1.3 Reactions of Hydrocarbons

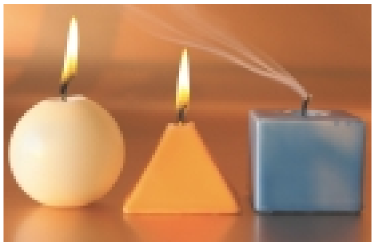


Figure 1
Hydrocarbons are found as solids, liquids, and gases, all of which burn to produce carbon dioxide and water, and large amounts of light and heat energy.

All hydrocarbons readily burn in air to give carbon dioxide and water, with the release of large amounts of energy (**Figure 1**); this chemical reaction accounts for the extensive use of hydrocarbons as fuel for our homes, cars, and jet engines. In other chemical reactions, alkanes are generally less reactive than alkenes and alkynes, a result of the presence of more reactive double and triple bonds in the latter. Aromatic compounds, with their benzene rings, are generally more reactive than the alkanes, and less reactive than the alkenes and alkynes. In this section, we will examine this trend in the chemical reactivity of hydrocarbons.

LAB EXERCISE 1.3.1

Preparation of Ethyne (p. 84)
How close does the actual yield come to the theoretical yield in the reaction between calcium carbide and water?

When we are representing reactions involving large molecules, it is often simpler to use a form of shorthand to represent the various functional groups. **Table 1** shows some of the commonly used symbols. For example, R—Ø represents any alkyl group attached to a benzene ring, and R—X represents any alkyl group attached to any halogen atom.

Table 1 Examples of Symbols Representing Functional Groups

Group	Symbol
alkyl group	R, R′, R″, etc. (R, R-prime, R-double prime)
halogen atom	X
phenyl group	Ø

Reactions of Alkanes

The characteristic reactions of saturated and unsaturated hydrocarbons can be explained by the types of carbon—carbon bonds in saturated and unsaturated hydrocarbons. Single covalent bonds between carbon atoms are relatively difficult to break, and thus alkanes are rather unreactive. They do undergo **combustion reactions** if ignited in air, making them useful fuels. Indeed, all hydrocarbons are capable of combustion to produce carbon dioxide and water. The reaction of propane gas, commonly used in gas barbecues, is shown below:

$$C_3H_{8(g)} + 5\ O_{2(g)} \rightarrow 3\ CO_{2(g)} + 4\ H_2O_{(g)}$$

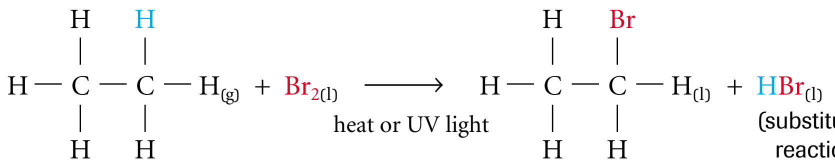
combustion reaction the reaction of a substance with oxygen, producing oxides and energy

substitution reaction a reaction in which a hydrogen atom is replaced by another atom or group of atoms; reaction of alkanes or aromatics with halogens to produce organic halides and hydrogen halides

alkyl halide an alkane in which one or more of the hydrogen atoms have been replaced with a halogen atom as a result of a substitution reaction

While the C—C bonds in alkanes are difficult to break, the hydrogen atoms may be *substituted* by a halogen atom in a **substitution reaction** with F_2, Cl_2, or Br_2. Reactions with F_2 are vigorous, but Cl_2 and Br_2 require heat or ultraviolet light to first dissociate the halogen molecules before the reaction will proceed. In each case, the product formed is a halogenated alkane; as the halogen atom(s) act as a functional group, halogenated alkanes are also referred to as an organic family called **alkyl halides**.

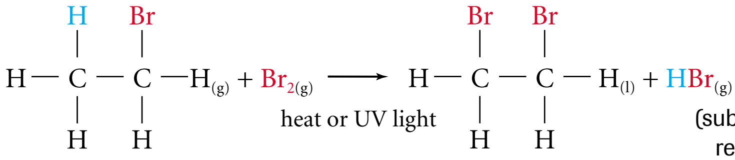
In the reaction of ethane with bromine, the orange colour of the bromine slowly disappears, and the presence of $HBr_{(g)}$ is indicated by a colour change of moist litmus paper from blue to red. A balanced equation for the reaction is shown below.



(substitution reaction)

bromoethane, (ethyl bromide)

As the reaction proceeds, the concentration of bromoethane increases and bromine reacts with it again, leading to the substitution of another of its hydrogen atoms, forming 1,2-dibromoethane.



