longest chain that contains the C=C bond. Notice that is it not the six-carbon chain across the page. The longest chain is 5 carbons. The C=C bond gets the lowest possible number. This compound is 2-ethyl-4-methylpent-1-ene.

**Activity source:** Exercise 22.1b is created by Samantha Sullivan Sauer, using images from Biovia Draw, licensed under CC BY-NC 4.0

Beta-carotene (found in spinach), capsanthin and capsorubin (both found in peppers), consist of long chained alkenes. Check out the infographics 22.1a. and 22.1b. for more details.

## Spotlight on Everyday Chemistry: Spinach and Bell Peppers

The vitamin A precursor found in both spinach and bell peppers is beta-carotene, an alkene. Beta-carotene consists of a long carbon chain with multiple double bonds with a substituted cyclohexene at each end. In addition, pigments and scents within bell peppers are alkenes. Specifically, chlorophyll contributes to the green pigment found in bell peppers and many other green plants. For more information see infographic 22.1a. and 22.1b.

**Infographic 22.1a.** Read more about "The Chemistry of Spinach (https://www.compoundchem.com/2018/07/17/spinach/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 22.1a [New tab].

**Infographic 22.1b.** Read more about "The Chemistry of Bell Peppers (https://www.compoundchem.com/2016/07/05/bell-peppers/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 22.1b [New tab].

## Naming Cycloalkenes

Cycloalkenes are named similarly, but because there is no chain end to begin from, we number the cycloalkene so that the double bond is between C1 and C2 and the first substituent has as low a number as possible. It's not necessary to indicate the position of the double bond in the name because it's always between C1 and C2. As with open-chain alkenes, the newer but not yet widely accepted naming rules place the locant immediately before the suffix in a cyclic alkene.
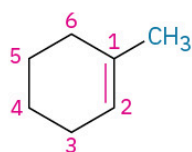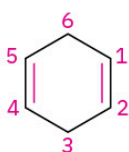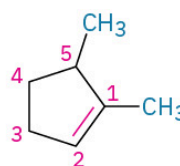
**1-Methylcyclohexene**

**1,4-Cyclohexadiene**

**(New: Cyclohexa-1,4-diene)**

**1,5-Dimethylcyclopentene**

**Figure 22.1h.** Examples of naming cycloalkenes. (credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0)
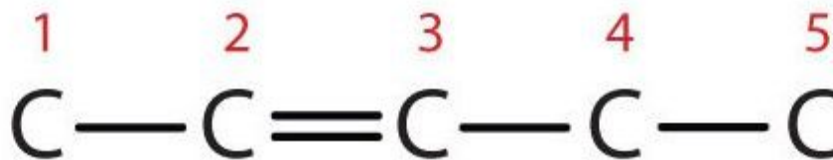
## Example 22.1c

Draw the structure for each compound.

1. 3-methyl-2-pentene
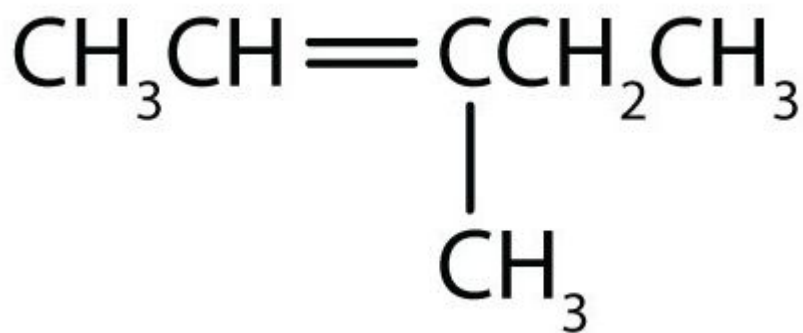2. cyclohexene

## Solution

1. First write the parent chain of five carbon atoms: C–C–C–C–C. Then add the double bond between the second and third carbon atoms:
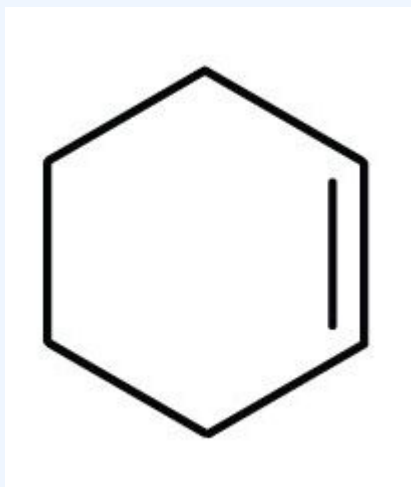


(credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

Now place the methyl group on the third carbon atom and add enough hydrogen atoms to give each carbon atom a total of four bonds.

$$CH_3CH=CCH_2CH_3$$
$$|$$
$$CH_3$$

(credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

- First, consider what each of the three parts of the name means. *Cyclo* means a ring compound, *hex* means 6 carbon atoms, and *–ene* means a double bond.
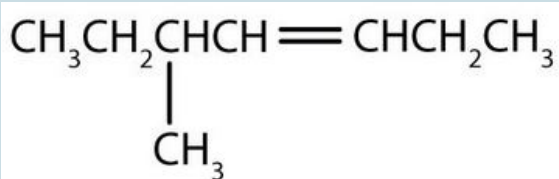


(credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

## Exercise 22.1a

Name each compound.

1. $CH_3CH_2CH_2CH_2CH_2CH=CHCH_3$

2. $CH_3CH_2CHCH = CHCH_2CH_3$ with $CH_3$ branch

**Check Your Answers:[1]**

Exercise source: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0

## Spotlight on Everyday Chemistry: Ethiopian Rooster Doro Wat

Doro wat is a common dish served at Christmas in Ethiopia. It consists of a spicy chicken stew with the flavours arising from alkenes and cycloalkenes. Three spices in particular are sotolon (flavour in fenugreek), linalool (flavour in coriander seeds) and 1,8-cineole (flavour in cardamon seeds). Linalool is shown below in Figure 22.1i.



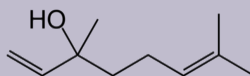**Figure 22.1i.** The molecular structure of linalool (credit: Image by Capaccio, CC BY-SA 3.0).

For more information on this dish refer to the infographic from Compound Interest: The Chemistry Advent Calendar 2023 (compoundchem.com). (https://www.compoundchem.com/2023advent/#day11)

# Alkynes

Hydrocarbon molecules with one or more triple bonds are called **alkynes**; they make up another series of

unsaturated hydrocarbons. Two carbon atoms joined by a triple bond have bond angles of 180°, giving these types of bonds a linear shape.

The simplest member of the alkyne series is ethyne, $C_2H_2$, commonly called acetylene as shown in Figure 22.1j. The Lewis structure for ethyne, a linear molecule, is:
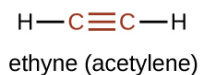
$$H-C\equiv C-H$$

ethyne (acetylene)

**Figure 22.1j.** The molecular structure of ethyne. (credit: *Chemistry (OpenStax)*, CC BY 4.0)

Acetylene is used in oxyacetylene torches for cutting and welding metals. The flame from such a torch can be very hot. Most acetylene, however, is converted to chemical intermediates that are used to make vinyl and acrylic plastics, fibers, resins, and a variety of other products.

Alkynes are similar to alkenes in both physical and chemical properties. For example, alkynes undergo many of the typical addition reactions of alkenes. Again, when comparing alkynes to alkanes, refer to Table 20.1b. Properties of Some Alkanes.

## Naming Alkynes

The International Union of Pure and Applied Chemistry (IUPAC) names for alkynes parallel those of alkenes, except that the family ending is *–yne* rather than *–ene*.

Alkynes follow the same naming rules as alkenes, using the same stem as alkanes, however they end in *-yne* to identify it as an alkyne.

Alkyne nomenclature follows the general rules for hydrocarbons replacing with the suffix *-yne*, and the position of the triple bond is indicated by giving the number of the first alkyne carbon in the chain.

1. Numbering the main chain begins at the end nearer the triple bond so that the triple bond receives as low a number as possible as illustrated in Figure 22.1k.

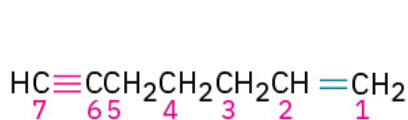$$CH_3CH_2CHCH_2C\equiv CCH_2CH_3$$

Begin numbering at the end nearer the triple bond.
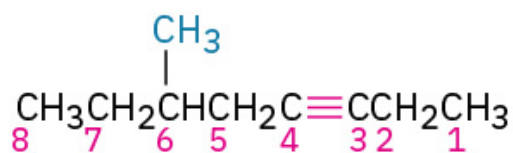
6-Methyl-3-octyne
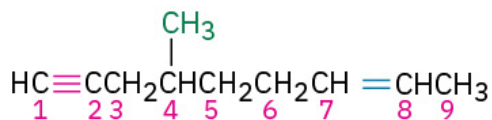(New: 6-Methyloct-3-yne)

**Figure 22.1k.** Numbering the alkyne at the end nearer the triple bond. (credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0)

Compounds with more than one triple bond are called diynes, triynes, and so forth; compounds containing both double and triple bonds are called enynes (not ynenes).

1. Numbering of an enyne chain starts from the end nearer the first multiple bond, whether double or triple. When there is a choice in numbering, double bonds receive lower numbers than triple bonds as shown in Figure 22.1l.

$$HC \equiv CCH_2CH_2CH_2CH = CH_2$$
$$\phantom{HC}7\phantom{\equiv}65\phantom{CH_2}4\phantom{CH_2}3\phantom{CH_2}2\phantom{CH}1$$

**1-Hepten-6-yne**
**(New: Hept-1-en-6-yne)**

$$\phantom{HC \equiv CCH_2}\overset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}\phantom{H}$$
$$HC \equiv CCH_2CHCH_2CH_2CH = CHCH_3$$
$$1\phantom{HC}23\phantom{CH_2}4\phantom{C}5\phantom{CH_2}6\phantom{CH_2}7\phantom{CH}8\phantom{=}9$$

**4-Methyl-7-nonen-1-yne**
**(New: 4-Methylnon-7-en-1-yne)**

**Figure 22.1l.** Examples of naming alkynes when numbering the double bond receives lower numbers than triple bonds. (credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0)

For a summary on how to name alkyne, watch Naming Alkynes shown below.

**Watch Naming Alkynes – IUPAC Nomenclature & Common Names – Youtube (13 min). (https://youtu.be/ouDS2tZU94g?)**

## Exercise 22.1b

Draw the structure for each compound.

a. acetylene
b. 3-methyl-1-hexyne

**Check Your Answers:[2]**

**Exercise source:** *Introduction to Chemistry: GOB (v. 1.0)*, CC BY-NC 3.0

## Exercise 22.1c

Name each alkyne.

    a. $CH_3CH_2CH_2C{\equiv}CH$

    b. $CH_3CH_2CH_2C{\equiv}CCH_3$

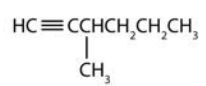**Check Your Answers:[3] Exercise source: _Intro Chem: GOB (v. 1.0),_ CC BY-NC 3.0**

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# Notes

1. 1) 2-octene 2) 5-methyl-3-heptene

2. a) H–C≡C–H b)

$$HC\equiv CCHCH_2CH_2CH_3$$
$$|$$
$$CH_3$$

3. a) 1-pentyne b) 2-hexyne

# 22.2 STRUCTURE OF ALKENES - CIS-TRANS ISOMERS

## Learning Objectives

By the end of this section, you will be able to:

- Recognize that alkenes that can exist as cis-trans isomers.
- Classify isomers as cis or trans.
- Draw structures for cis-trans isomers given their names.

There is free rotation about the carbon-to-carbon single bonds (C–C) in alkanes. In contrast, the structure of alkenes requires that the carbon atoms of a double bond and the two atoms bonded to each carbon atom all lie in a single plane, and that each doubly bonded carbon atom lies in the center of a triangle. This part of the molecule's structure is rigid; rotation about doubly bonded carbon atoms is *not* possible without rupturing the bond. Look at the two chlorinated hydrocarbons in Figure 22.2a.
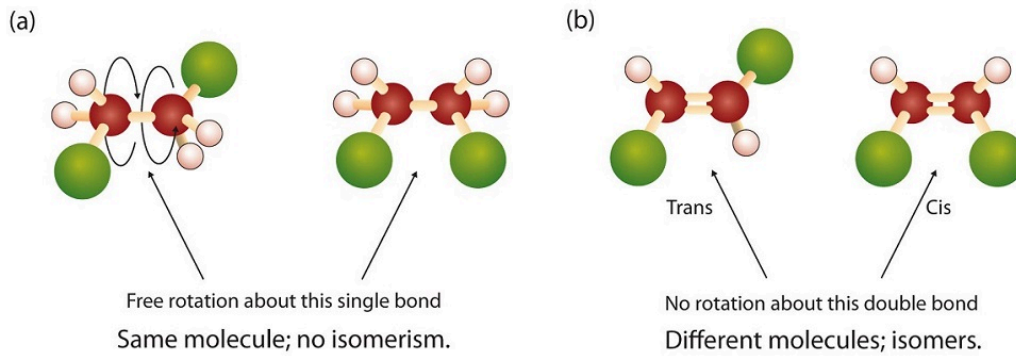
(a)

(b)

Trans　　　　　　　Cis

Free rotation about this single bond

No rotation about this double bond

Same molecule; no isomerism.

Different molecules; isomers.

**Figure 22.2a.** Rotation about Bonds. In 1,2-dichloroethane (a), free rotation about the C–C bond allows the two structures to be interconverted by a twist of one end relative to the other. In 1,2-dichloroethene (b), restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond are significant. (Credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0 ; edited by Ball et al.)

In 1,2-dichloroethane (part (a) of Figure 22.2b.), there is free rotation about the C–C bond. The two models shown represent exactly the same molecule; they are *not* isomers. You can draw structural formulas that look different, but if you bear in mind the possibility of this free rotation about single bonds, you should recognize that these two structures represent the same molecule:
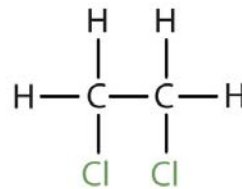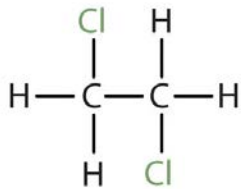
**Figure 22.2b.**1, 2-dichloroethane on the left (a) and 1.2-dichloroethane on the left (b). (Credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0)

In 1,2-dichloroethene (part (b) of Figure 22.2b.), however, restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond become significant. This

leads to a special kind of isomerism. The isomer in which the two chlorine (Cl) atoms lie on the same side of the molecule is called the cis isomer (Latin *cis,* meaning "on this side") and is named cis-1,2-dichloroethene. The isomer with the two Cl atoms on opposite sides of the molecule is the trans isomer (Latin *trans,* meaning "across") and is named *trans*-1,2-dichloroethene. These two compounds are cis-trans isomers (or geometric isomers), compounds that have different configurations (groups permanently in different places in space) because of the presence of a rigid structure in their molecule.

Consider the alkene with the condensed structural formula $CH_3CH=CHCH_3$. We could name it 2-butene, but there are actually two such compounds; the double bond results in cis-trans isomerism (Figure 22.2c.).
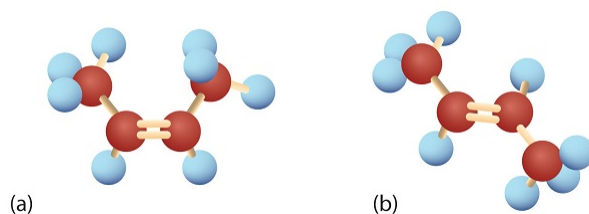


(a)        (b)

**Figure 22.2c.** Ball-and-Spring Models of (a) Cis-2-Butene and (b) Trans-2-Butene. Cis-trans isomers have different physical, chemical, and physiological properties. (Credit: *Intro Chem: GOB (V. 1.0).,* CC BY-NC-SA 3.0 ; edited by Ball et al.)

*Cis*-2-butene has both methyl groups on the same side of the molecule. *Trans*-2-butene has the methyl groups on opposite sides of the molecule. Their structural formulas are as follows according to Figure 22.2d.
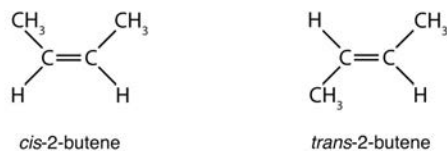


cis-2-butene        trans-2-butene

**Figure 22.2d.** Models of (left) Cis-2-Butene and (right) Trans-2-Butene. (Credit: *Intro Chem : GOB (V. 1.0).,* CC BY-NC-SA 3.0).

Note, however, that the presence of a double bond does **not** necessarily lead to cis-trans isomerism (Figure 22.2e.). We can draw two *seemingly* different propenes:
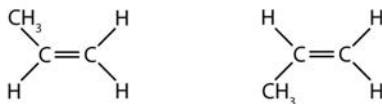


**Figure 22.2e.** Different views of the propene molecule (flip vertically). These are not isomers. (Credit: *Intro Chem: GOB (V. 1.0).,* CC BY-NC-SA 3.0).

However, these two structures are not really different from each other. If you could pick up either molecule

from the page and flip it over top to bottom, you would see that the two formulas are identical. Thus, there are two requirements for cis-trans isomerism:

1. Rotation must be restricted in the molecule.
2. There must be two nonidentical groups on each doubly bonded carbon atom.

In these propene structures, the second requirement for cis-trans isomerism is not fulfilled. One of the doubly bonded carbon atoms does have two different groups attached, but the rules require that *both* carbon atoms have two different groups. In general, the following statements hold true in cis-trans isomerism:

- Alkenes with a $C=CH_2$ unit do not exist as cis-trans isomers.
- Alkenes with a $C=CR_2$ unit, where the two R groups are the same, do not exist as cis-trans isomers.
- Alkenes of the type R–CH=CH–R can exist as cis and trans isomers; cis if the two R groups are on the same side of the carbon-to-carbon double bond, and trans if the two R groups are on opposite sides of the carbon-to-carbon double bond.

## Advanced Note: E/Z Isomerization

If a molecule has a $C=C$ bond with one non-hydrogen group attached to each of the carbons, cis/trans nomenclature described above is enough to describe it. However, if you have three different groups (or four), then the cis/trans approach is insufficient to describe the different isomers, since we do not know which two of the three groups are being described. For example, if you have a $C=C$ bond, with a methyl group and a bromine on one carbon, and an ethyl group on the other, it is neither trans nor cis, since it is not clear whether the ethyl group is trans to the bromine or the methyl.

Cis-trans isomerism also occurs in cyclic compounds. In ring structures, groups are unable to rotate about any of the ring carbon–carbon bonds. Therefore, groups can be either on the same side of the ring (cis) or on opposite sides of the ring (trans). For our purposes here, we represent all cycloalkanes as planar structures, and we indicate the positions of the groups, either above or below the plane of the ring. Refer to Figure 22.2f. to compare cis-1,2-dimethylcyclopropane and trans-1,2-dimethylcyclopropane.



Cis-1,2-dimethylcyclopropane        Trans-1,2-dimethylcyclopropane

**Figure 22.2f.** Cis-1,2-dimethylcyclopropane and trans-1,2-dimethylcyclopropane. (Credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

For a look at the types of isomerism in organic chemistry. Refer back to Infographic 20.3a.

## Example 22.2a

Which compounds can exist as cis-trans (geometric) isomers? Draw them.

1. $CHCl=CHBr$
2. $CH_2=CBrCH_3$
3. $(CH_3)_2C=CHCH_2CH_3$
4. $CH_3CH=CHCH_2CH_3$

### Solution

All four structures have a double bond and thus meet rule 1 for cis-trans isomerism.

1. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom (H and Cl on one and H and Br on the other). It exists as both cis and trans isomers:
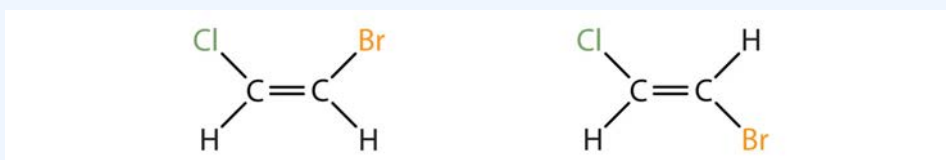


(Credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

- This compound has two hydrogen atoms on one of its doubly bonded carbon atoms; it fails rule 2 and does not exist as cis and trans isomers.
- This compound has two methyl ($CH_3$) groups on one of its doubly bonded carbon atoms. It fails rule 2 and does not exist as cis and trans isomers.
- This compound meets rule 2; it has two nonidentical groups on *each* carbon atom and exists as both cis and trans isomers:
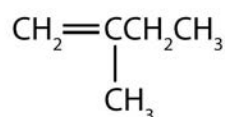


(Credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).
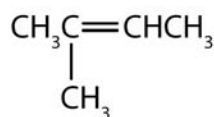
## Exercise 22.2a

Which compounds can exist as cis-trans isomers?

a. $CH_2=CHCH_2CH_2CH_3$

b. $CH_3CH=CHCH_2CH_3$

c. $CH_3CH_2CH=CHCH_2CH_3$

d.



(Credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

e.



(Credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

**Check Your Answers:[1]**

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# Notes

1. a) no cis-trans isomers b) cis-trans isomers are possible c) cis-trans isomers are possible d) no cis-trans isomers e) no cis-trans isomers

# 22.3 REACTIONS OF ALKENES AND ALKYNES

<div style="background-color:olive">

## Learning Objectives

By the end of this section, you will be able to:

- Write equations for the addition reactions of alkenes and alkynes with hydrogen, halogens, and water
- Describe Markovnikov's Rule as it applies to addition reactions
- Describe chemical tests to test for the presence of unsaturated hydrocarbons.

</div>

## Addition Reactions

Alkenes are valued mainly for addition reactions, in which one of the bonds in the double bond is broken. Each of the carbon atoms in the bond can then attach another atom or group while remaining joined to each other by a single bond. Examples of addition reactions include hydrogenation, halogenation and hydration.

### Hydrogenation of Alkenes

Perhaps the simplest addition reaction is hydrogenation—a reaction with hydrogen ($H_2$) in the presence of a catalyst such as nickel (Ni) or platinum (Pt). An example of the addition reaction between ethylene and hydrogen is shown in Figure 22.3a.
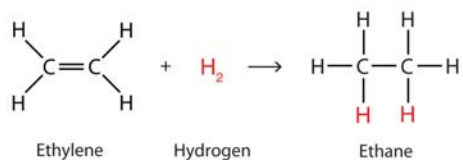


**Figure 22.3a**. Addition reaction of ethylene with hydrogen to produce ethane. (Credit: *Intro Chemistry: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

The product is an alkane having the same carbon skeleton as the alkene.

## Halogenation of Alkenes

Alkenes also readily undergo halogenation—the addition of halogens. Indeed, the reaction with bromine ($Br_2$) can be used to test for alkenes. Bromine solutions are brownish red. When we add a $Br_2$ solution to an alkene, the colour of the solution disappears because the alkene reacts with the bromine as shown in Figure 22.3b.



Ethylene          Bromine          1,2-Dibromoethane
                (brownish-red)        (colorless)

**Figure 22.3b**. The halogenation of ethylene and bromine to produce 1,2-dibromoethane. (Credit: *Intro Chemistry: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

## Hydration of Alkenes

Another important addition reaction is that between an alkene and water to form an alcohol. This reaction, called hydration as shown in Figure 22.3c., requires a catalyst—usually a strong acid, such as sulfuric acid ($H_2SO_4$).
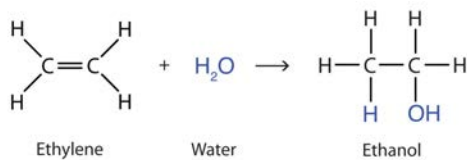


Ethylene          Water          Ethanol

**Figure 22.3c.** Hydration of ethylene and water to produce ethanol (Credit: *Intro Chemistry: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

The hydration reaction is discussed in a later chapter, where we deal with this reaction in the synthesis of alcohols.

### Example 22.3a

Write the equation for the reaction between $CH_3CH=CHCH_3$ and each substance.

a.  H₂ (Ni catalyst)

b.  Br₂

c.  H₂O (H₂SO₄ catalyst)

## Solution
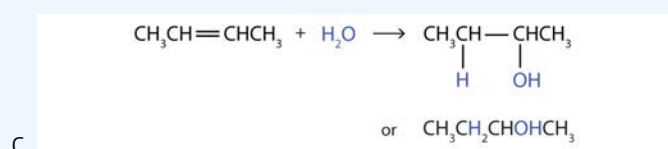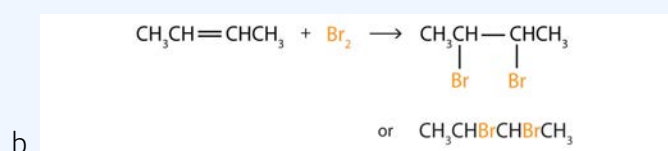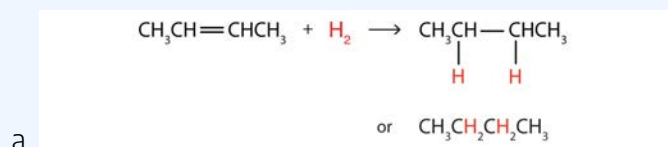
In each reaction, the reagent adds across the double bond.

a.
$$CH_3CH{=}CHCH_3 \ + \ H_2 \ \longrightarrow \ CH_3CH{-}CHCH_3$$
with H and H below the CH—CH
$$\text{or} \quad CH_3CH_2CH_2CH_3$$

b.
$$CH_3CH{=}CHCH_3 \ + \ Br_2 \ \longrightarrow \ CH_3CH{-}CHCH_3$$
with Br and Br below the CH—CH
$$\text{or} \quad CH_3CHBrCHBrCH_3$$

c.
$$CH_3CH{=}CHCH_3 \ + \ H_2O \ \longrightarrow \ CH_3CH{-}CHCH_3$$
with H and OH below the CH—CH
$$\text{or} \quad CH_3CH_2CHOHCH_3$$

**Image credit:** *Intro Chemistry: GOB (V. 1.0).*, CC BY-NC-SA 3.0.

# Exercise 22.3a

Write the equation for each reaction.

a.  $CH_3CH_2CH{=}CH_2$ with $H_2$ (Ni catalyst)

b.  $CH_3CH{=}CH_2$ with $Cl_2$

c.  $CH_3CH_2CH{=}CHCH_2CH_3$ with $H_2O$ ($H_2SO_4$ catalyst)

## Check Your Answers:[1]

**Source:** Exercise 22.3a is adapted from *Fundamentals of GOB Chem,* CC BY-NC-SA 4.0 with answer images drawn by Samantha Sullivan Sauer / Biovia Draw, CC BY-NC 4.0

# Markovnikov's Rule

In the addition any unsymmetrical hydrogen-based molecule (e.g. HX or $H_2O$) to an alkene, the H attaches to the carbon with fewer alkyl substituents and the X attaches to the carbon with more alkyl substituents. Examples of the rule is demonstrated in Figure 22.3d.
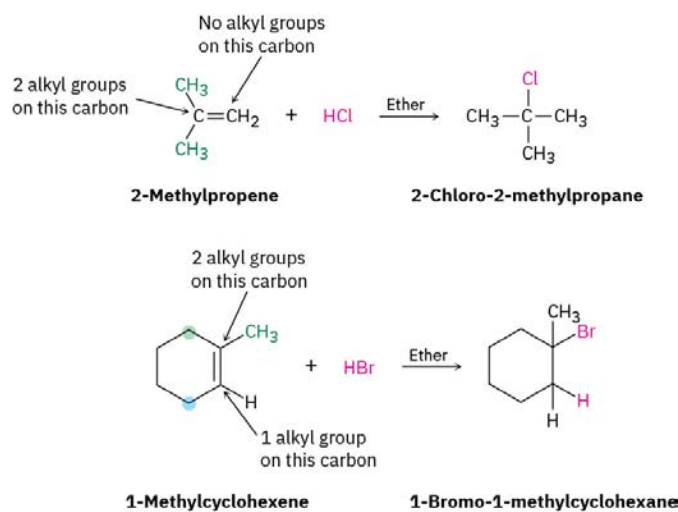


**Figure 22.3d.** Addition reactions using Markovnikov's rule for the reactions of 2-methylpropene with HCl (top) and 1-methylcylcohexene with HBr (bottom). (credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0).

When both double-bonded carbon atoms have the same degree of substitution, a mixture of addition products results as demonstrated in Figure 22.3e.
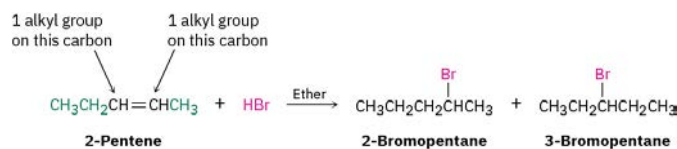


**Figure 22.3e.** Addition reaction when the double-bonded carbon has the same degree of substitution as shown when 2-pentene reacts with HBr. (credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0).

Because carbocations are involved as intermediates in these **electrophilic addition reactions**, Markovnikov's rule can be restated in the following way:

> **Markovnikov's rule restated** In the addition of HX or $H_2O$ to an alkene, the more highly substituted carbocation is formed as the intermediate rather than the less highly substituted one.

For example, in Figure 22.3f., addition of $H^+$ to 2-methylpropene yields the intermediate *tertiary* carbocation rather than the alternative primary carbocation, and addition to 1-methylcyclohexene yields a tertiary cation rather than a secondary one. Why should this be?
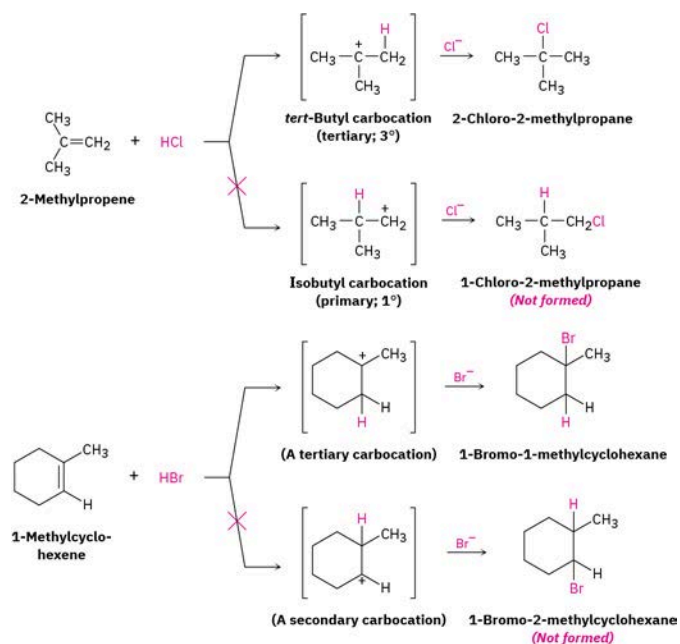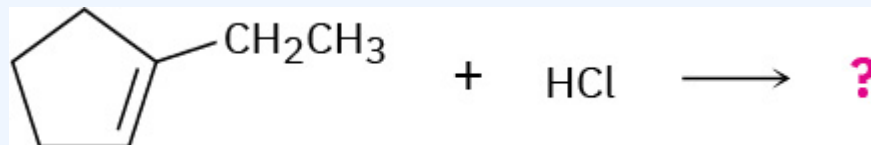
**Figure 22.3f.** Addition reaction involving the addition of $H^+$ to 2-methylpropene to yield intermediate *tertiary* carbocation (credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0).

## Example 22.3b

What product would you expect from reaction of HCl with 1-ethylcyclopentene?



(credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0).

## Strategy

When solving a problem that asks you to predict a reaction product, begin by looking at the functional group(s) in the reactants and deciding what kind of reaction is likely to occur. In the present instance, the reactant is an alkene that will probably undergo an electrophilic addition reaction with HCl. Next, recall what you know about electrophilic addition reactions to predict the product. You know that electrophilic addition reactions follow Markovnikov's rule, so $H^+$ will add to the double-bond carbon that has one alkyl group (C2 on the ring) and the Cl will add to the double-bond carbon that has two alkyl groups (C1 on the ring).

## Solution

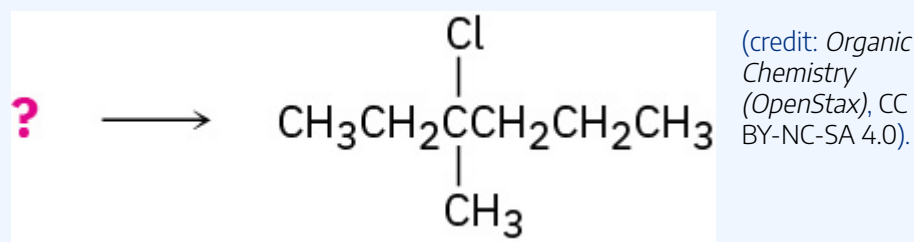The expected product is 1-chloro-1-ethylcyclopentane.
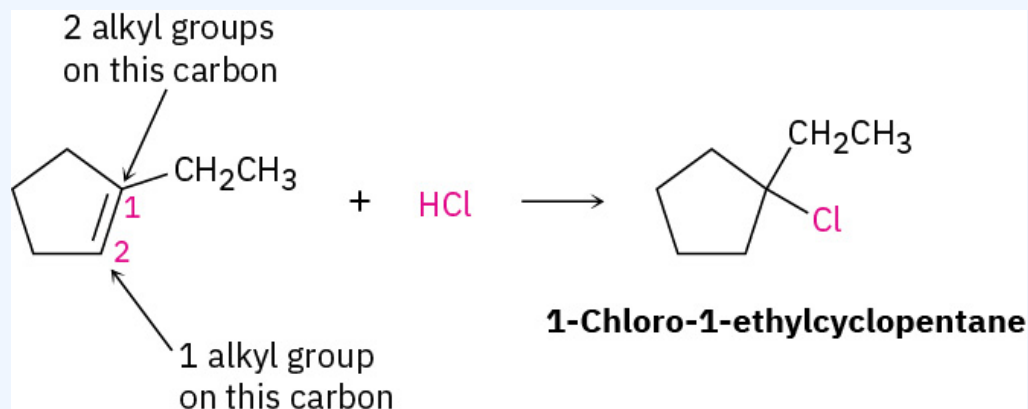


(credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0).

## Example 22.3c

### Synthesizing a Specific Compound

What alkene would you start with to prepare the following alkyl halide? There may be more than one possibility.



(credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0).

## Strategy

When solving a problem that asks how to prepare a given product, always work backward. Look at the product, identify the functional group(s) it contains, and ask yourself, "How can I prepare that functional group?" In the present instance, the product is a tertiary alkyl chloride, which can be prepared by reaction of an alkene with HCl. The carbon atom bearing the –Cl atom in the product must be one of the double-bond carbons in the reactant. Draw and evaluate all possibilities.
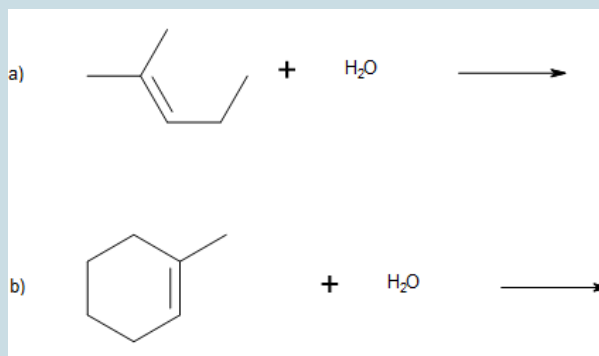
## Solution

There are three possibilities, all of which could give the desired product according to Markovnikov's rule.
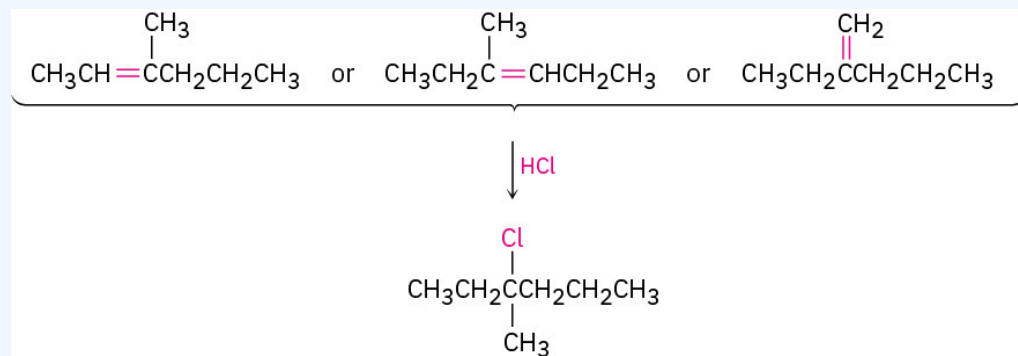


(credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0).

## Exercise 22.3b

Draw the major product formed from these reactions.



### Check Your Answers:[2]

**Activity source:** Exercise 22.3b is created by Samantha Sullivan Sauer, using images from Biovia Draw, licensed under CC BY-NC 4.0

For more details on alkene addition reactions including the concept of Markonikov's rule, watch Alkene Addition Reactions below.

**Watch Alkene Addition Reactions: Crash Course Organic Chemistry #16 (youtube.com) (https://youtu.be/3WbjKwRqOhk?) (13 min).**

# Polymerization

The most important commercial reactions of alkenes are *polymerizations*, reactions in which small molecules, referred to in general as monomers (from the Greek *monos*, meaning "one," and *meros*, meaning "parts"), are assembled into giant molecules referred to as polymers (from the Greek *poly*, meaning "many," and *meros*, meaning "parts"). For more information on polymerization see Chapter 27: Polymers.

# Sourcing of Alkenes

In summary, recall that organic functional groups can be converted into other functional groups through reactions. To look at the sourcing of alkenes, refer to the map of some of the more common reactions to convert functional groups can be found in Section 19.6 – General Reactions of Carbon in Infographic 19.6a.

# Reactions of Alkynes

Chemically, the alkynes are similar to the alkenes. Alkynes can undergo addition, hydration and hydrogenation (or reduction) reactions.

## Halogenation of Alkynes

Since the C≡C″>C≡C functional group has two π bonds, alkynes typically react even more readily, and react with twice as much reagent in addition reactions. The reaction of acetylene with bromine is a typical example as shown in Figure 22.3g.
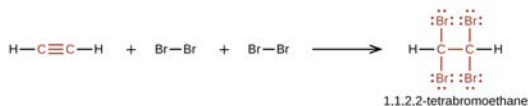


**Figure 22.3g.** Addition reaction involving acetylene and bromine (credit: *Chemistry: Atoms First 2e (OpenStax)*, CC BY 4.0)

Acetylene and the other alkynes also burn readily. An acetylene torch takes advantage of the high heat of combustion for acetylene.

As a general rule, electrophiles undergo addition reactions with alkynes much as they do with alkenes. Take the reaction of alkynes with HX, for instance. The reaction often can be stopped with the addition of 1

equivalent of HX, but reaction with an excess of HX leads to a dihalide product. For example, reaction of 1-hexyne with 2 equivalents of HBr yields 2,2-dibromohexane. As the following examples indicate, the regiochemistry of addition follows Markovnikov's rule, with halogen adding to the more highly substituted side of the alkyne bond and hydrogen adding to the less highly substituted side. Trans stereochemistry of H and X normally, although not always, occurs in the product.

**HBr addition**

CH₃CH₂CH₂CH₂C≡CH  →(HBr / CH₃CO₂H)→  CH₃CH₂CH₂CH₂C=CH (Br H)  →(HBr / CH₃CO₂H)→  CH₃CH₂CH₂CH₂C—CH (Br H / Br H)

1-Hexyne          2-Bromo-1-hexene          2,2-Dibromohexane

(credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0).

**HCl addition**

CH₃CH₂C≡CCH₂CH₃  →(HCl / CH₃CO₂H)→  (Cl / CH₃CH₂ C=C CH₂CH₃ / H)  →(HCl / CH₃CO₂H)→  CH₃CH₂C—CCH₂CH₃ (Cl H / Cl H)

3-Hexyne          (Z)-3-Chloro-3-hexene          3,3-Dichlorohexane
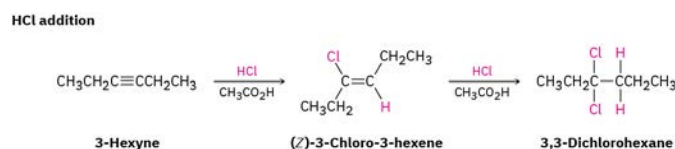
**Figure 22.3h.** HBr addition to 1-hexyne (top) and HCl addition to 3-hexyne (bottom). (credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0).

Bromine and chlorine also add to alkynes to give addition products, and trans stereochemistry again results as demonstrated in Figure 22.3i. below.

**Br₂ addition**

CH₃CH₂C≡CH  →(Br₂ / CH₂Cl₂)→  (Br / CH₃CH₂ C=C H / Br)  →(Br₂ / CH₂Cl₂)→  CH₃CH₂C—CH (Br Br / Br Br)

1-Butyne          (E)-1,2-Dibromo-1-butene   1,1,2,2-Tetrabromobutane

**Figure 22.3i.** Br₂ addition to 1-butyne.  (credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0).

The mechanism of alkyne addition is similar but not identical to that of alkene addition. When an electrophile such as HBr adds to an alkene, the reaction takes place in two steps and involves an alkyl carbocation intermediate. If HBr were to add by the same mechanism to an alkyne, an analogous vinylic carbocation would be formed as the intermediate as shown in Figure 22.3j.
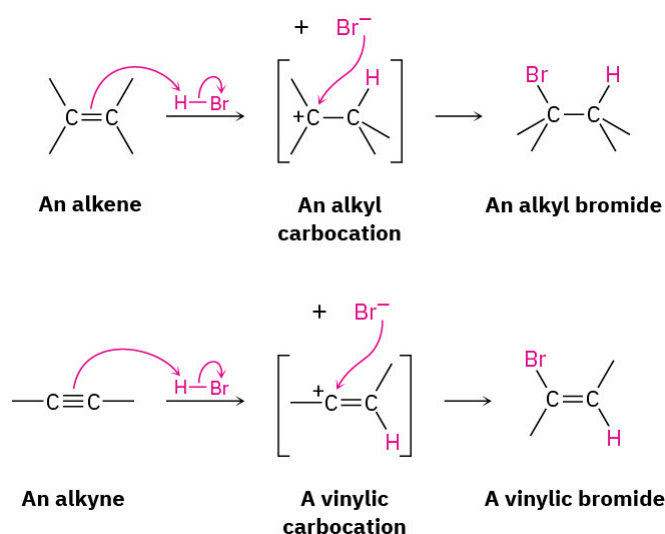
**Figure 22.3j.** The mechanism of alkene and alkyne addition involving carbocation intermediate. (credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0).