1,2-dibromoethane

(substitution reaction)

Additional bromines may be added, resulting in a mixture of brominated products that (because of differences in physical properties) can be separated by procedures such as distillation.

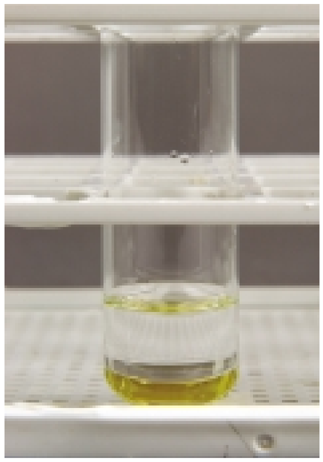


Figure 2
The reaction of cyclohexene and bromine water, $Br_{2(aq)}$, is rapid, forming a layer of brominated cyclohexane (clear).

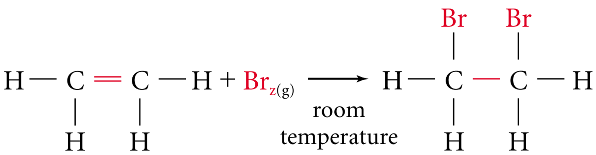
Reactions of Alkenes and Alkynes

Alkenes and alkynes exhibit much greater chemical reactivity than alkanes. For example, the reaction of these unsaturated hydrocarbons with bromine is fast, and will occur at room temperature (**Figure 2**). (Recall that the bromination of alkanes requires heat or UV light.) This increased reactivity is attributed to the presence of the double and triple bonds. This characteristic reaction of alkenes and alkynes is called an **addition reaction** as atoms are *added* to the molecule with *no loss of hydrogen atoms*.

Alkenes and alkynes can undergo addition reactions not only with halogens, but also with hydrogen, hydrogen halides, and water, given the appropriate conditions. Examples of these reactions are shown below.

addition reaction a reaction of alkenes and alkynes in which a molecule, such as hydrogen or a halogen, is added to a double or triple bond

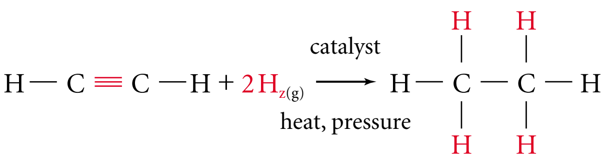
Halogenation (with Br_2 or Cl_2)



ethene 1,2-dibromoethane

(addition reaction)

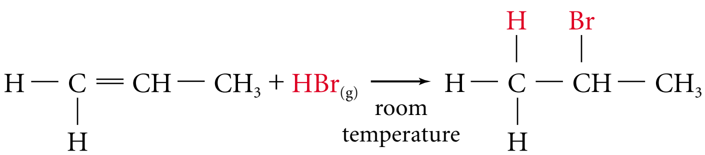
Hydrogenation (with H_2)



ethyne ethane

(addition reaction)

Hydrohalogenation (with hydrogen halides)



propene 2-bromopropane

(addition reaction)

Table 2 Prefixes for Functional Groups

Functional group	Prefix
–F	fluoro
–Cl	chloro
–Br	bromo
–I	iodo
–OH	hydroxy
$–NO_2$	nitro
$–NH_2$	amino

DID YOU KNOW?

Margarine
Vegetable oils consist of molecules with long hydrocarbon chains containing many double bonds; these oils are called "polyunsaturated." The oils are "hardened" by undergoing hydrogenation reactions to produce more saturated molecules, similar to those in animal fats such as lard.

Hydration (with H_2O)

$$\mathrm{H-CH{=}CH-CH_3} + \mathrm{HOH} \xrightarrow[\text{catalyst}]{\mathrm{H_2SO_4}} \begin{array}{ccccc} \mathrm{H} & & \mathrm{OH} & & \\ | & & | & & \\ \mathrm{H_2C} & - & \mathrm{CH} & - & \mathrm{CH_3} \end{array} \quad \text{(addition reaction)}$$

propene → 2-hydroxypropane (an alcohol)

Markovnikov's Rule

When molecules such as H_2, consisting of two *identical* atoms, are added to a double bond, only one possible product is formed; in other words, addition of identical atoms to either side of the double bond results in identical products.