A vinylic carbocation has an *sp*-hybridized carbon and generally forms less readily than an alkyl carbocation (Figure 22.3j.). As a rule, a secondary vinylic carbocation forms about as readily as a primary alkyl carbocation, but a primary vinylic carbocation is so difficult to form that there is no clear evidence it even exists. Thus, many alkyne additions occur through more complex mechanistic pathways.

## Hydration of Alkynes

Hydration of alkynes also can take place. Alkynes don't react directly with aqueous acid but will undergo hydration readily in the presence of mercury(II) sulfate as a Lewis acid catalyst. The reaction occurs with Markovnikov regiochemistry, so the −OH group adds to the more highly substituted carbon and the −H attaches to the less highly substituted one as demonstrated in Figure 22.3k.
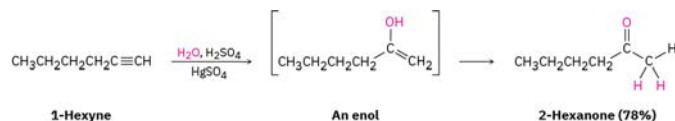


**Figure 22.3k.** Hydration of 1-hexyne to produce 2-hexanone. (credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0).

Interestingly, the actual product isolated from alkyne hydration is not a vinylic alcohol, or enol (*ene* + *ol*), but is instead a ketone.

# Hydrogenation of Alkynes

Lastly, hydrogenation (reduction) of alkynes is another chemical reaction that can take place. Alkynes are reduced to alkanes by addition of $H_2$ over a metal catalyst. The reaction in Figure 22.3l., occurs in two steps through an alkene intermediate, and measurements show that the first step in the reaction is more exothermic than the second.
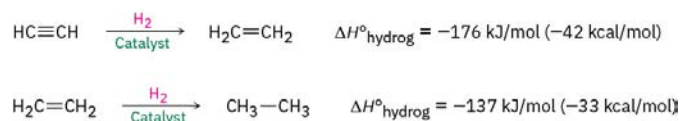
$$HC{\equiv}CH \xrightarrow[\text{Catalyst}]{H_2} H_2C{=}CH_2 \quad \Delta H°_{\text{hydrog}} = -176 \text{ kJ/mol } (-42 \text{ kcal/mol})$$

$$H_2C{=}CH_2 \xrightarrow[\text{Catalyst}]{H_2} CH_3{-}CH_3 \quad \Delta H°_{\text{hydrog}} = -137 \text{ kJ/mol } (-33 \text{ kcal/mol})$$

**Figure 22.3l.** Reduction of alkyne with $H_2$ over a metal with an alkene intermediate catalyst. (credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0).

Complete reduction to the alkane occurs when palladium on carbon (Pd/C) is used as catalyst, but hydrogenation can be stopped at the alkene stage if the less active *Lindlar catalyst* is used. The Lindlar catalyst is a finely divided palladium metal that has been precipitated onto a calcium carbonate support and then deactivated by treatment with lead acetate and quinoline, an aromatic amine. The hydrogenation occurs with syn stereochemistry, giving a cis alkene product.
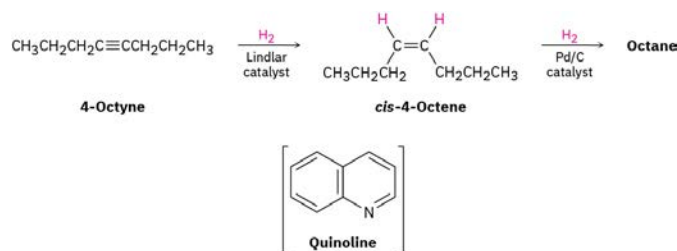


**Figure 22.3m.** Complete reduction of 4-octyne. (credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0).

The alkyne hydrogenation reaction has been explored extensively by the Hoffmann–LaRoche pharmaceutical company, where it is used in the commercial synthesis of vitamin A. The cis isomer of vitamin A produced initially on hydrogenation is converted to the trans isomer by heating as shown in Figure 22.3n.
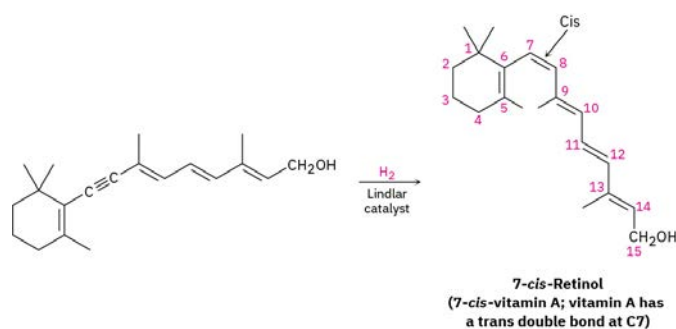
**7-cis-Retinol**
**(7-cis-vitamin A; vitamin A has**
**a trans double bond at C7)**

**Figure 22.3n.** The cis isomer of vitamin A produced initially on hydrogenation is converted to the trans isomer by heating (credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0).

An alternative method for the conversion of an alkyne to an alkene uses sodium or lithium metal as the reducing agent in liquid ammonia as solvent. This method is complementary to the Lindlar reduction because it produces trans rather than cis alkenes. For example, in Figure 22.3o., 5-decyne gives *trans*-5-decene on treatment with lithium in liquid ammonia.



**5-Decyne**  **trans-5-Decene (78%)**

**Figure 22.3o.** 5-decyne gives *trans*-5-decene on treatment with lithium in liquid ammonia. (credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0).

## Spotlight on Everyday Chemistry: 2022 Nobel Prize in Chemistry

Alkynes were involved in the concept of "click" chemistry where an azide is added to an alkyne with a copper catalyst allowing the two molecules to click together forming a cyclic molecule. The click chemistry concept was awarded the 2022 Nobel Prize in Chemistry to Carolyn R. Bertozzi, Morten Meldal and K. Barry Sharpless. For more information refer to infographic 22.3a.
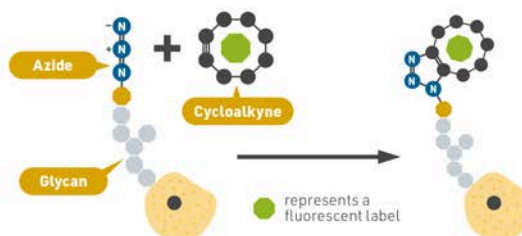
**Infographic 22.3a.** Read more about "The 2022 Nobel Prize in Chemistry (https://www.compoundchem.com/2022/10/05/2022nobelchemistry/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 22.3a [New tab].

# Testing for Presence of Alkenes/Alkynes

There are several ways to test for the presence of carbon-carbon double bonds and triple bonds (unsaturated hydrocarbons). One such method, as previously mentioned above, is the bromine test. Here the organic

compound containing a double or triple C-C bond is mixed with an aqueous solution of bromine (or chlorine). With bromine, there is a visible colour change resulting when bromine is added to the double or triple bond (Figure 22.3p. and Figure 22.3q.). Before addition, the bromine is brownish-red. After addition the solution is colourless. If the solution stays brownish-red, it is a negative result and the compound being tested is saturated. This means there is no opportunity for addition.
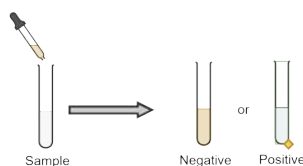


**Figure 22.3p.** Bromine test for presence of double or triple carbon-carbon bond. Positive result is a colourless solution. Negative result is a brownish-red solution (credit: Samantha Sullivan Sauer, Created with Chemix (https://chemix.org), Chemix license)
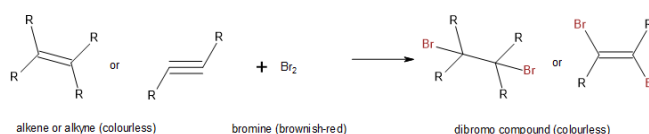


**Figure 22.3q.** Bromine test for presence of unsaturated hydrocarbons (credit: Samantha Sullivan Sauer, using Biovia Draw, CC BY-NC 4.0)

A second such test to confirm the presence of a carbon-carbon double or triple bond (unsaturated hydrocarbon) is the oxidation or permanganate test (Figure 22.3s.). This test is also known as the Baeyer test. Here, potassium permanganate, $KMnO_4$, is used as an oxidizing agent to convert the alkene or alkyne to a diol (two alcohol functional groups in the same molecule). The visual colour change is from dark purple (permanganate solution) to dark green (manganate solution) then to black precipitate (manganese dioxide) (Figure 22.3r.). If the solution stays purple, it is a negative result and the compound being tested is saturated. This means there is no opportunity for oxidation. This test can give conflicting results in that any other components in the molecule or solution that are mildly reducing will also give a positive result.
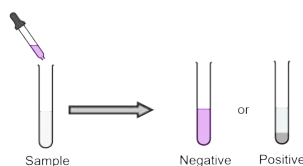
**Figure 22.3r.** Permanganate test for presence of double or triple carbon-carbon bond.  Positive result is a black precipitate.  Negative result is a purplish solution (credit: Samantha Sullivan Sauer, Created with Chemix (https://chemix.org), Chemix license)
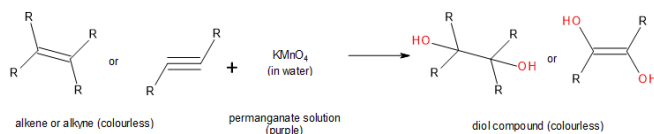


**Figure 22.3s.** Permanganate test for presence of unsaturated hydrocarbons (credit: Samantha Sullivan Sauer, using Biovia Draw, CC BY-NC 4.0)

## Links to Enhanced Learning

- Watch E/Z Alkenes, Electrophilic Addition, & Carbocations: Crash Course Organic Chemistry (https://youtu.be/B8qaENT_k0A) Crash Course Organic Chemistry #14 by Crash Course.
- Watch Alkene Redox Reactions (https://youtu.be/HYSRwaMo3tY) Crash Course Organic Chemistry #17 by Crash Course.
- Watch Alkyne Reactions & Tautomerization (https://youtu.be/zFSHoaScfwY) Crash Course Organic Chemistry #18 by Crash Course (https://www.youtube.com/@crashcourse).

# Attribution & References

Except where otherwise noted, this page is written and adapted by David Wegman, Adrienne Richards and Samantha Sullivan Sauer from

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- "Reactions of Alkynes" section is adapted from "18.1 Hydrocarbons (https://boisestate.pressbooks.pub/chemistry/chapter/21-1-hydrocarbons/)" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)*

- "7.8 Orientation of Electrophilic Additions: Markovnikov's Rule", "9.3 Reactions of Alkynes: Addition of HX and X2", "9.4 Hydration of Alkynes ", and "9.5 Reduction of Alkynes" In *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/1-why-this-chapter)* by John McMurray, CC BY-NC-SA 4.0. Access for free at *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/1-why-this-chapter)*

- "21.1 Hydrocarbons"  In *Chemistry: Atoms First 2e (OpenStax)* by Paul Flowers, Edward J. Neth, William R. Robinson, Klaus Theopold & Richard Langley, CC BY 4.0

- Testing for Presence of Alkenes/Alkynes section is adapted by Samantha Sullivan Sauer from "4.6.2.1: Chemistry of Manganese" by Jim Clark In *Inorganic Chemistry II (CHEM4210)* , CC BY-NC 4.0 and "Reactions of Alkenes with Bromine" by Jim Clark In *Supplemental Modules (Organic Chemistry)*, CC BY-NC 4.0

## Notes
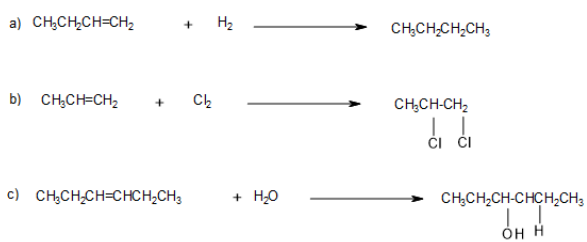


1.
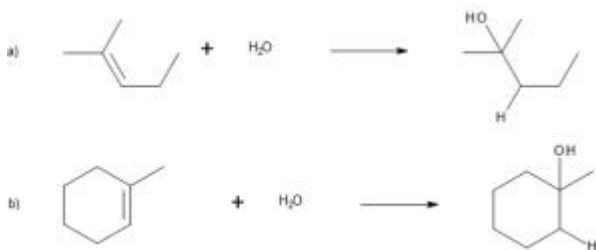


2.

# 22.4 AROMATIC COMPOUNDS - STRUCTURE AND NAMING

## Learning Objectives

By the end of this section, you will be able to:

- Describe the bonding in benzene and the way typical reactions of benzene differ from those of the alkenes.
- Recognize aromatic compounds from structural formulas.
- Name aromatic compounds given formulas.
- Write formulas for aromatic compounds given their names.

Next, we consider a class of hydrocarbons with molecular formulas like those of unsaturated hydrocarbons, but which, unlike the alkenes, do not readily undergo addition reactions. These compounds comprise a distinct class, called aromatic hydrocarbons, with unique structures and properties. Historically, benzene-like substances were called **aromatic** hydrocarbons because they had distinctive aromas. Today, an aromatic compound is any compound that contains a benzene ring or has certain benzene-like properties (but not necessarily a strong aroma). You can recognize the aromatic compounds in this text by the presence of one or more benzene rings in their structure. Some representative aromatic compounds and their uses are listed in Table 22.4a., where the benzene ring is represented as $C_6H_5$.

The simplest of these compounds. Benzene ($C_6H_6$) is of great commercial importance, but it also has noteworthy health effects.

The formula $C_6H_6$ seems to indicate that benzene has a high degree of unsaturation. (Hexane, the saturated hydrocarbon with six carbon atoms has the formula $C_6H_{14}$—eight more hydrogen atoms than benzene.) However, despite the seeming low level of saturation, benzene is rather unreactive. It does not, for example, react readily with bromine, which, is a test for unsaturation.

To explain the surprising properties of benzene, chemists suppose the molecule has a cyclic, hexagonal, planar structure of six carbon atoms with one hydrogen atom bonded to each. We can write a structure with

alternate single and double bonds, either as a full structural formula or as a line formula as shown in Figure 22.4a.
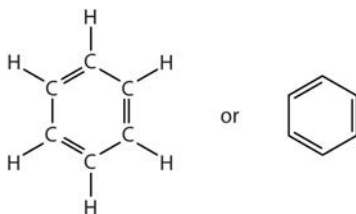


**Figure 22.4a.** Benzene ring structural arrangement versions (credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

However, these structures do not explain the unique properties of benzene. Furthermore, experimental evidence indicates that all the carbon-to-carbon bonds in benzene are equivalent, and the molecule is unusually stable. Chemists often represent benzene as a hexagon with an inscribed circle as in Figure 22.4b.



**Figure 22.4b**. Benzene ring represented as a hexagon with an inscribed circle (credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

The inner circle indicates that the valence electrons are shared equally by all six carbon atoms (that is, the electrons are *delocalized*, or spread out, over all the carbon atoms). It is understood that each corner of the hexagon is occupied by one carbon atom, and each carbon atom has one hydrogen atom attached to it. Any other atom or groups of atoms substituted for a hydrogen atom must be shown bonded to a particular corner of the hexagon. We use this modern symbolism, but many scientists still use the earlier structure with alternate double and single bonds.

**Table 22.4a.** *Some Representative Aromatic Compounds*

| Name | Structure | Typical Uses |
|---|---|---|
| aniline | $C_6H_5–NH_2$ | starting material for the synthesis of dyes, drugs, resins, varnishes, perfumes; solvent; vulcanizing rubber |
| benzoic acid | $C_6H_5–COOH$ | food preservative; starting material for the synthesis of dyes and other organic compounds; curing of tobacco |
| bromobenzene | $C_6H_5–Br$ | starting material for the synthesis of many other aromatic compounds; solvent; motor oil additive |
| nitrobenzene | $C_6H_5–NO_2$ | starting material for the synthesis of aniline; solvent for cellulose nitrate; in soaps and shoe polish |
| phenol | $C_6H_5–OH$ | disinfectant; starting material for the synthesis of resins, drugs, and other organic compounds |
| toluene | $C_6H_5–CH_3$ | solvent; gasoline octane booster; starting material for the synthesis of benzoic acid, |

**Table source:** "13.8: Structure and Nomenclature of Aromatic Compounds" In *Basics of GOB Chemistry (Ball et al.)*, CC BY-NC-SA 4.0.

Many aromatic based compounds have pleasant odours but they are generally toxic with some being carcinogenic. Users should avoid inhaling any vapours. Lighter weight aromatic hydrocarbons are highly flammable and have a sooty flame. Like all hydrocarbons, aromatics are less dense than water and not soluble in water. Their boiling points tend to increase in molar mass, but their melting points are independent on molar mass. Symmetry in the molecule leads to much higher melting points. (Roberts & Caserio, 1977).
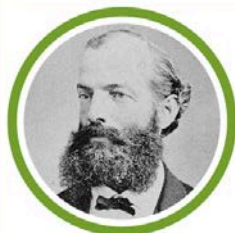
## Spotlight on Everyday Chemistry: August Kekule and The Benzene Structure

August Kekule was the first one to depict the benzene structure as a ring-like structure with alternating single and double bonds. For more information refer to infographic 22.4a. below.

**Infographic 22.4a.** Read more about "Today in Chemistry History: August Kekulé and the structure of benzene (https://www.compoundchem.com/2020/09/07/kekule/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 22.4a [New tab].

## Example 22.4a – Identifying Aromatic Compounds

Which compounds are aromatic?
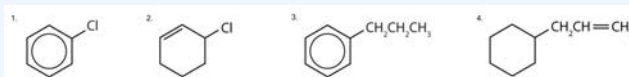


(credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

## Solution

1. The compound has a benzene ring (with a chlorine atom substituted for one of the hydrogen

atoms); it is aromatic.

2. The compound is cyclic, but it does not have a benzene ring; it is not aromatic.
3. The compound has a benzene ring (with a propyl group substituted for one of the hydrogen atoms); it is aromatic.
4. The compound is cyclic, but it does not have a benzene ring; it is not aromatic.

## Spotlight on Everyday Chemistry: Benzene Health Hazards and Connection to Common Medical Ingredients

Benzene is a liquid that smells like gasoline, boils at 80°C, and freezes at 5.5°C. Most of the benzene used commercially comes from petroleum. It is employed as a starting material for the production of detergents, drugs, dyes, insectici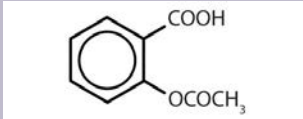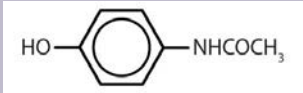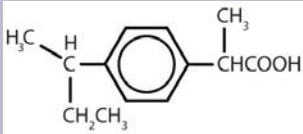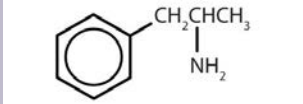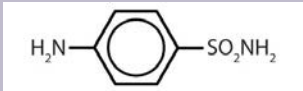des, and plastics. It was formerly used to decaffeinate coffee and was a significant component of many consumer products, such as paint strippers, rubber cements, and home dry-cleaning spot removers. It was removed from many product formulations in the 1950s, but others continued to use benzene in products until the 1970s when it was associated with leukemia deaths. Benzene is still important in industry as a precursor in the production of plastics (such as Styrofoam and nylon), drugs, detergents, synthetic rubber, pesticides, and dyes. It is used as a solvent for such things as cleaning and maintaining printing equipment and for adhesives such as those used to attach soles to shoes. Benzene is now known to have both short- and long-term toxic effects. The inhalation of large concentrations can cause nausea and even death due to respiratory or heart failure, while repeated exposure leads to a progressive disease in which the ability of the bone marrow to make new blood cells is eventually destroyed. This results in a condition called *aplastic anemia*, in which there is a decrease in the numbers of both the red and white blood cells.

Though benzene alone has been shown to potentially affect your health, substances containing the benzene ring are common in both animals and plants. Plants can synthesize the benzene ring from carbon dioxide, water, and inorganic materials. Animals cannot synthesize it, but they are dependent on certain aromatic compounds for survival and therefore must obtain them from food. Phenylalanine, tyrosine, and tryptophan (essential amino acids) and vitamins K, $B_2$ (riboflavin), and $B_9$ (folic acid) all contain the benzene ring. Many important drugs, a few of which are shown in Table 22.4b., also feature a benzene ring.

**Table 22.4b. Some Drugs That Contain a Benzene Ring (Image Credits:** *Intro Chem: GOB (V. 1.0).*, **CC BY-NC-SA 3.0).**

| Name | Structure |
|------|-----------|
| aspirin |  |
| acetaminophen |  |
| ibuprofen |  |
| amphetamine |  |
| sulfanilamide |  |

# Naming Aromatic Compounds

## Naming Monosubstituted Benzenes

In the International Union of Pure and Applied Chemistry (IUPAC) system, aromatic hydrocarbons are named as derivatives of benzene. Figure 22.4c. shows four examples. In these structures, it is immaterial whether the single substituent is written at the top, side, or bottom of the ring: a hexagon is symmetrical, and therefore all positions are equivalent.
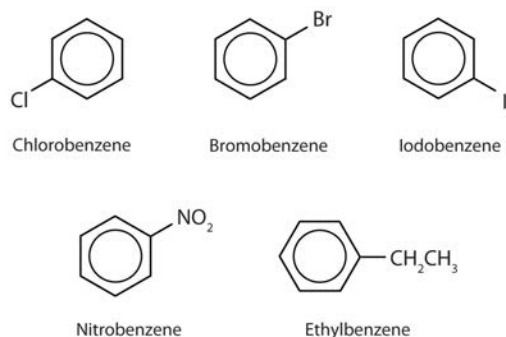
**Figure 22.4c.** Some Benzene Derivatives. These compounds are named in the usual way with the group that replaces a hydrogen atom named as a substituent group: Cl as chloro, Br as bromo, I as iodo, $NO_2$ as nitro, and $CH_3CH_2$ as ethyl (credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

Although some compounds are referred to exclusively by IUPAC names, some are more frequently denoted by common names, as is indicated in Table 22.4a. and shown in Figure 22.4d.
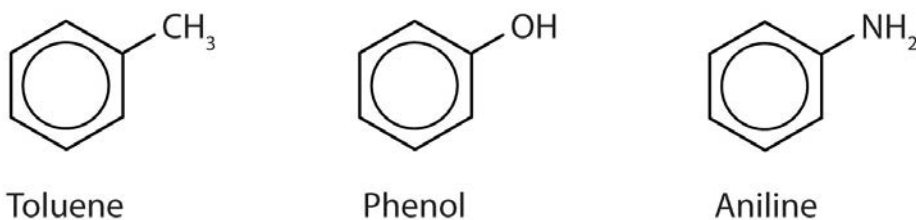


**Figure 22.4d.** Common aromatic structures representing toluene, phenol and aniline (credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

## Naming Polysubstituted Benzenes

When there is more than one substituent, the corners of the hexagon are no longer equivalent, so we must designate the relative positions. There are three possible disubstituted benzenes, and we can use numbers to distinguish them (Figure 22.4e.). We start numbering at the carbon atom to which one of the groups is attached and count toward the carbon atom that bears the other substituent group by the shortest path.
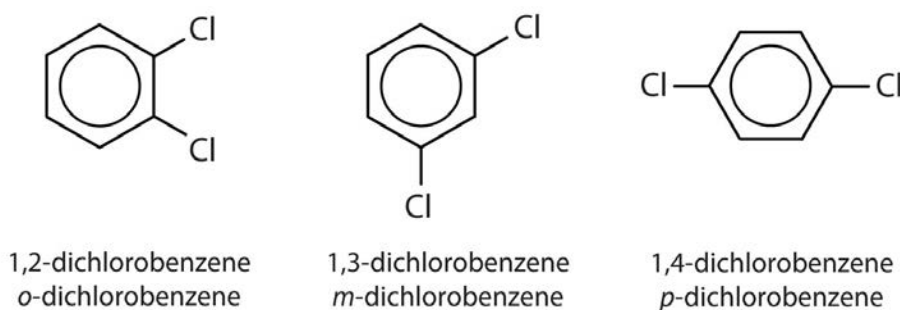
**Figure 22.4e.** The three isomeric dichlorobenzenes (credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

1,2-dichlorobenzene
*o*-dichlorobenzene

1,3-dichlorobenzene
*m*-dichlorobenzene

1,4-dichlorobenzene
*p*-dichlorobenzene

The structural differences in the three dichlorobenzene compounds in Figure 22.4e. lead to differences in physical properties. Table 22.4c. highlights some of the key physical properties of dichlorobenzenes.

**Table 22.4c. Physical properties of dichlorobenzenes (Data sources credit: National Center for Biotechnology Information, 2024a, b, c)**

| Compound | Chemical Formula | Molecular Weight | Boiling Point | Melting Point |
|---|---|---|---|---|
| 1,2-dichlorobenzene (o-dichlorobenzene) | $C_6H_4Cl_2$ | 147.00 g/mol | 180°C | -17°C |
| 1,3-dichlorobenzene (m-dichlorobenzene) | $C_6H_4Cl_2$ | 147.00 g/mol | 173°C | -25°C |
| 1,4-dichlorobenzene (p-dichlorobenzene) | $C_6H_4Cl_2$ | 147.00 g/mol | 174°C | 53°C |

In Figure 22.4e., common names are also used: the prefix *ortho* (*o-*) for 1,2-disubstitution, *meta* (*m-*) for 1,3-disubstitution, and *para* (*p-*) for 1,4-disubstitution. The substituent names are listed in alphabetical order. The first substituent is given the lowest number. When a common name is used, the carbon atom that bears the group responsible for the name is given the number 1 as demonstrated in Figure 22.4f.

1-Bromo-4-chlorobenzene
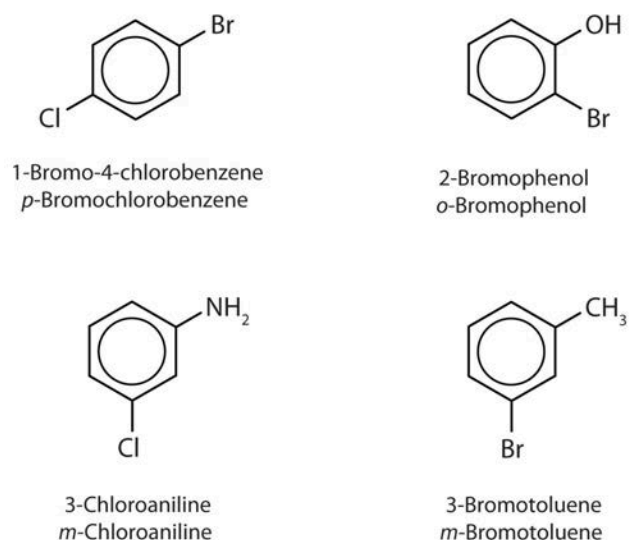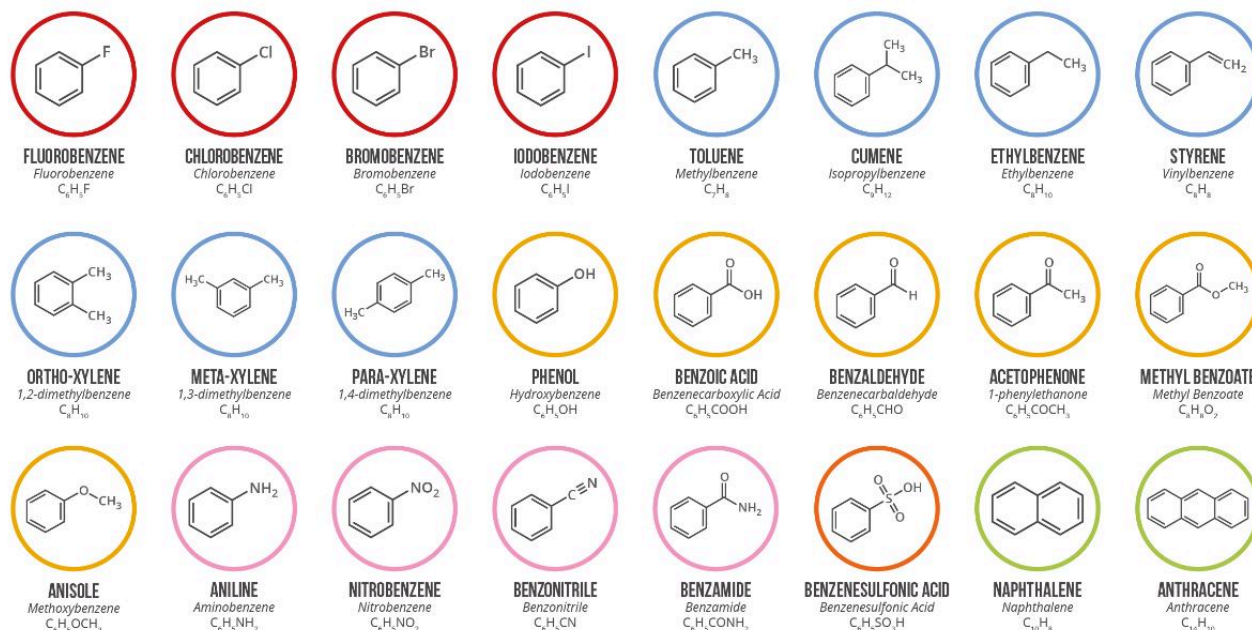*p*-Bromochlorobenzene

2-Bromophenol
*o*-Bromophenol

3-Chloroaniline
*m*-Chloroaniline

3-Bromotoluene
*m*-Bromotoluene

**Figure 22.4f.** Common names using ortho, meta and para and where the carbon atom that bears the group responsible for the name is given the number 1 (credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

Infographic 22.4b. shows a section of benzene derivatives with their IUPAC and common names.



# BENZENE DERIVATIVES IN ORGANIC CHEMISTRY

A WIDE VARIETY OF IMPORTANT ORGANIC COMPOUNDS ARE DERIVED FROM BENZENE, BY REPLACING ONE OF THE HYDROGENS WITH A DIFFERENT FUNCTIONAL GROUP. THEY CAN HAVE BOTH COMMON & SYSTEMATIC NAMES, WHICH CAN BE CONFUSING; HERE, COMMON NAMES ARE SHOWN PRIMARILY, WITH SYSTEMATIC NAMES SHOWN IN ITALICS.

● HALOGEN-CONTAINING ● HYDROCARBON DERIVATIVES ● OXYGEN-CONTAINING ● NITROGEN-CONTAINING ● SULFUR-CONTAINING ● POLYAROMATICS

**FLUOROBENZENE** *Fluorobenzene* $C_6H_5F$

**CHLOROBENZENE** *Chlorobenzene* $C_6H_5Cl$

**BROMOBENZENE** *Bromobenzene* $C_6H_5Br$

**IODOBENZENE** *Iodobenzene* $C_6H_5I$

**TOLUENE** *Methylbenzene* $C_7H_8$

**CUMENE** *Isopropylbenzene* $C_9H_{12}$

**ETHYLBENZENE** *Ethylbenzene* $C_8H_{10}$

**STYRENE** *Vinylbenzene* $C_8H_8$

**ORTHO-XYLENE** *1,2-dimethylbenzene* $C_8H_{10}$

**META-XYLENE** *1,3-dimethylbenzene* $C_8H_{10}$

**PARA-XYLENE** *1,4-dimethylbenzene* $C_8H_{10}$

**PHENOL** *Hydroxybenzene* $C_6H_5OH$

**BENZOIC ACID** *Benzenecarboxylic Acid* $C_6H_5COOH$

**BENZALDEHYDE** *Benzenecarbaldehyde* $C_6H_5CHO$

**ACETOPHENONE** *1-phenylethanone* $C_6H_5COCH_3$

**METHYL BENZOATE** *Methyl Benzoate* $C_8H_8O_2$

**ANISOLE** *Methoxybenzene* $C_6H_5OCH_3$

**ANILINE** *Aminobenzene* $C_6H_5NH_2$

**NITROBENZENE** *Nitrobenzene* $C_6H_5NO_2$

**BENZONITRILE** *Benzonitrile* $C_6H_5CN$

**BENZAMIDE** *Benzamide* $C_6H_5CONH_2$

**BENZENESULFONIC ACID** *Benzenesulfonic Acid* $C_6H_5SO_3H$

**NAPHTHALENE** *Naphthalene* $C_{10}H_8$

**ANTHRACENE** *Anthracene* $C_{14}H_{10}$

**Infographic 22.4b.** Read more about "Benzene Derivatives in Organic Chemistry" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 22.4b [New tab].

## Example 22.4b

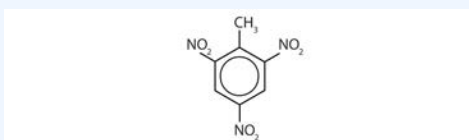Name each compound using both the common name and the IUPAC name.
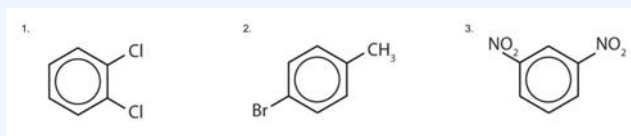


(credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

### Solution

1. The benzene ring has two chlorine atoms (dichloro) in the first and second positions. The compound is *o*-dichlorobenzene or 1,2-dichlorobenzene.
2. The benzene ring has a methyl ($CH_3$) group. The compound is therefore named as a derivative of toluene. The bromine atom is on the fourth carbon atom, counting from the methyl group. The compound is *p*-bromotoluene or 4-bromotoluene.
3. The benzene ring has two nitro ($NO_2$) groups in the first and third positions. It is *m*-dinitrobenzene or 1,3-dinitrobenzene.

Note: The nitro ($NO_2$) group is a common substituent in aromatic compounds. Many nitro compounds are explosive, most notably 2,4,6-trinitrotoluene (TNT).
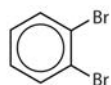


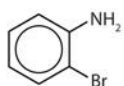(credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

## Exercise 22.4a

Name each compound using both the common name and the IUPAC name.

1. 

2. 

**Check Your Answers:**[1]

**Exercise and image credit:** *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0

## Naming Compounds with an Aromatic Substituent

Sometimes an aromatic group is found as a substituent bonded to a nonaromatic entity or to another aromatic ring. The group of atoms remaining when a hydrogen atom is removed from an aromatic compound is called an aryl group. The most common aryl group is derived from benzene ($C_6H_6$) by removing one hydrogen atom ($C_6H_5$) and is called a *phenyl* group (Figure 22.4g.), from *pheno*, an old name for benzene.
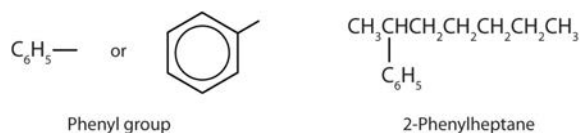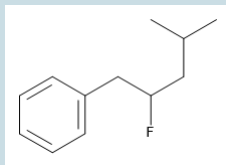


**Figure 22.4g**. Different ways to represent the phenyl group using a condensed structure, line structure and phenyl as a substituent (credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

## Exercise 22.4b

Name this compound.

(credit: Samantha Sullivan Sauer / Biovia Draw, CC BY-NC 4.0.)

## Check Your Answer:[2]

**Activity source:** Exercise 22.4b is created by Samantha Sullivan Sauer, using images from Biovia Draw, licensed under CC BY-NC 4.0

## Spotlight on Everyday Chemistry: Benzene Derivatives in Sunscreen and New Car Smell

A number of sunscreens that are UVA and UVB blockers are made with ingredients that contain benzene structures. For a detailed look at the various substituted benzene ingredients, see infographic 22.4c. below.

# THE CHEMISTRY OF SUNSCREEN

Summer sun brings with it the risk of sunburn, so we'll all be slapping on the sunscreen to guard against it. But what are the chemicals that keep you from turning as red as a lobster? This graphic looks at them and how they work.

**sunprotect** spray lotion *by Sainsbury's*

**30** spf **high** protection

## TYPES OF UV RADIATION

### UVA 320-400nm
wavelength

Accounts for 95% of solar UV radiation reaching Earth's surface. Penetrates deepest into skin, and contributes to skin cancer via indirect DNA damage.

### UVB 290-320nm
wavelength

Accounts for 5% of solar UV radiation reaching Earth's surface. Causes direct DNA damage, and is one of the main contributors to skin cancer.

### UVC 290-100nm
wavelength

Filtered out by ozone in the Earth's atmosphere, and as a result does not reach the surface of the Earth, and doesn't cause skin damage.

**17** SUNSCREEN ACTIVE INGREDIENTS APPROVED IN THE USA

**28** SUNSCREEN ACTIVE INGREDIENTS APPROVED IN THE EU

Inorganic chemicals in sunscreen, such as zinc oxide and titanium oxide, both absorb and scatter UV light. Organic chemicals are also used – the chemical bonds in these absorb UV radiation, with the chemical structure affecting whether they absorb UVA, UVB, or both. Several different chemicals are used in sunscreen to ensure full protection.
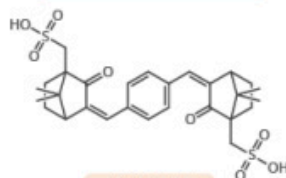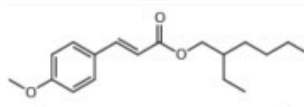
## UVA BLOCKERS
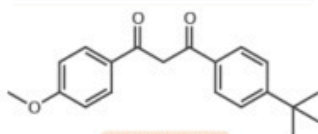
AVOBENZONE
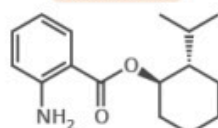
MENTHYL ANTHRANILATE

ECAMSULE

## UVB BLOCKERS

OCTYL METHOXYCINNAMATE
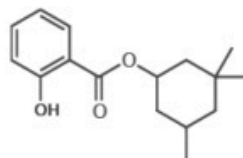
HOMOSALATE

### OTHER UVB BLOCKERS
(Italicised = not approved in USA)

| | |
|---|---|
| PABA | Octylocrylene |
| Padimate O | Ensulizole |
| Cinoxate | *Octyl triazone* |
| Octyl salicylate | *Enzacamene* |
| Trolamine salicylate | *Amiloxate* |

## UVA & UVB BLOCKERS
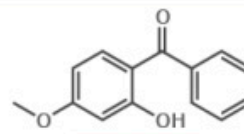
OXYBENZONE
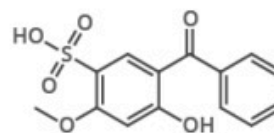
SULISOBENZONE

### OTHER UVA & UVB BLOCKERS
(Italicised = not approved in USA)

| | |
|---|---|
| Dioxybenzone | *Neo Heliopan AP* |
| *Mexoryl XL* | *Uvinul A Plus* |
| *Tinosorb S* | *UVAsorb HEB* |
| *Tinosorb M* | |

All currently approved in EU, Canada & Australia

**Infographic 22.4c.**  Read more about "The Science of Sunscreen & How it Protects Your Skin (https://www.compoundchem.com/2014/06/05/sunscreenchemicals/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 22.4c [New tab].

Not only are benzene compounds found in products we use such as sunscreen, but they can also be found in objects we handle. A new car for example will often have a "new car smell". This smell is associated with numerous volatile organic compounds (VOCs) that are made up of compounds that contain a benzene ring. For more information about the types of VOCs found within a new car see Infographic 22.4d.

*Aroma Chemistry*

# THE AROMA OF NEW CARS

**60+**

The approximate number of volatile organic compounds (VOCs) detected in the interior of new cars. Not all of these will have odours, but many may be contributors to the characteristic 'new car smell', so it's not the result of one specific compound.

The approximate percentage decay of total VOC levels per week in new car interiors. They can also vary depending on conditions - concentrations will be decreased by ventilation of the car, but can be increased by increased temperatures within the car.

**20%**

## THE MOST COMMONLY FOUND COMPOUNDS
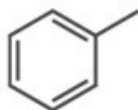
TOLUENE
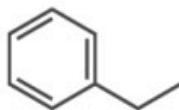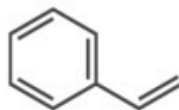
ETHYLBENZENE

STYRENE
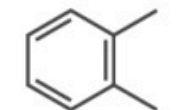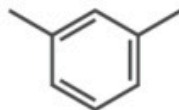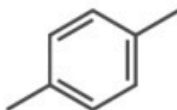
XYLENES (p-XYLENE, m-XYLENE AND o-XYLENE)
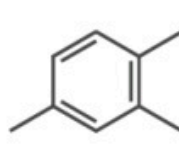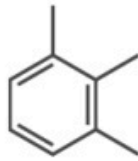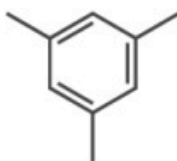
TRIMETHYLBENZENES (1,3,5-, 1,2,3- AND 1,2,4-TRIMETHYLBENZENE
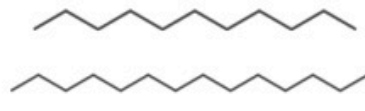
VARIOUS ALKANES

## WHERE DO THEY COME FROM?

### ARE THEY HARMFUL?

**PLASTIC** MOLDINGS **CARPET** UPHOLSTERY ADHESIVES **LUBRICANTS** GASOLINE LEATHER & VINYL TREATMENTS

A 2007 study found little toxicity in new car odours under lab conditions. However, although concentrations of these compounds are still very low, they can be above recommended indoor guidelines for VOCs for the first 6 months after a car's manufacture. This could lead to headaches, sensory irritations and minor allergic responses. Manufacturers are now taking measures to reduce the levels of these compounds in new cars.

## Polycyclic Aromatic Hydrocarbons

Some common aromatic hydrocarbons consist of fused benzene rings—rings that share a common side. These compounds are called polycyclic aromatic hydrocarbons (PAHs). A few examples are shown in Figure 22.4h.
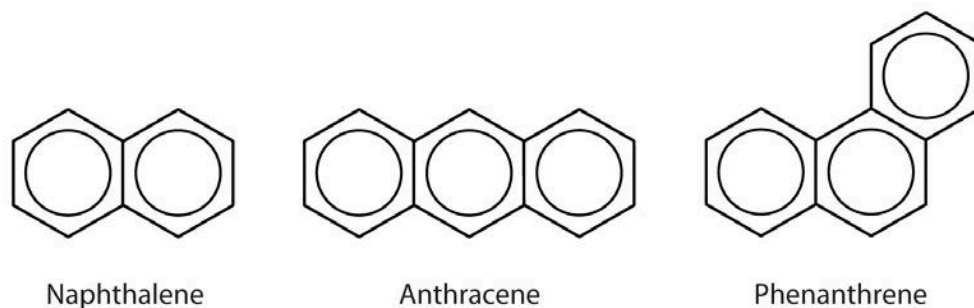
**Figure 22.4h.** Examples of polycyclic aromatic compounds naphthalene, anthracene and phenanthrene. (credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

The three examples (naphthalene, anthracene and phenanthrene), shown here are colourless, crystalline solids generally obtained from coal tar. Naphthalene has a pungent odour and is used in mothballs. Anthracene is used in the manufacture of certain dyes. Steroids, a large group of naturally occurring substances, contain the phenanthrene structure.

## Spotlight on Everyday Chemistry: Glow Sticks

Glow sticks are effectively used at night so that you can be visible or to add some fun to an event. They come in all sorts of colours such as red, orange, yellow, green and blue. Benzene containing compounds are responsible for the various colours produced. Additionally, the reaction that allows the glow stick to glow, is from the reactions involving benzene containing compounds. Next time you use a glow stick, you can thank the benzene rings! For more information, see infographic 22.4e. below.
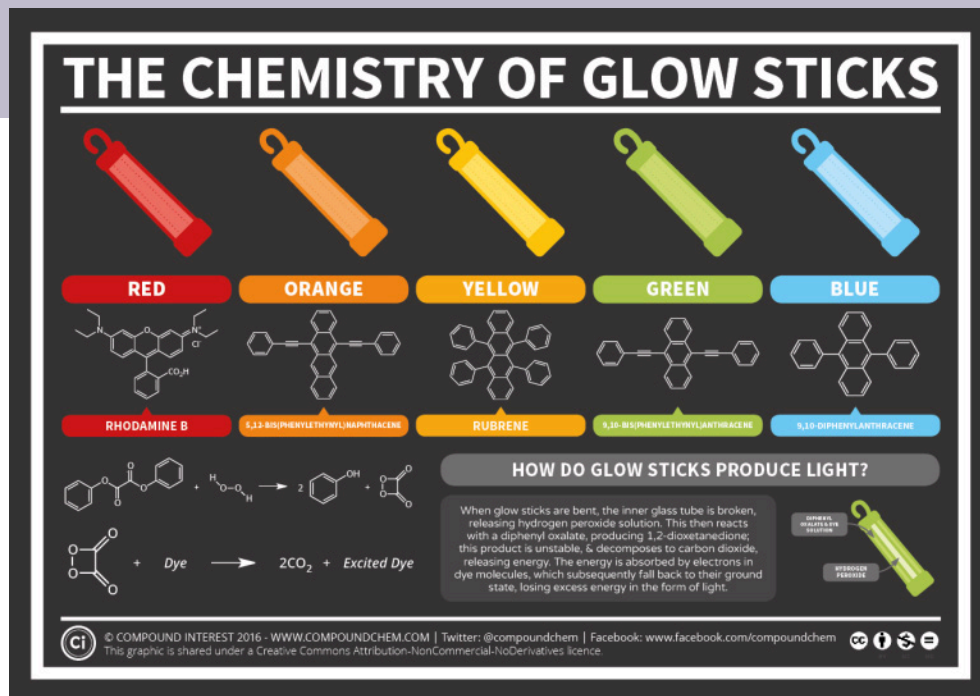
**THE CHEMISTRY OF GLOW STICKS**

# Attribution & References

Except where otherwise noted, this page is adapted by David Wegman, Adrienne Richards and Samantha Sullivan Sauer from "13.8: Aromatic Compounds and the Structure of Benzene" and "13.9: Naming Aromatic Compounds" In *Map: Fundamentals of General Organic and Biological Chemistry (McMurry et al.)* by LibreTexts, licensed under CC BY-NC-SA 3.0. / A derivative of *Basics of GOB (Ball et al.)*, CC BY-NC-SA 4.0 a LibreTexts version of *Introduction to Chemistry: GOB (v. 1.0)*, CC BY-NC 3.0.

## References cited in-text

National Center for Biotechnology Information (2024a). *PubChem Compound Summary for CID 7239, 1,2-Dichlorobenzene (https://pubchem.ncbi.nlm.nih.gov/compound/1_2-Dichlorobenzene).* Retrieved January 14, 2024. .

National Center for Biotechnology Information (2024b).*PubChem Compound Summary for CID 10943, 1,3-Dichlorobenzene (https://pubchem.ncbi.nlm.nih.gov/compound/1_3-Dichlorobenzene.).* Retrieved January 14, 2024.

National Center for Biotechnology Information (2024c). *PubChem Compound Summary for CID 4685, 1,4-Dichlorobenzene (https://pubchem.ncbi.nlm.nih.gov/compound/1_4-Dichlorobenzen).* Retrieved January 14, 2024.

Roberts, J. D., & Caserio, M. C. (1977). *Basic Principles of Organic Chemistry,* (2nd ed.) W. A. Benjamin, Inc.

## Notes

1. 1) 1,2-dibromobenzene or o-dibromobenzene 2) 1-amino-2-bromobenzne or o-aminobromobenzene or o-bromoaniline

2. 2-fluoro-4-methyl-1-phenylpentane

# 22.5 AROMATIC REACTIONS

## Electrophilic Aromatic Substitution

Before seeing how electrophilic aromatic substitutions occur, let's briefly recall about electrophilic alkene additions. When a reagent such as HCl adds to an alkene, the electrophilic hydrogen ion approaches the $\pi$ electrons of the double bond and forms a bond to one carbon, leaving a positive charge at the other carbon. This carbocation intermediate then reacts with the nucleophilic $Cl^-$ ion to yield the addition product as shown in Figure 22.5a.



**Alkene**          **Carbocation intermediate**          **Addition product**
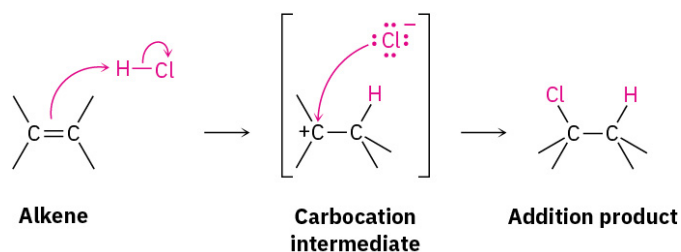
**Figure 22.5a.** Electrophilic substitution of ethene with HCl gives a carbocation intermediate. (credit: *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/16-1-electrophilic-aromatic-substitution-reactions-bromination)*, CC BY-NC-SA 4.0)

An electrophilic aromatic substitution reaction begins in a similar way, but there are a number of differences. One difference is that aromatic rings are less reactive toward electrophiles than alkenes. For example, $Br_2$ in $CH_2Cl_2$ solution reacts instantly with most alkenes but does not react with benzene at room temperature. For bromination of benzene to take place, a catalyst such as $FeBr_3$ is needed. The catalyst makes the

$Br_2$ molecule more electrophilic by polarizing it to give a FeBr4–Br+FeBr4–Br+">FeBr4–Br+ species that reacts as if it were $Br^+$. The polarized $Br_2$ molecule then reacts with the nucleophilic benzene ring to yield a nonaromatic carbocation intermediate that is doubly allylic and has three resonance forms as shown in Figure 22.5b.
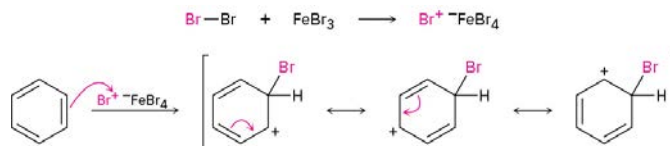


**Figure 22.5b.** The bromination of benzene using FeBr₃ as a catalyst yielding three resonance forms of nonaromatic carbocation intermediate. (credit: *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/16-1-electrophilic-aromatic-substitution-reactions-bromination)*, CC BY-NC-SA 4.0)

Although more stable than a typical alkyl carbocation because of resonance, the intermediate in electrophilic aromatic substitution is nevertheless much less stable than the starting benzene ring itself, with its 150 kJ/mol (36 kcal/mol) of aromatic stability. Thus, the reaction of an electrophile with a benzene ring is endergonic, has a substantial activation energy, and is rather slow. Figure 22.5c. shows an energy diagram comparing the reaction of an electrophile with an alkene and with benzene. The benzene reaction is slower (higher $\Delta G^\ddagger$) because the starting material is more stable. Additionally, the benzene reaction is slower than the alkene reaction because of the stability of the aromatic ring.
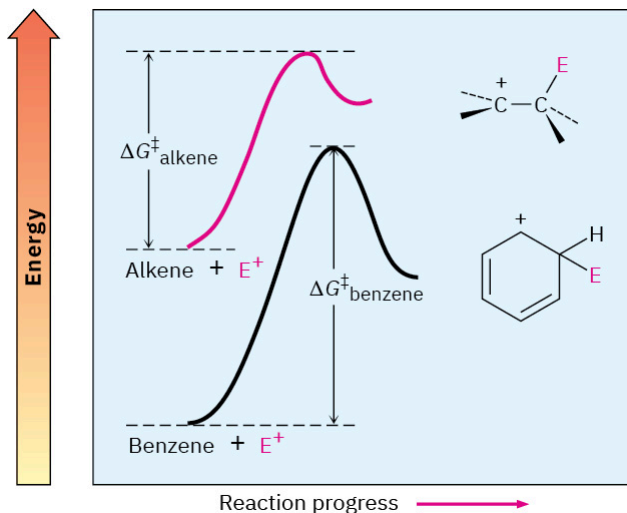


**Figure 22.5c.** A comparison of the reactions of an electrophile ($E^+$) with an alkene and with benzene to see the $\Delta G^\ddagger$ difference. (credit: *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/16-1-electrophilic-aromatic-substitution-reactions-bromination)*, CC BY-NC-SA 4.0)

Another difference between alkene addition and aromatic substitution occurs after the carbocation intermediate has formed. Instead of adding $Br^-$ to give an addition product, the carbocation intermediate

loses H$^+$ from the bromine-bearing carbon to give a substitution product. The net effect of reaction of Br$_2$ with benzene is the substitution of H$^+$ by Br$^+$ by the overall mechanism shown in Figure 22.5d. The reaction occurs in two steps and involves a resonance-stabilized carbocation intermediate.
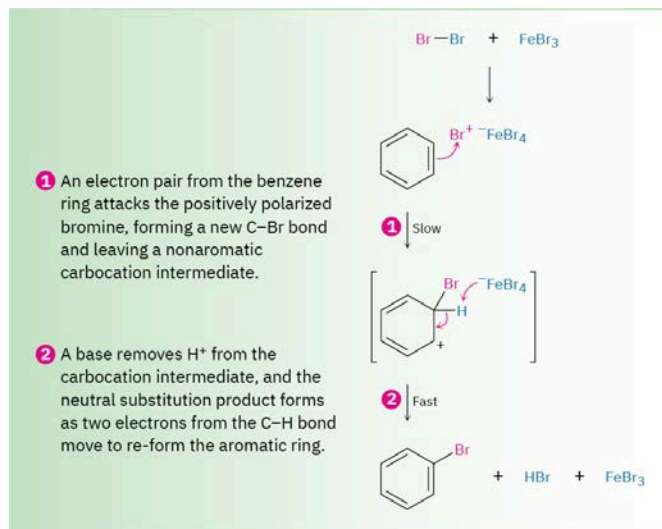


**Figure 22.5d.** Overall mechanism of the bromination of benzene using FeBr$_3$ as a catalyst to yield bromobenzene, HBr and FeBr$_3$. (credit: *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/16-1-electrophilic-aromatic-substitution-reactions-bromination)*, CC BY-NC-SA 4.0)

In summary, electrophilic aromatic substitution of benzene with HBr using FeBr$_3$ as a catalyst yields bromobenzene (Figure 22.5e.).
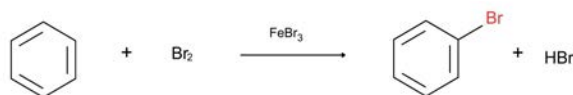


**Figure 22.5e.** General electrophilic aromatic substitution of benzene with Br$_2$ using FeBr$_3$ as a catalyst yields bromobenzene. (credit: Samantha Sullivan Sauer / Biovia Draw, CC BY-NC 4.0.)

**Watch Intro to Electrophilic Aromatic Substitution: Crash Course Organic Chemistry #37 (youtube.com) (https://youtu.be/vuSF5yhKRxA?) (12 min).**

## Aromatic Halogenation

Chlorine and iodine can be introduced into aromatic rings by electrophilic substitution reactions just as bromine can, but fluorine is too reactive and only poor yields of monofluoroaromatic products are obtained by direct fluorination. Instead, other sources of "F$^+$" are used, in which a fluorine atom is bonded to a positively charged nitrogen. One of the most common such reagents goes by the acronym F-TEDA-BF$_4$ in the presence of trifluoromethanesulfonic acid (TfOH). (You don't need to know the full name of F-TEDA,

which is sold under the name Selectfluor.). An example in Figure 22.5f. shows the electrophilic substitution of toluene using F-TEDA-BF$_4$ as a catalyst to yield *o*-fluorotoluene and *p*-fluorotoluene.
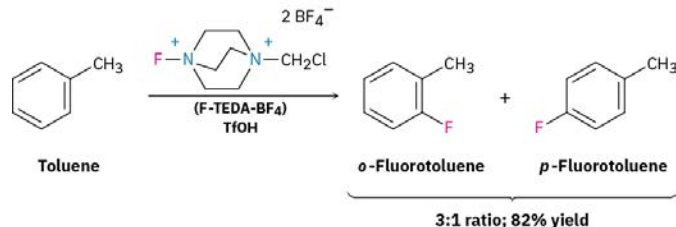


**Figure 22.5f.** Electrophilic substitution of toluene using F-TEDA-BF$_4$ as a catalyst to yield *o*-fluorotoluene and *p*-fluorotoluene in a 3:1 ratio respectively. (credit: *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/16-2-other-aromatic-substitutions)*, CC BY-NC-SA 4.0)

More than 20% of all pharmaceutical agents sold contain fluorine, including 30% of the top 100 drugs sold. Sitagliptin (Januvia), used to treat type 2 diabetes, fluoxetine (Prozac), an antidepressant, and atorvastatin (Lipitor), a statin used to lower cholesterol, are examples (Figure 22.5g.).
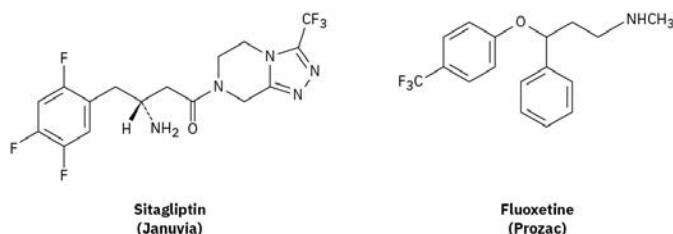


**Figure 22.5g.** Structural representations of Sitagliptin (Januvia) and fluoxetine (Prozac). (credit: *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/16-2-other-aromatic-substitutions)*, CC BY-NC-SA 4.0)

Aromatic rings react with Cl$_2$ in the presence of FeCl$_3$ catalyst to yield chlorobenzenes, just as they react with Br$_2$ and FeBr$_3$ (Figure 22.5h.). This kind of reaction is used in the synthesis of numerous pharmaceutical agents, including the antiallergy medication loratadine, marketed as Claritin.
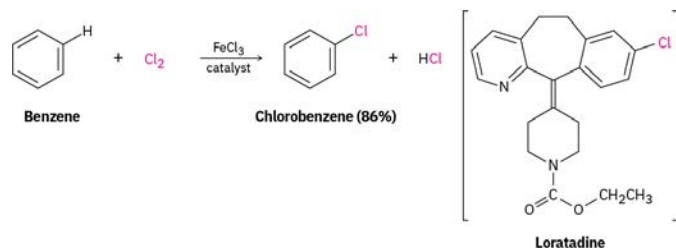


**Figure 22.5h.** Benzene reacting with Cl$_2$ in the presence of FeCl$_3$ catalyst to yield chlorobenzenes (left). This process is also used to synthesize loratadine, marketed as Claritin (right). (credit: *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/16-2-other-aromatic-substitutions)*, CC BY-NC-SA 4.0)

Iodine itself is unreactive toward aromatic rings, so an oxidizing agent such as hydrogen peroxide or a copper salt such as $CuCl_2$ must be added to the reaction. These substances accelerate the iodination reaction by oxidizing $I_2$ to a more powerful electrophilic species that reacts as if it were $I^+$. The aromatic ring then reacts with $I^+$ in the typical way, yielding a substitution product (Figure 22.5i.).
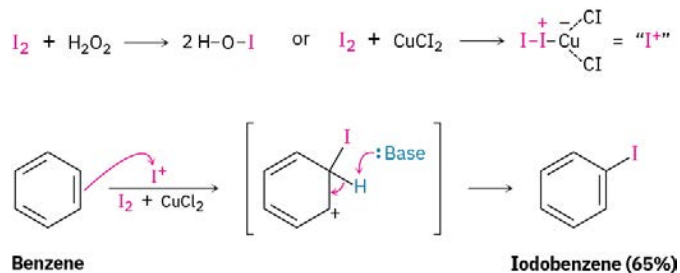


**Figure 22.5i.** Benzene reacting with iodine in the presence of an oxidizing agent copper salt ($CuCl_2$) to yield iodobenzene. (credit: *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/16-2-other-aromatic-substitutions)*, CC BY-NC-SA 4.0)

Electrophilic aromatic halogenations also occur in the biosynthesis of many naturally occurring molecules, particularly those produced by marine organisms. In humans, the best-known example occurs in the thyroid gland during the biosynthesis of thyroxine, a hormone involved in regulating growth and metabolism. The amino acid tyrosine is first iodinated by thyroid peroxidase, and two of the iodinated tyrosine molecules then couple (Figure 22.5j.). The electrophilic iodinating agent is an $I^+$ species, perhaps hypoiodous acid (HIO), that is formed from iodide ion by oxidation with $H_2O_2$.
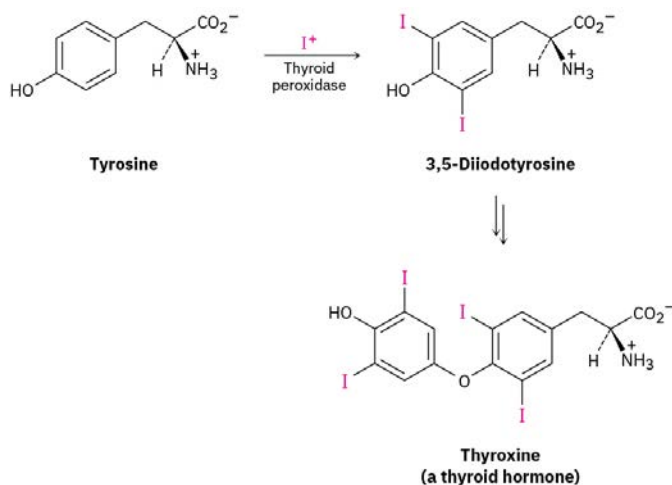


**Figure 22.5j.** Tyrosine is iodinated with thyroid peroxidase to produce thyroxine (a thyroid hormone). (credit: *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/16-2-other-aromatic-substitutions)*, CC BY-NC-SA 4.0)

# Aromatic Nitration

Aromatic rings are nitrated by reaction with a mixture of concentrated nitric and sulfuric acids. The electrophile is the nitronium ion, $NO_2^+$, which is formed from $HNO_3$ by protonation and loss of water. The nitronium ion reacts with benzene to yield a carbocation intermediate, and loss of $H^+$ from this intermediate gives the neutral substitution product, nitrobenzene (Figure 22.5k.). The mechanism for electrophilic nitration of an aromatic ring is shown below (Figure 22.5k.).
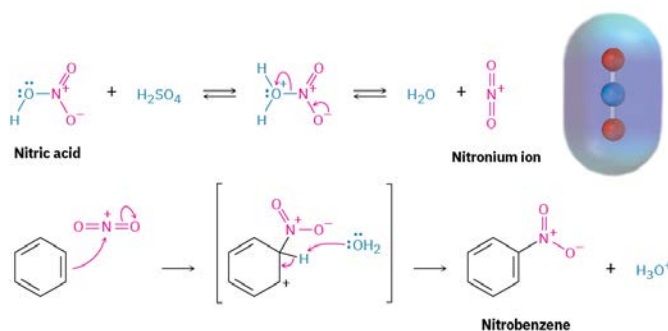


**Figure 22.5k.** Nitration of benzene occurs with a mixture of sulfuric acid and nitric acid to yield nitrobenzene. (credit: *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/16-2-other-aromatic-substitutions)*, CC BY-NC-SA 4.0)

An electrostatic potential map of the reactive electrophile $NO_2^+$ shows that the nitrogen atom is most positive.

Electrophilic nitration of an aromatic ring does not occur in nature but is particularly important in the laboratory because the nitro-substituted product can be reduced by reagents such as iron, tin, or $SnCl_2$ to yield the corresponding *arylamine,* $ArNH_2$. Attachment of an amino group ($-NH_2$) to an aromatic ring by the two-step nitration/reduction sequence is a key part of the industrial synthesis of many dyes and pharmaceutical agents. For example (Figure 22.5l.), nitrobenzene in the presence of Fe, $H_3O^+$ and $OH^-$ yields aniline.
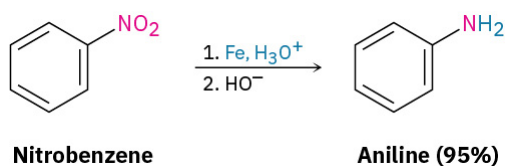


**Figure 22.5l.** Electrophilic nitration of nitrobenzene in the presence of Fe, $H_3O^+$ and $OH^-$ to yield aniline. (credit: *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/16-2-other-aromatic-substitutions)*, CC BY-NC-SA 4.0)

# Aromatic Sulfonation

Aromatic rings can be sulfonated by reaction with so-called fuming sulfuric acid, a mixture of $H_2SO_4$ and $SO_3$ (Figure 22.5m.). The reactive electrophile is either $HSO3+HSO3+">HSO_3^+$ or neutral $SO_3$, depending on reaction conditions, and substitution occurs by the same two-step mechanism seen previously for bromination and nitration. Note, however, that the sulfonation reaction is readily reversible. It can occur either forward or backward, depending on the reaction conditions. Sulfonation is favoured in strong acid, but desulfonation is favoured in hot, dilute aqueous acid.
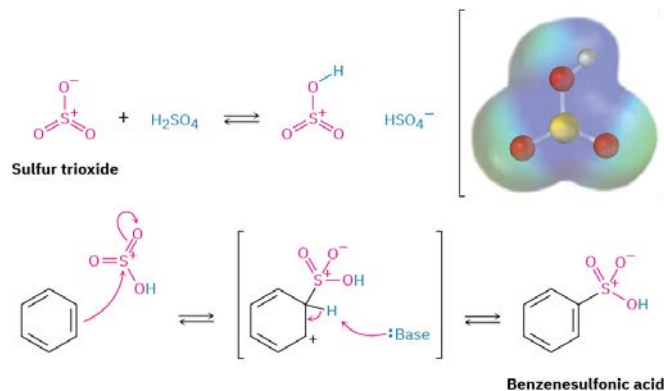


**Figure 22.5m**. Sulfonation of benzene using a mixture of sulfur trioxide and sulfuric acid yields benzenesulfonic acid. (credit: *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/16-2-other-aromatic-substitutions)*, CC BY-NC-SA 4.0)

Aromatic sulfonation does not occur naturally but is widely used in the preparation of dyes and pharmaceutical agents. For example, the sulfa drugs, such as sulfanilamide (Figure 22.5n.), were among the first clinically useful antibiotics. Although largely replaced today by more effective agents, sulfa drugs are still used in the treatment of meningitis and urinary tract infections. These drugs are prepared commercially by a process that involves aromatic sulfonation as its key step.
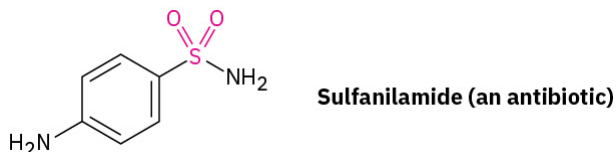


**Figure 22.5n.** The molecular structure of sulfanilamide (an antibiotic). (credit: *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/16-2-other-aromatic-substitutions)*, CC BY-NC-SA 4.0)

# Aromatic Hydroxylation

Direct hydroxylation of an aromatic ring to yield a hydroxybenzene (a *phenol*) is difficult and rarely done in

the laboratory but occurs much more frequently in biological pathways. An example (Figure 22.5o.) is the hydroxylation of *p*-hydroxyphenylacetate to give 3,4-dihydroxyphenylacetate. The reaction is catalyzed by *p*-hydroxyphenylacetate-3-hydroxylase and requires molecular oxygen plus the coenzyme reduced flavin adenine dinucleotide, abbreviated $FADH_2$.
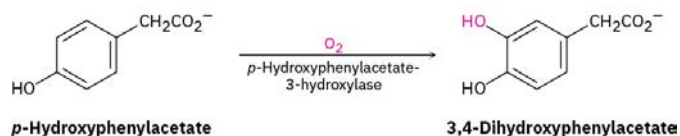


**Figure 22.5o.** Hydroxylation of *p*-hydroxyphenylacetate to give 3,4-dihydroxyphenylacetate as example of a biological pathway. (credit: *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/ pages/16-2-other-aromatic-substitutions)*, CC BY-NC-SA 4.0)

## Oxidation of Alkyl Side Chains

Despite its unsaturation, the benzene ring is inert to strong oxidizing agents such as $KMnO_4$, which will cleave alkene carbon–carbon bonds. It turns out, however, that the presence of the aromatic ring has a dramatic effect on the reactivity of alkyl side chains. These side chains react rapidly with oxidizing agents and are converted into carboxyl groups, $-CO_2H$. The net effect is conversion of an alkylbenzene into a benzoic acid, $Ar-R \rightarrow Ar-CO2HAr-R \rightarrow Ar-CO2H">Ar-R \rightarrow Ar-CO_2H$. Butylbenzene is oxidized by aqueous $KMnO_4$ to give benzoic acid, for instance (Figure 22.5p.).
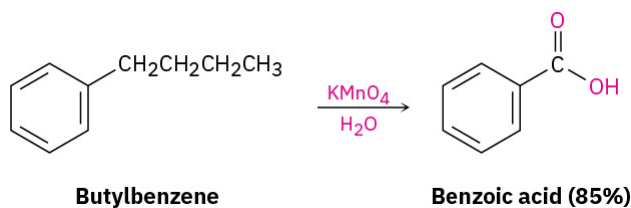


**Figure 22.5p.** Butylbenzene is oxidized by aqueous $KMnO_4$ to give benzoic acid. (credit: *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/ 16-8-oxidation-of-aromatic-compounds)*, CC BY-NC-SA 4.0)

A similar oxidation is employed industrially for the preparation of the terephthalic acid used in the production of polyester fibers. Worldwide, approximately 118 million tons per year of terephthalic acid is produced by oxidation of *p*-xylene, using air as the oxidant and Co(III) salts as catalyst.

**p-Xylene**  **Terephthalic acid**
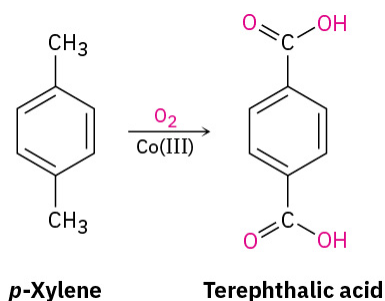
**Figure 22.5q.** Preparation of the terephthalic acid by oxidation of *p*-xylene, using air as the oxidant and Co(III) salts as catalyst (credit: *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/ 16-8-oxidation-of-aromatic-compounds)*, CC BY-NC-SA 4.0)

The mechanism of side-chain oxidation is complex and involves reaction of C–H bonds at the position next to the aromatic ring to form intermediate benzylic radicals. *tert*-Butylbenzene has no benzylic hydrogens, however, and is therefore inert (Figure 22.5r.).
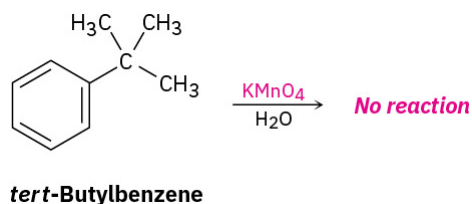


**tert-Butylbenzene**

**Figure 22.5r.** *tert*-Butylbenzene given it has no benzylic hydrogens produces no reaction. (credit: *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/ 16-8-oxidation-of-aromatic-compounds)*, CC BY-NC-SA 4.0)

Analogous side-chain oxidations occur in various biosynthetic pathways. The neurotransmitter norepinephrine, for instance, is biosynthesized from dopamine by a benzylic hydroxylation reaction. The process is catalyzed by the copper-containing enzyme dopamine $\beta$-monooxygenase and occurs by a radical mechanism. A copper–oxygen species in the enzyme first abstracts the pro-R benzylic hydrogen to give a radical, and a hydroxyl is then transferred from copper to carbon.

## Catalytic Hydrogenation of Aromatic Rings

Just as aromatic rings are generally inert to oxidation, they're also inert to catalytic hydrogenation under conditions that reduce typical alkene double bonds. As a result, it's possible to reduce an alkene double bond selectively in the presence of an aromatic ring. For example (Figure 22.5s.), 4-phenyl-3-buten-2-one is reduced

to 4-phenyl-2-butanone using a palladium catalyst at room temperature and atmospheric pressure. Neither the benzene ring nor the ketone carbonyl group is affected.
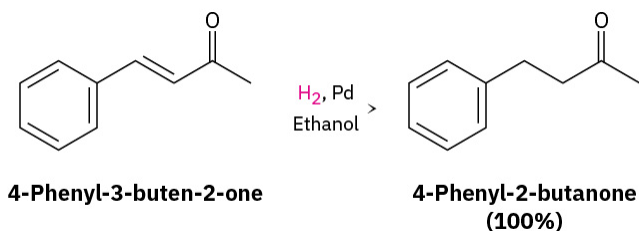


**4-Phenyl-3-buten-2-one**  **4-Phenyl-2-butanone**
**(100%)**

**Figure 22.5s.** 4-phenyl-3-buten-2-one is reduced to 4-phenyl-2-butanone using a palladium catalyst at room temperature and atmospheric pressure and there is no effect on the benzene ring. (credit: *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/16-9-reduction-of-aromatic-compounds)*, CC BY-NC-SA 4.0)

To hydrogenate an aromatic ring, it's necessary either to use a platinum catalyst with hydrogen gas at a pressure of several hundred atmospheres or to use a more effective catalyst such as rhodium on carbon. Under these conditions, aromatic rings are converted into cyclohexanes. For example, *o*-xylene yields 1,2-dimethylcyclohexane, and 4-*tert*-butylphenol gives 4-*tert*-butylcyclohexanol as shown in Figure 22.5t.



*o*-Xylene  *cis*-1,2-Dimethyl-cyclohexane

**4-*tert*-Butylphenol**  *cis*-4-*tert*-Butyl-cyclohexanol
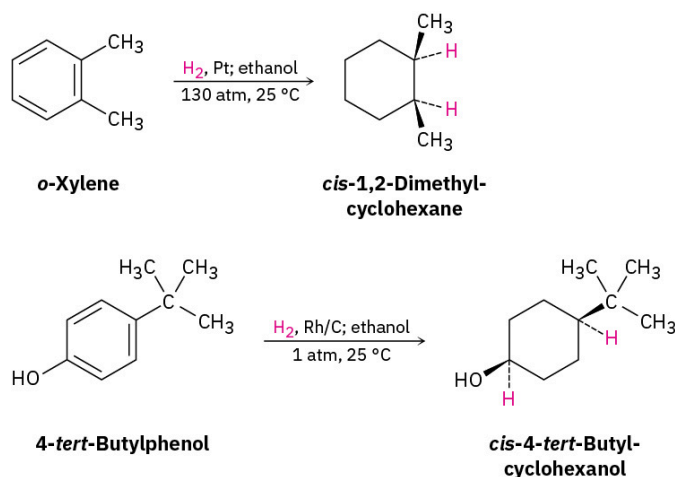
**Figure 22.5t.** Hydrogenation of aromatic compounds o-xylene yields 1,2-dimethylcyclohexane (top) and 4-tert-butylphenol yields 4-*tert*-butylcyclohexanol (bottom). (credit: *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/16-9-reduction-of-aromatic-compounds)*, CC BY-NC-SA 4.0)

For a detailed summary of the various reaction pathways that aromatic compounds undergo, refer to infographic 22.5a.
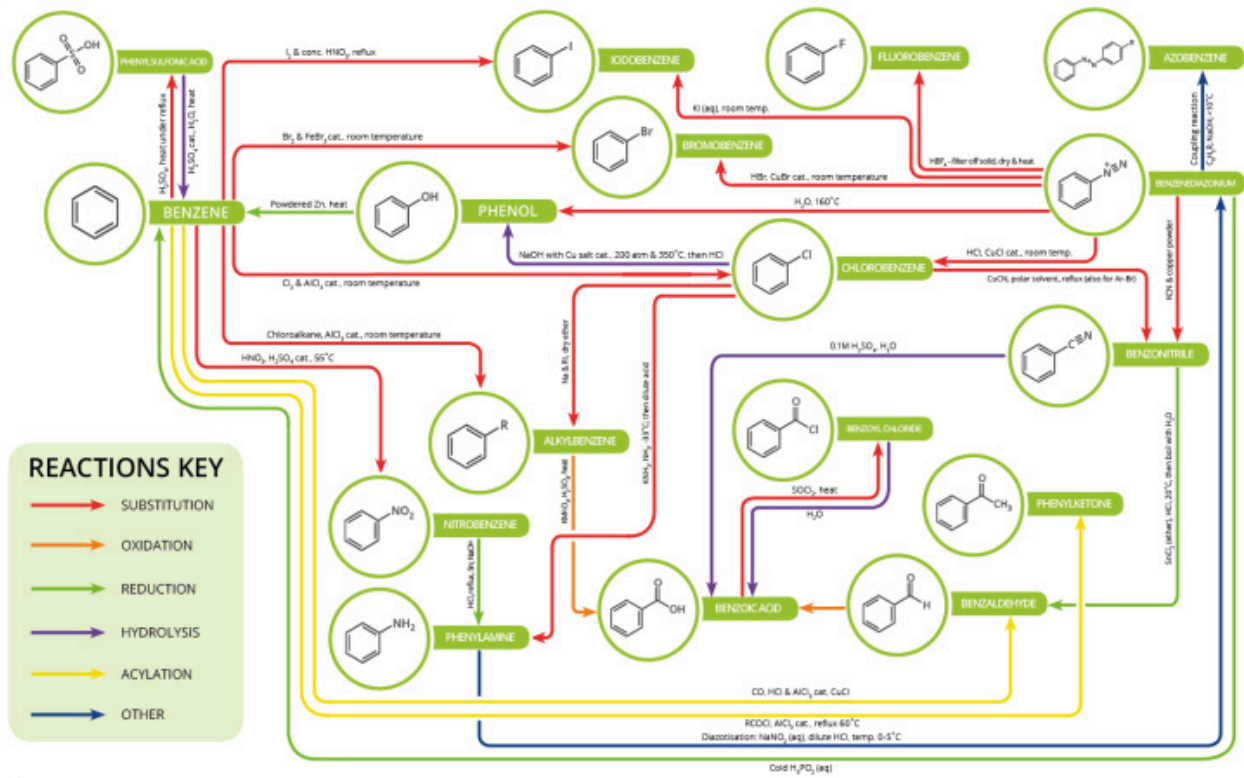
**Infographic 22.5a.** Read more about "Aromatic Chemistry Reactions Map (https://www.compoundchem.com/2014/02/23/aromatic-chemistry-reactions-map/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text summary of infographic 22.5a [New tab].

**Watch Diazonium Salts & Nucleophilic Aromatic Substitution: Crash Course Organic Chemistry #47 (youtube.com) (https://youtu.be/aPdxwMJVwf4?) (14 min).** Some aspects of this video may not apply to this text.

## Friedel-Crafts Reactions

Friedel-Crafts reactions involve the acylation of benzene and substituted benzenes. An **acyl group** is an alkyl group attached to a carbon-oxygen double bond. If "R" represents any alkyl group, then an acyl group has the formula RCO-. **Acylation** means substituting an acyl group into something – in this case, into a benzene ring. A hydrogen on the ring is replaced by a group like methyl or ethyl and so on.

The most commonly used acyl group is $CH_3CO$-. This is called the ethanoyl group, and in this case the reaction is sometimes called "ethanoylation". In the example which follows we are substituting a $CH_3CO$- group into the ring, but you could equally well use any other acyl group. The most reactive substance

containing an acyl group is an acyl chloride (also known as an acid chloride). These have the general formula RCOCl. Benzene is treated with a mixture of ethanoyl chloride, $CH_3COCl$, and aluminium chloride as the catalyst. The mixture is heated to about 60°C for about 30 minutes. A ketone called phenylethanone (old name: acetophenone) is formed as shown in Figure 22.5u.



**Figure 22.5u.** Benzene reacts with $CH_3COCl$ and aluminum chloride as the catalyst to produce phenylethanone. (credit: *Supplemental Modules (Organic Chemistry)*, CC BY-NC 4.0).

Note in Figure 22.5u., that the aluminum chloride isn't written into these equations because it is acting as a catalyst. If you wanted to include it, you could write $AlCl_3$ over the top of the arrow.

The reaction is just the same with methylbenzene except that you have to worry about where the acyl group attaches to the ring relative to the methyl group. Normally, the methyl group in methylbenzene directs new groups into the 2- and 4- positions (assuming the methyl group is in the 1- position). In acylation, though, virtually all the substitution happens in the 4- position (Figure 22.5v.).
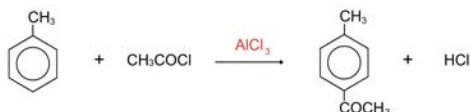


**Figure 22.5v.** The reaction of methylbenzene with $CH_3COCl$ and aluminum chloride as the catalyst to move the new group into the 4-position. (credit: *Supplemental Modules (Organic Chemistry)*, CC BY-NC 4.0).

Alkylation means substituting an alkyl group into something – in this case into a benzene ring. A hydrogen on the ring is replaced by a group like methyl or ethyl and so on. Benzene reacts at room temperature with a chloroalkane (for example, chloromethane or chloroethane) in the presence of aluminum chloride as a catalyst. In Figure 22.5w., a methyl group is substituted, but any other alkyl group could be used in the same way. Substituting a methyl group gives methylbenzene.

**Figure 22.5w.** The reaction of chloromethane with benzene and aluminum chloride as the catalyst to produce an alkylated benzene.(credit: *Supplemental Modules (Organic Chemistry)*, CC BY-NC 4.0).

Friedel-Crafts reactions are also involved in industrial processes such as the manufacturing of ethylbenzene (Figure 22.5x.). Ethylbenzene is an important industrial chemical used to make styrene (phenylethene), which in turn is used to make polystyrene – poly(phenylethene). It is manufactured from benzene and ethene. There are several ways of doing this, some of which use a variation on Friedel-Crafts alkylation.
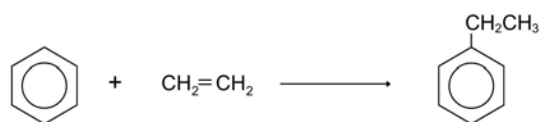


**Figure 22.5x.** The reaction of benzene with ethene to produce ethylbenzene using a catalyst. (credit: *Supplemental Modules (Organic Chemistry)*, CC BY-NC 4.0).

## Attribution & References

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- "16.1 Electrophilic Aromatic Substitution Reactions: Bromination", "16.2 Other Aromatic Substitutions", "16.8 Oxidation of Aromatic Compounds" and "16.9 Reduction of Aromatic Compounds" In *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/1-why-this-chapter)* by John McMurray, CC BY-NC-SA 4.0. Access for free at *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/1-why-this-chapter)*
- "Friedel-Crafts Reactions" by Jim Clark In *Supplemental Modules (Organic Chemistry)* is shared under a CC BY-NC 4.0

# CHAPTER 22 - SUMMARY

## 22.1 Alkenes and Alkynes – Structure and Naming

Any hydrocarbon containing either a double or triple bond is an unsaturated hydrocarbon. Alkenes have a carbon-to-carbon double bond. The general formula for alkenes with one double bond is $C_nH_{2n}$. Alkenes can be straight chain, branched chain, or cyclic. Alkynes have a carbon-to-carbon triple bond. The general formula for alkynes with one triple bond is $C_nH_{2n-2}$.  or cyclic. Simple alkenes and alkynes often have common names, but all of them can be named by the system of the International Union of Pure and Applied Chemistry. The physical properties of alkenes are quite similar to those of alkanes. Like other hydrocarbons, alkenes are insoluble in water but soluble in organic solvents.

## 22.2 Structure of Alkenes – Cis-Trans Isomers

Cis-trans isomers (or geometric isomers) are characterized by molecules that differ only in their configuration around a rigid part of the structure, such as a carbon–to-carbon double bond or a ring. The molecule having two identical (or closely related) atoms or groups on the same side is the cis isomer; the one having the two groups on opposite sides is the trans isomer.

## 22.3 Reactions of Alkenes and Alkynes

More reactive than alkanes, alkenes and alkynes both undergo addition reactions across the double or triple bond:

- Addition of hydrogen (hydrogenation): $CH_2=CH_2 + H_2 \rightarrow CH_3CH_3$
- Addition of halogen (halogenation): $CH_2=CH_2 + X_2 \rightarrow XCH_2CH_2X$ (where X = F, Cl, Br, or I.)
- Addition of water (hydration): $CH_2=CH_2 + HOH \rightarrow HCH_2CH_2OH$

Markovnikov's Rule applies to unsymmetrical additions.  In the addition of HX or $H_2O$ to an alkene, the more highly substituted carbocation is formed as the intermediate rather than the less highly substituted one. There are several tests used to determine the presence of a double or triple bond: bromine test and permanganate test.

# 22.4 Aromatic Compounds – Structure and Naming

The cyclic hydrocarbon *benzene* ($C_6H_6$) has a ring of carbon atoms. The molecule seems to be unsaturated, but it does not undergo the typical reactions expected of alkenes. The electrons that might be fixed in three double bonds are instead *delocalized* over all six carbon atoms. A hydrocarbon containing one or more benzene rings (or other similarly stable electron arrangements) is an aromatic hydrocarbon, and any related substance is an aromatic compound. One or more of the hydrogen atoms on a benzene ring can be replaced by other atoms. When two hydrogen atoms are replaced, the product name is based on the relative position of the replacement atoms (or atom groups). A 1,2-disubstituted benzene is designated as an *ortho* (*o-*) isomer; 1,3-, a *meta* (*m-*) isomer; and 1,4-, a *para* (*p-*) isomer. An aromatic group as a substituent is called a phenyl group. A polycyclic aromatic hydrocarbon (PAH) has fused benzene rings sharing a common side.

# 22.5 Aromatic Reactions

Aromatic compounds undergo substitution and oxidation reactions. A benzene ring can be substituted with a halogen atom (using $X_2$ and $FeX_3$), a substituted benzene can be halogenated (add X), a benzene can be nitrated (adding $-NO_2$) or sulfonated (adding $-HSO_3$), and a substituted benzene can be hydroxylated (add $-OH$). Side chain oxidation occurs with an alkylated benzene leaving the benzene ring intact and changing any carbon chain to benzoic acid. Friedel-Crafts reactions allow for substitution of an alkyl chain onto a benzene ring.

# Attribution & References

Except where otherwise noted, this page is written and adapted by David Wegman, Adrienne Richards and Samantha Sullivan Sauer from "13.S: Unsaturated and Aromatic Hydrocarbons (Summary)", in *Basics of General, Organic, and Biological Chemistry (Ball et al.)* by David W. Ball, John W. Hill, and Rhonda J. Scott via LibreTexts, licensed under CC BY-NC-SA 4.0. / A LibreTexts version of *Introduction to Chemistry: GOB (v. 1.0),* CC BY-NC 3.0.

# CHAPTER 22 - REVIEW

## 22.1 Alkenes and Alkynes – Structure and Naming

1. Briefly identify the important distinctions between a saturated hydrocarbon and an unsaturated hydrocarbon. **Check answer** [1]
2. Briefly identify the important distinctions between an alkene and an alkane.
3. Classify each compound as saturated or unsaturated. Identify each as an alkane, an alkene, or an alkyne. **Check answer**[2]
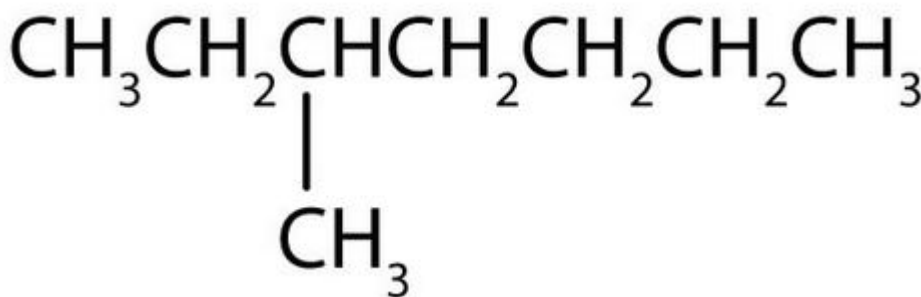
a.

$$CH_3CH_2CHCH_2CH_2CH_2CH_3$$
$$|$$
$$CH_3$$

(credit: *Intro Chem : GOB (v. 1.0)*, CC BY-NC 3.0)

b. $CH_3CH_2C{\equiv}CCH_3$

$$CH_3CH{=}CCH_2CH_2CH_2CH_3$$
$$|$$
$$CH_3$$
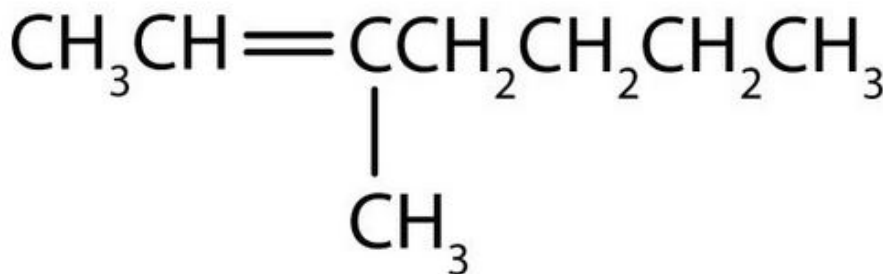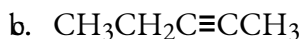
(credit: *Intro Chem : GOB (v. 1.0)*, CC BY-NC 3.0)

4. Briefly describe the physical properties of alkenes. How do these properties compare to those of the alkanes? **Check answer**[3]
5. Without consulting tables, arrange the following alkenes in order of increasing boiling point: 1-butene, ethene, 1-hexene, and propene. **Check answer**[4]
6. Without referring to a table or other reference, predict which member of each pair has the higher boiling point. **Check answer**[5]

   1-pentene or 1-butene

3-heptene or 3-nonene

7. Which is a good solvent for cyclohexene, pentane or water?

8. Draw the structure of each compound
   a. 2-methyl-2-pentene **Check answer**[6]
   b. 2,3-dimethyl-1-butene **Check answer**[7]
   c. cyclohexene **Check answer**[8]

9. Name each compound. **Check answer**[9]
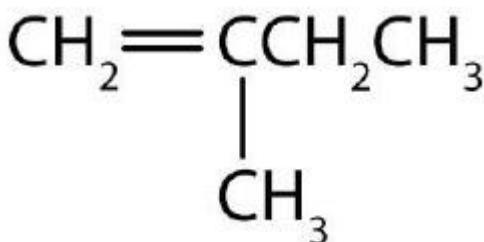
$$CH_2{=}CCH_2CH_3$$
$$|$$
$$CH_3$$

(credit: *Intro Chem: GOB (v. 1.0)*, CC BY-NC 3.0)

a.

$$CH_3CH{=}CHCH_2CHCH_2CH_3$$
$$|$$
$$CH_3$$

(credit: *Intro Chem: GOB (v. 1.0)*, CC BY-NC 3.0)

b.

$$CH_3$$
$$|$$
$$CH_3CCH{=}CCH_2CH_3$$
$$|\quad\quad|$$
$$CH_3\quad CH_3$$
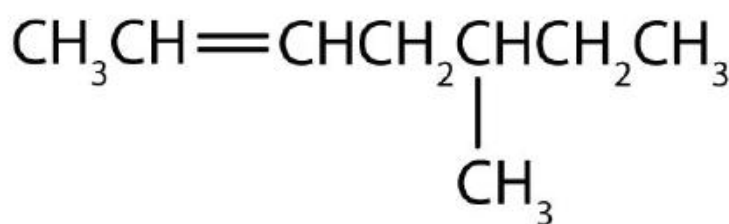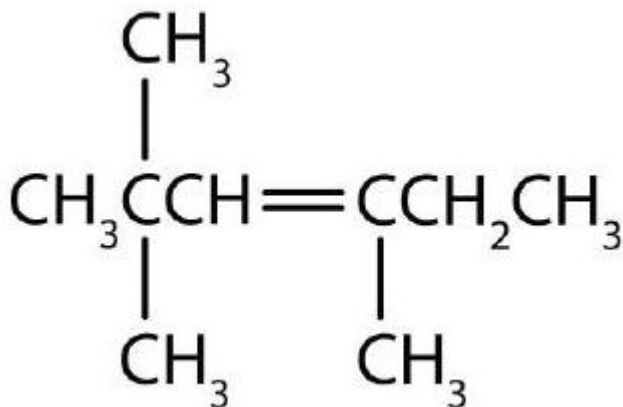
(credit: *Intro Chem: GOB (v. 1.0)*, CC BY-NC 3.0)

c.

10. Briefly identify the important differences between an alkene and an alkyne. How are they similar? **Check answer**[10]

11. The alkene $(CH_3)_2CHCH_2CH{=}CH_2$ is named 4-methyl-1-pentene. What is the name of $(CH_3)_2CHCH_2C{\equiv}CH$? **Check answer**[11]

12. Draw the structure for each compound.

    a. ethyne **Check answer**[12]

    b. 3-methyl-1-hexyne **Check answer**[13]

    c. 4-methyl-2-hexyne

    d. 3-octyne

13. Name each alkyne. **Check answer**[14]

    a. $CH_3CH_2CH_2C{\equiv}CH$

    b. $CH_3CH_2CH_2C{\equiv}CCH_3$

14. What is wrong with each name? Draw the structure and give the correct name for each compound.

    a. 2-methyl-4-heptene

    b. 2-ethyl-2-hexene

    c. 2,2-dimethyl-3-pentene

# 22.2 Structure of Alkenes – Cis-Trans Isomers

1. What are cis-trans (geometric) isomers? What two types of compounds can exhibit cis-trans isomerism? **Check answer**[15]

2. Classify each compound as a cis isomer, a trans isomer, or neither. **Check answer**[16]



(credit: *Intro Chem: GOB (v. 1.0)*, CC BY-NC 3.0)

3. Do alkynes show cis-trans isomerism? Explain. **Check answer**[17]

4. Draw the structures of the cis-trans isomers for each compound. Label them cis and trans. If no cis-trans isomers exist, write none.

    a. 2-bromo-2-pentene **Check answer**[18]

    b. 3-hexene **Check answer**[19]

    c. 4-methyl-2-pentene **Check answer**[20]
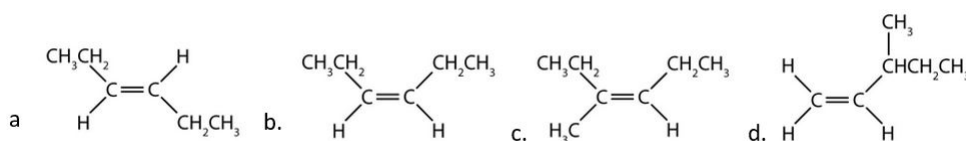
    d. 1,1-dibromo-2-butene **Check answer**[21]

    e. 2-butenoic acid ($CH_3CH{=}CHCOOH$) **Check answer**[22]

5. Draw the structures of the cis-trans isomers for each compound. Label them cis and trans. If no cis-trans isomers exist, write none.

    a. 2,3-dimethyl-2-pentene

    b. 1,1-dimethyl-2-ethylcyclopropane

    c. 1,2-dimethylcyclohexane

    d. 5-methyl-2-hexene

e.  1,2,3-trimethylcyclopropane

## 22.3 Reactions of Alkenes and Alkynes

1.  What is the principal difference in properties between alkenes and alkanes? How are they alike? **Check answer**[23]

2.  If $C_{12}H_{24}$ reacts with HBr in an addition reaction, what is the molecular formula of the product? **Check answer**[24]

3.  Complete each equation.

    a.  $(CH_3)_2C=CH_2 + Br_2 \rightarrow$ **Check answer**[25]

    b.  CH2=C(CH3)CH2CH3+H2→Ni">CH$_2$=C(CH$_3$)CH$_2$CH$_3$+H$_2$ → (with Ni) **Check answer**[26]



(credit: *Intro Chem: GOB (v. 1.0)*, CC BY-NC 3.0)

$$+ \ H_2O \xrightarrow{H_2SO_4}$$
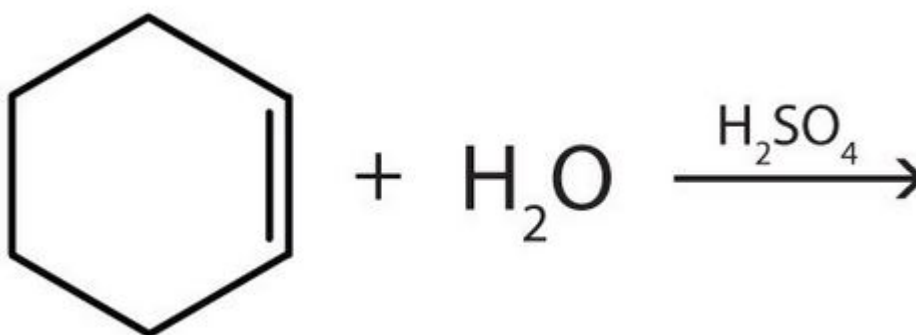
    c.  **Check answer**[27]

4.  When three isomeric pentenes—X, Y, and Z—are hydrogenated, all three form 2-methylbutane. The addition of $Cl_2$ to Y gives 1,2-dichloro-3-methylbutane, and the addition of $Cl_2$ to Z gives 1,2-dichloro-2-methylbutane. Draw the original structures for X, Y, and Z.

5.  Describe Markovnikov's Rule and give an example of water adding to an alkene that shows the application of this rule.

6.  Pentane and 1-pentene are both colourless, low-boiling liquids. Describe a simple test that distinguishes the two compounds. Indicate what you would observe. **Check answer**[28]

## 22.4 Aromatic Compounds – Structure and Naming

1.  Briefly identify the important characteristics of an aromatic compound. **Check answer**[29]

2.  Briefly describe the bonding in benzene. **Check answer**[30]

3.  What does the circle mean in the chemist's representation of benzene? **Check answer**[31]

4.  What is meant by the prefixes *meta*, *ortho*, or *para*? Give the name and draw the structure for a

compound that illustrates each. **Check answer**[32]

5. What is a phenyl group? Give the structure for 3-phenyloctane. **Check answer**[33]

6. Is each compound aromatic? **Check answer**[34]
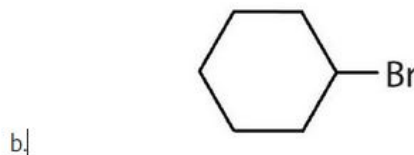


a.

b.

7. Is each compound aromatic? **Check answer**[35]



a.

b.
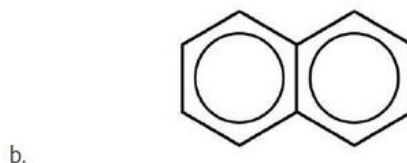
8. Draw the structure for each compound.
   a. toluene **Check answer**[36]
   b. *m*-diethylbenzene **Check answer**[37]
   c. 3,5-dinitrotoluene **Check answer**[38]

9. Name each compound with its IUPAC name. **Check answer**[39]



a.

b.

c.

d.
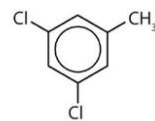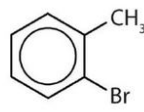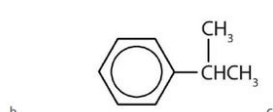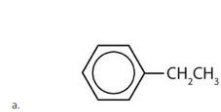
10. What is wrong with each name? **Check answer**[40]
   a. 2-bromobenzene
   b. 3,3-dichlorotoluene
   c. 1,4-dimethylnitrobenzene

## 22.5 Aromatic Reactions

1. How do the typical reactions of benzene differ from those of the alkenes? **Check answer**[41]
2. Monobromination of toluene gives a mixture of three bromotoluene products. Draw and name them.
3. How many products might be formed on chlorination of o-xylene (o-dimethylbenzene), m-xylene, and p-xylene?
4. What is the major monosubstitution product from the Friedel–Crafts reaction of benzene with

1-chloro-2-methylpropane in the presence of AlCl$_3$?

5. What aromatic products would you obtain from the KMnO4 oxidation of the following substances?

a. 

(credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0)

b. 

(credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0)
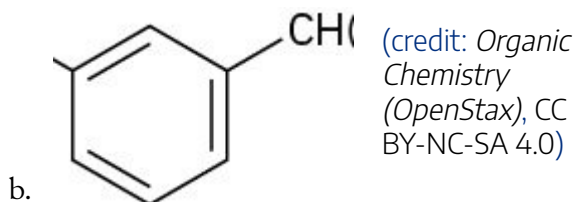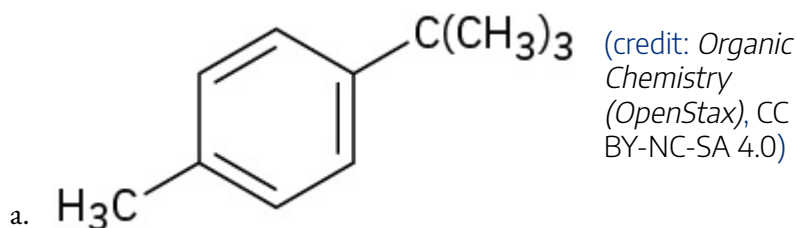
## Links to Enhanced Learning

Create your own organic nomenclature quiz to identify, name and draw alkenes and alkynes using Organic Nomenclature (orgchem101.com). You can customize the types of questions you receive and get instant feedback.

# Attribution & References

Except where otherwise noted, this page (including images in solutions) is adapted by David Wegman, Adrienne Richards and Samantha Sullivan Sauer from

- " 13.E: Unsaturated and Aromatic Hydrocarbons (Exercises) ", in *Basics of General, Organic, and Biological Chemistry (Ball et al.)* by David W. Ball, John W. Hill, and Rhonda J. Scott via LibreTexts, licensed under CC BY-NC-SA 4.0. / A derivative of *Introduction to Chemistry: GOB (v. 1.0)*, CC BY-NC 3.0.
- "16.1 Electrophilic Aromatic Substitution Reactions: Bromination", "16.2 Other Aromatic Substitutions", "16.3 Alkylation and Acylation of Aromatic Rings: The Friedel–Crafts Reaction", "16.8 Oxidation of Aromatic Compounds" and "16.9 Reduction of Aromatic Compounds" In *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/1-why-this-chapter)* by John

- Images in solutions are from the original sources noted above, except:
  - ○ 22.1 Questions 8 and 12b: *Intro Chem : GOB (v. 1.0),* CC BY-NC 3.0
  - ○ 22.2 Question 4b, e: *Intro Chem: GOB (v. 1.0),* CC BY-NC 3.0
  - ○ 22.3 Question 3c: *Intro Chem: GOB (v. 1.0),* CC BY-NC 3.0
  - ○ 22.4 Questions 4, 5, 8: *Intro Chem: GOB (v. 1.0),*CC BY-NC 3.0

# Notes

1. Unsaturated hydrocarbons have double or triple bonds and are quite reactive; saturated hydrocarbons have only single bonds and are rather unreactive.

2. An alkene has a double bond; an alkane has single bonds only. a) saturated; alkane b) unsaturated; alkyne c) unsaturated; alkene

3. Alkenes have physical properties (low boiling points, insoluble in water) quite similar to those of their corresponding alkanes.

4. ethene < propene < 1-butene < 1-hexene

5. a) 1-pentene b)3-nonene

6.

$$CH_3C=CHCH_2CH_3$$
$$|$$
$$CH_3$$

7.

$$CH_2=CCHCH_3$$
with $CH_3$ above the second carbon and $CH_3$ below the third carbon
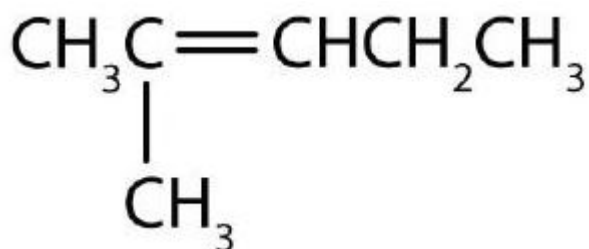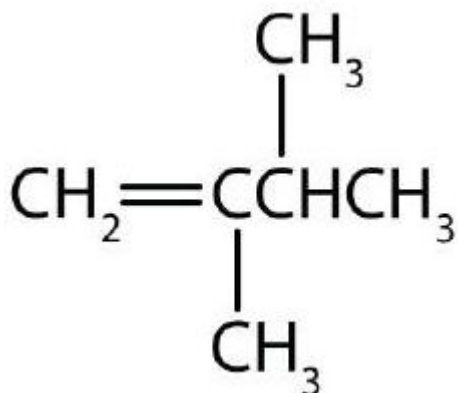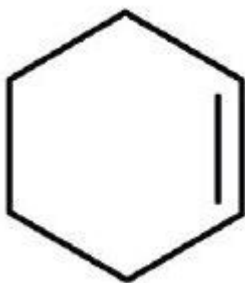
8.

9.  1. 2-methyl-1-butene 2. 5-methyl-2-heptene 3. 2,2,4-trimethyl-3-hexene

10.  Alkenes have double bonds; alkynes have triple bonds. Both undergo addition reactions.

11.  4-methyl-1-pentyne

12.  H–C≡C–H
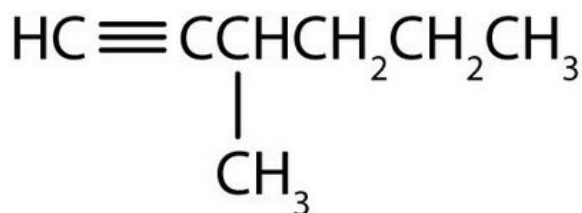


13.

14.  1. 1-pentyne 2. 2-hexyne

15.  Cis-trans isomers are compounds that have different configurations (groups permanently in different places in space) because of the presence of a rigid structure in their molecule. Alkenes and cyclic compounds can exhibit cis-trans isomerism.

16.  1. trans (the two hydrogen atoms are on opposite sides) 2. cis (the two hydrogen atoms are on the same side, as are the two ethyl groups) 3. cis (the two ethyl groups are on the same side) 4. neither (flipping the bond does not change the molecule. There are no isomers for this molecule).

17.  No; a triply bonded carbon atom can form only one other bond. It would have to have two groups attached to show cis-trans isomerism.

18.  none. There are two distinct geometric isomers, but since there are there are four different groups off the double bond, these are both cis/trans isomers (they are technically E/Z isomers discussed elsewhere).



19.



20.



21.

22. 
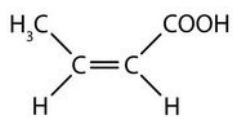
cis      trans
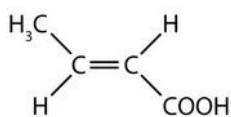
23. Alkenes undergo addition reactions; alkanes do not. Both burn.

24. $C_{12}H_{24}Br_2$

25. $(CH_3)_2CBrCH_2Br$

26. $CH_3CH(CH_3)CH_2CH_3$
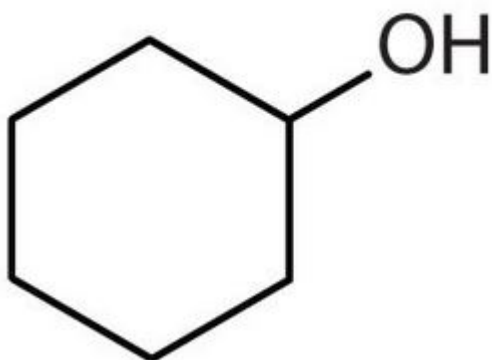
27. 

28. Add bromine solution (reddish-brown) to each. Pentane will not react, and the reddish-brown colour persists; 1-pentene will react, leaving a colourless solution.

29. An aromatic compound is any compound that contains a benzene ring or has certain benzene-like properties.

30. Valence electrons are shared equally by all six carbon atoms (that is, the electrons are delocalized).

31. The six electrons are shared equally by all six carbon atoms.



m-dinitrobenzene or 1,3-dinitrobenzene
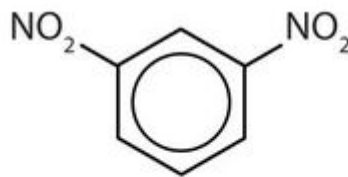
32. meta = 1,3 disubstitution; (answers will vary)             ortho = 1,2
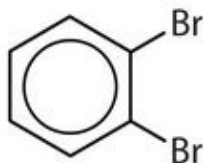


o-dibromobenzene or 1,2-dibromobenzene

disubstitution

para = 1,4 disubstitution or 1-bromo-4-chlorobenzene
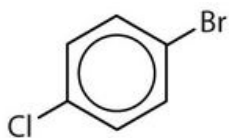
p-bromochlorobenzene or 1-bromo-2-chlorobenzene



33.  phenyl group: $C_6H_5$ or

3-phenyloctane:

$$CH_3CH_2CHCH_2CH_2CH_2CH_2CH_3$$
$$|$$
$$C_6H_5$$
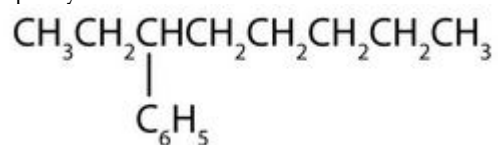
34.  a) yes b) no
35.  a) no b) yes
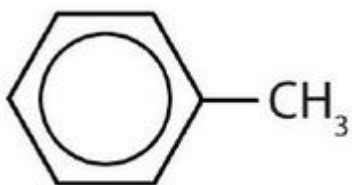


36.
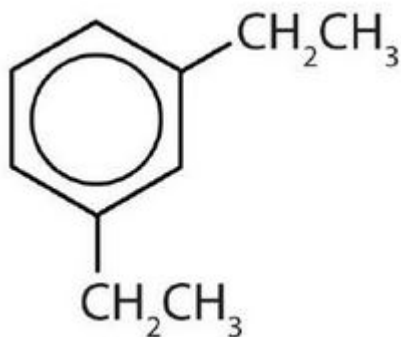


37.
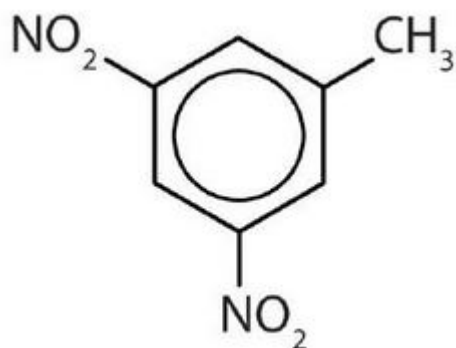


38.

39. a) ethylbenzene b) isopropylbenzene c) o-bromotoluene d) 3,5-dichlorotoluene

40. a) number not needed b) can't have two groups on one carbon atom on a benzene ring c) can't have a substituent on the same carbon atom as the nitro group

41. Benzene is rather unreactive toward addition reactions compared to an alkene.

# CHAPTER 22 - INFOGRAPHIC DESCRIPTIONS

## Infographics used in Chapter 22

- 22.0a The Chemistry of Tomatoes
- 22.1a The Chemistry of Spinach
- 22.1b The Chemistry of Bell Peppers
- 22.3a The 2022 Nobel Prize in Chemistry
- 22.4a Today in Chemistry History: August Kekulé and the structure of benzene
- 22.4b Benzene Derivatives in Organic Chemistry
- 22.4c The Science of Sunscreen & How it Protects Your Skin
- 22.4d The Chemicals Behind the 'New Car Smell
- 22.4e The Chemistry of Glow Sticks
- 22.5a Aromatic Chemistry Reactions Map

## 22.0a The Chemistry of Tomatoes

Should tomatoes be stored in the fridge? Chilling damages cell membranes in tomatoes, and inhibits enzyme activity, which can lead to a drastic loss of volatile compounds. Some of these, such as the C6 (six carbon) volatiles, do not contribute significantly to flavour, but others, such as geranial, have a noted impact on factors such as sweetness. Taking tomatoes out of the fridge for 24 hours can lead to some recovery of volatile compounds, however, though only within a week of fridge storage. It's also worth noting that storing ripe tomatoes in the fridge can obviously be beneficial, to stop them from going off! (Z)-3-Hexenal is also a significant volatile compound in tomatoes.

What causes the colour of tomatoes?

Green tomatoes are also coloured because of the presence of chlorophyll. As they ripen, the pigment lycopene develops; this compound absorbs light across mos tof the visible light spectrum, except the red portion, causing the tomatoes to appear red. It absorbs most visible light as a result of its highly conjugated structure – that is to say, it has lots of alternating double and single bonds. Lycopene absorbs all but the longest wavelengths of visible light.

*Read more about "The Chemistry of Tomatoes [New tab] (https://www.compoundchem.com/2014/10/02/tomatoes/)" by Andy Brunning / Compound Interest, CC BY-NC-ND*

## 22.1a The Chemistry of Spinach

Compared to many other vegetables, spinach does have a higher iron content. However, iron in vegetables tends to have a low bioavailability, meaning it is not easily absorbed in the body.

According to USDA food consumption database; Scrimshaw (1991): Spinach: 2.6mg iron per 100grams, 1.7% absorbed (0.44mg). Sirloin steak: 2.5mg iron per 100 grams, 20% absorbed (0.50mg).

Low absorption of iron is partly due to the polyphenol compounds in spinach binding iron – not due to its oxalic acid content (as previously thought). Though it might not be a great source of iron, it's a good source of Vitamin A in the form of carotenoids (for example Beta-carotene).

Spinach contains high amounts of oxalic acid which leaves your teeth with a 'chalky' feeling. The oxalic acid reacts with the calcium ions in the spinach and your saliva forming poorly soluble calcium oxalate crystals which coat your teeth creating 'spinach teeth'.

*Read more about "The Chemistry of Spinach [New tab] (https://www.compoundchem.com/2018/07/17/spinach/)" by Andy Brunning / Compound Interest, CC BY-NC-ND*

## 22.1b The Chemistry of Bell Peppers

Bell peppers go through a spectrum of colours as they ripen.

Chlorophyll, used by plants for photosynthesis, gives bell peppers their initial green colour. As the pepper ripens, chlorophyll decomposes and a range of carotenoid pigments (lutein, violaxathin, and beta-carotene) appear, which give yellow and orange hues. Eventually red carotenoid pigments including capsanthin and capsorubin appear, which are exclusively found in peppers.

Chlorophyll A: $R = -CH_3$
Chlorophyll B: $R = -CHO$

The aroma of bell peppers also develops as they ripen.

Green peppers: the smell is largely due to 2-methoxy-3-isobutylpyrazine ("bell pepper pyrazine"). Other minor contributors include: (E,Z)-2,6-nonadienal ("cucumber aldehyde"). The concentrations of most volatile compounds drop during ripening, with the exception of (E)-2-hexenal and (E)-2-hexenol, lending a sweeter, fruitier note to the aroma.

*Read more about "The Chemistry of Bell Peppers [New tab] (https://www.compoundchem.com/2016/07/05/bell-peppers/)" by Andy Brunning / Compound Interest, CC BY-NC-ND*

## 22.3a The 2022 Nobel Prize in Chemistry

The 2022 Nobel Prize in Chemistry, awarded jointly to Carolyn R. Bertozzi, Morten Meldal and K. Barry Sharpless for their development of click chemistry and bioorthogonal chemistry.

Barry Sharpless coined the concept "click" chemistry in 2001. Click chemistry refers to reactions which efficiently snap together small molecules with simple reaction conditions and no unwanted byproducts.

Independently, Barry Sharpless and Morten Mendal developed the first click reaction: a reaction in which an azide is added to an alkyne with a copper catalyst. The two reagents click together to form a single cyclic product, with the copper catalyst making the reaction quick and selective. Chemists could add groups onto the azide and alkyne to change the product formed by the reaction.

Carolyn Bertozzi introduced the concept of bioorthologanal chemistry – chemical reactions that happen in cells without affecting their normal chemistry – in 2003. Copper is toxic to living cells, so she modified the original click reaction to produce a copper-free version. She used this reaction to track molecules called glycans on cell surfaces, which she had been investigating since the early 1990s.

Additional click chemistry reactions have developed, useful in the synthesis of new drugs. Bioorthologonal reactions allow researchers to study biological molecules and help identify targets of new drugs, and are also being trialed to produce 'clickable' antibodies to target cancerous tumours.

*Read more about "The 2022 Nobel Prize in Chemistry [New tab] (https://www.compoundchem.com/2022/10/05/2022nobelchemistry/)" by Andy Brunning / Compound Interest, CC BY-NC-ND*

## 22.4a Today in Chemistry History: August Kekulé and the structure of benzene

Today in Chemistry History: August Kekulé.

Kekulé was born on 7 September 1829.

Kekulé is best known for work on the structure of benzene. He claimed he deciphered its ring-shaped structure after a daydream about a snake eating its own tail. He depicted the benzene ring as a flat molecule with alternating single and double bonds between carbon atoms. Original structure was an irregular hexagon with different bond lengths between the carbon atoms, which we now know isn't the case, and it did not fully explain benzene's reactivity and stability.

In 1929 Kathleen Lonsdale used X-ray crystallography to show all carbon-carbon bonds in a benzene ring are the same length, meaning they are delocalised. This explains benzene's stability. Lonsdale proved it was flat molecule.

*Read more about "Today in Chemistry History: August Kekulé and the structure of benzene [New tab] (https://www.compoundchem.com/2020/09/07/kekule/)" by Andy Brunning / Compound Interest, CC BY-NC-ND*

## 22.4b Benzene Derivatives in Organic Chemistry

A wide variety of important organic compounds are derived from benzene, by replacing one of the hydrogens with a different functional group. They can have both common and systematic names, which can be confusing.

**Different benzene derivatives**

| Functional group | Common name | Systematic name | Chemical formula |
| --- | --- | --- | --- |
| Halogen-containing | Fluorobenzene | Fluorobenzene | $C_6H_5F$ |
| Halogen-containing | Chlorobenzene | Chlorobenzene | $C_6H_5Cl$ |
| Halogen-containing | Bromobenzene | Bromobenzene | $C_6H_5Br$ |
| Halogen-containing | Iodobenzene | Iodobenzene | $C_6H_5I$ |
| Hydrocarbon derivatives | Toluene | Methylbenzene | $C_7H_8$ |
| Hydrocarbon derivatives | Cumene | Isopropylbenzene | $C_9H_{12}$ |
| Hydrocarbon derivatives | Ethylbenzene | Ethylbenzene | $C_8H_{10}$ |
| Hydrocarbon derivatives | Styrene | Vinylbenzene | $C_8H_8$ |
| Hydrocarbon derivatives | Ortho-xylene | 1,2-dimenthylbenzene | $C_8H_{10}$ |
| Hydrocarbon derivatives | Meta-xylene | 1,3-dimenthylbenzene | $C_8H_{10}$ |
| Hydrocarbon derivatives | Para-xylene | 1,4-dimenthylbenzene | $C_8H_{10}$ |
| Oxygen-containing | Phenol | Hydrobenzene | $C_6H_5OH$ |
| Oxygen-containing | Benzoic acid | Benzenecarboxylic Acid | $C_6H_5COOH$ |
| Oxygen-containing | Benzaldehyde | Benzenecarbaldehyde | $C_6H_5CHO$ |
| Oxygen-containing | Acetophenone | 1-phenylethanone | $C_6H_5COCH_3$ |
| Oxygen-containing | Methyl Benzoate | Methyl Benzoate | $C_8H_8O_2$ |
| Oxygen-containing | Anisole | Methoxybenzene | $C_6H_5OCH_3$ |
| Nitrogen-containing | Aniline | Aminobenzene | $C_6H_5NH_2$ |
| Nitrogen-containing | Nitrobenzene | Nitrobenzene | $C_6H_5NO_2$ |
| Nitrogen-containing | Benzonitrile | Benzonitrile | $C_6H_5CN$ |
| Nitrogen-containing | Benzamide | Benzamide | $C_6H_5CONH_2$ |
| Sulfur-containing | Benzenesulfonic Acid | Benzenesulfonic Acid | $C_6H_5CO_3H$ |

| Polyaromatics | Naphthalene | Naphthalene | $C_{10}H_8$ |
| Polyaromatics | Anthracene | Anthracene | $C_{14}H_{10}$ |

*Read more about "Benzene Derivatives in Organic Chemistry [New tab] (https://www.compoundchem.com/2014/09/01/benzene-derivatives-in-organic-chemistry/)" by Andy Brunning / Compound Interest, CC BY-NC-ND*

## 22.4c The Science of Sunscreen & How it Protects Your Skin

Types of UV radiation:

- UVA: (wavelength 320-400nm) accounts for 95% of solar UV radiation reaching Earth's surface. Penetrates deepest into skin, contributes to skin cancer via indirect DNA damage. UVA blockers: Avobenzone, Menthyl Anthranilate, Ecamsule.
- UVB: (wavelength 290-320nm) accounts for 5% of solar UV radiation reaching Earth's surface. Causes direct DNA damage, one of main contributors to skin cancer. UVB blockers: Octyl Methoxycinnamate, Homosalate, PABA, Padimate O, Cinoxate, Octyl Salicylate, Trolamine Salicylate, Octylocrylene, Ensulizole. UVB blockers not approved in the USA: Octly Triazone, Enzacamene, Amiloxate.
- UVC: (wavelength 290-100nm) filtered by ozone in Earth's atmosphere and does not reach the surface, as a result does not cause skin damage.

Inorganic chemicals in sunscreen (ie. Zinc oxide, titanium oxide) both absorb and scatter UV light.

Organic chemical also used – the chemical bonds absorb UV radiation, with the chemical structure affecting whether they absorb UVA, UVB or both. Several different chemicals are used in sunscreen to ensure full protection.

UVA and UVB blockers, all approved in EU, Canada, Australia: oxybenzone, Sulisobenzone, Dioxybenzone. UVB blockers not approved in the USA, all approved in EU, Canada, Australia: Mexoryl XL, Tinososorb S, Tinosorb M, Neo Heliopan AP, Uvinual A Plus, UVAsorb HEB.

17 sunscreen active ingredients approved in the USA.

28 sunscreen ingredients approved in the EU.

*Read more about "The Science of Sunscreen & How it Protects Your Skin [New tab] (https://www.compoundchem.com/2014/06/05/sunscreenchemicals/)" by Andy Brunning / Compound Interest, CC BY-NC-ND*

## 22.4d The Chemicals Behind the 'New Car Smell

60+ is the approximate number of volatile organic compounds (VOCs) detected in the interior of new cars. Not a;; of these ill have odours, but many may be contributors to the characteristics of 'new car smell', no it's not the result of one specific compound.

20% is the approximate percentage decay of total VOC levels per week in new car interiors. They can also vary depending on conditions – concentrations will be decreased by ventilation of the car, but can be increased by increased temperatures within the car.

The most common found compounds: Toluene, Ethylbenzene, Styrene, Xylenes (p-Xylene, m-Xylene, and o-Xylene), Trimethylbenzenes (1,3,5-, and 1,2,4-Trimethylbenzene), various alkanes.

They come from: plastic, moldings, carpets, upholstery, adhesives, lubricants, gasoline, leather and vinyl treatments.

A 2007 study found little toxicity in the new car odours under lab conditions, However, although concentrations of these compounds are still very low, they can be above recommended indoor guidelines for VOCs for the first 6 months after a car's manufacture. This could lead to headaches, sensory irritations and minor allergic responses. Manufacturers are now taking measure to reduce the levels of these compounds in new cars.

*Read more about "The Chemicals Behind the 'New Car Smell' [New tab] (https://www.compoundchem.com/ 2014/06/16/newcarsmell/)" by Andy Brunning / Compound Interest, CC BY-NC-ND*

## 22.4e The Chemistry of Glow Sticks

When glow sticks are bent the inner glass tube is broken, releasing hydrogen peroxide solution. This then reacts with diphenyl oxalate, producing 1,2-dioxtanedione; this product is unstable, and decomposes to carbon dioxide, releasing energy. The energy is absorbed by electrons in dye molecules, which subsequently fall back to their ground state, losing excess energy in the form of light.

- Rhodamine B produces red colour.
- 5,12-BIS(Phenylethynyl)Naphthacene produces orange colour.
- Rubrene produces yellow colour.
- 9,10-BIS(Phenylethynyl)Anthracene produce green colour.
- 9,10-Diphenylanthracene produce blue colour.

*Read more about "The Chemistry of Glow Sticks [New tab] (https://www.compoundchem.com/2014/10/14/ glowsticks/)" by Andy Brunning / Compound Interest, CC BY-NC-ND*

## 22.5a Aromatic Chemistry Reactions Map

**Aromatic functional group interconversions**

| Starting compound | Type of Reaction | Reaction Conditions | Resulting Compound |
|---|---|---|---|
| Alkylbenzene | Oxidation | $KmnO_4, H_2SO_4$ heat | Benzoic acid |
| Benzaldehyde | Oxidation | not listed | Benzoic acid |
| Benzenediazonium | Substitution | $HBF_4$ filter off solid, dry and heat | Fluorobenzene |
| Benzenediazonium | Coupling | $C_6H_5R$, NaOH, less than 10 degree Celsius | Azobenzene |
| Benzenediazonium | Substitution | $HCl, CuCl$ cat., room temperature | Chlorobenzene |
| Benzenediazonium | Substitution | $H_2O$, 160 degree Celsius | Phenol |
| Benzenediazonium | Substitution | $KCN$ and copper powder | Benzonitrile |
| Benzenediazonium | Substitution | $HBr, CuCr$ cat., room temperature | Bromobenzene |
| Benzenediazonium | Substitution | $Kl(aq)$, room temperature | Iodobenzene |
| Benzenediazonium | Reduction | cold $H_3PO_2(aq)$ | Benzene |
| Benzene | Substitution | $H_2SO_4$, heat under reflux | Phenylsulfonic acid |
| Benzene | Substitution | $I_2$ & conc. $HNO_3$. reflux | Iodobenzene |
| Benzene | Substitution | $Br_2$ & $FeBr_3$ cat., room temperature | Bromobenzene |
| Benzene | Substitution | $Cl_2$ & $AlCl_3$ cat., room temperature | Chlorobenzene |
| Benzene | Substitution | Chloroalkane, $AlCl_3$ cat., room temperature | Alkylbenzene |
| Benzene | Substitution | $HNO_3, H_2SO_4$ cat., 55 degrees Celsius | Nitrobenzene |
| Benzene | Acylation | $CO, HCl$ & $AlCl_3$ cat., $CuCl$ | Benzaldehyde |

| Benzene | Acylation | $RCOCl$, $AlCl_3$ cat., reflux 60 degree Celsius | Phenylketone |
|---|---|---|---|
| Benzonitrile | Reduction | reduction of $SnCl_2(ether)$, $HCl$, 20 degree Celsius then boil with $H_2O$ | Benzaldehyde |
| Benzonitrile | Hydrolysis | 0.1M $H_2SO_4$, $H_2O$ | Benzoic acid |
| Benzoic acid | Substitution | $SOCl_2$ heat | Benzoyl chloride |
| Benzoyl chloride | Hydrolysis | $H_2O$ | Benzoic acid |
| Chlorobenzene | Substitution | $KNH_2NH_3$ -33 degrees Celsius, then dilute acid | Phenylamine |
| Chlorobenzene | Substitution | $Na$ & $Rl$, dry ether | Alkylbenzene |
| Chlorobenzene | Hydrolysis | $NaOH$ with $Cu$ salt cat., 200 atm and 350 degree Celsius then $HCl$ | Phenol |
| Chlorobenzene | Substitution | $CuCN$, polar solvent, reflux (also for $Ar-Br$) | Benzontirile |
| Nitrobenzene | Reduction | $HCl$, reflux, $Sn$; $NaOH$ | Phenylamine |
| Phenol | Reduction | powdered $Zn$, heat | Benzene |
| Phenylamine | Diazotisation | $NaNO_2(aq)$, dilute $HCl$, temperature 0-5 degree Celsius | Benzenediazonium |
| Phenylsulfonic Acid | Hydrolysis | $H_2SO_4$ cat., $H_2O$, heat | Benzene |

*Read more about "Aromatic Chemistry Reactions Map [New tab] (https://www.compoundchem.com/2014/02/23/aromatic-chemistry-reactions-map/)" by Andy Brunning / Compound Interest, CC BY-NC-ND*

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