When molecules of *nonidentical* atoms are added, however, two *different* products are theoretically possible. For example, when HBr is added to propene, the H may add to C atom 1, or it may add to C 2; two different products are possible, as shown below.

$$\mathrm{H-CH{=}CH-CH_3} + \mathrm{HBr} \longrightarrow \begin{array}{ccccc} \mathrm{H_2C} & - & \mathrm{CH} & - & \mathrm{CH_3} \\ | & & | & & \\ \mathrm{H} & & \mathrm{Br} & & \end{array} \quad \text{or} \quad \begin{array}{ccccc} \mathrm{H_2C} & - & \mathrm{CH} & - & \mathrm{CH_3} \\ | & & | & & \\ \mathrm{Br} & & \mathrm{H} & & \end{array}$$

propene; 2-bromopropane (main product); 1-bromopropane

Experiments show that, in fact, only one main product is formed. The product can be predicted by a rule known as Markovnikov's rule, first stated by Russian chemist V. V. Markovnikov (1838–1904).

> **Markovnikov's Rule**
>
> When a hydrogen halide or water is added to an alkene or alkyne, the hydrogen atom bonds to the carbon atom within the double bond that *already has more hydrogen atoms*. This rule may be remembered simply as "the rich get richer."

As illustrated in the reaction of propene above, the first C atom has two attached H atoms, while the second C atom has only one attached H atom. Therefore, the "rich" C1 atom "gets richer" by gaining the additional H atom; the Br atom attaches to the middle C atom. The main product formed in this reaction is 2-bromopropane.

SAMPLE problem — Predicting Products of Addition Reactions

What compound will be produced when water reacts with 2-methyl-1-pentene?

First, write the structural formula for 2-methyl-1-pentene.

$$\begin{array}{ccccccc} \mathrm{CH_3} & \mathrm{CH_2} & \mathrm{CH_2} & \mathrm{C} & = & \mathrm{CH_2} \\ 5 & 4 & 3 & 2\,| & & 1 \\ & & & \mathrm{CH_3} & & \end{array}$$

Next, identify the C atom within the double bond that has more H atoms attached. Since carbon 1 has two H atoms attached, and carbon 2 has no H atoms attached, the H atom in the HOH adds to carbon 1, and the OH group adds to carbon 2.

We can now predict the product of the reaction.

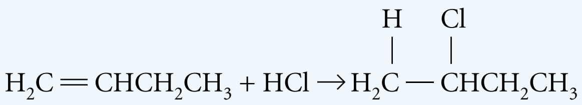
$$\begin{array}{cccccc} \mathrm{CH_3} & \mathrm{CH_2} & \mathrm{CH_2} & \mathrm{C} & = & \mathrm{CH_2} \\ 5 & 4 & 3 & 2\,| & & 1 \\ & & & \mathrm{CH_3} & & \end{array} + \mathrm{HOH} \longrightarrow \begin{array}{cccccc} & & & \mathrm{OH} & & \mathrm{H} \\ & & & | & & | \\ \mathrm{CH_3} & \mathrm{CH_2} & \mathrm{CH_2} & \mathrm{C} & - & \mathrm{CH_2} \\ 5 & 4 & 3 & 2\,| & & 1 \\ & & & \mathrm{CH_3} & & \end{array}$$

The compound produced is 2-hydroxy-2-methylpentane.

Example

Draw structural diagrams to represent an addition reaction of an alkene to produce 2-chlorobutane.

Solution

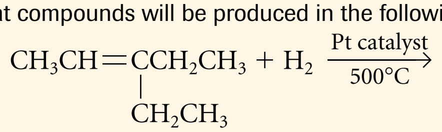


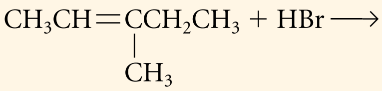
1-butene

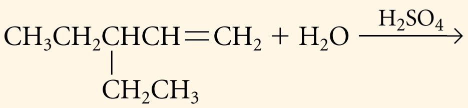
Practice

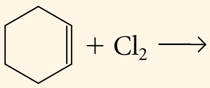
Understanding Concepts

1. What compounds will be produced in the following addition reactions?

(a) 

(b) 

(c) 

(d) 

Synthesis: Choosing Where to Start

Addition reactions are important reactions that are often used in the synthesis of complex organic molecules. Careful selection of an alkene as starting material allows us to strategically place functional groups such as a halogen or a hydroxyl group ($-OH$) in desired positions on a carbon chain. As we will see later in this chapter, the products of these addition reactions can in turn take part in further reactions to synthesize other organic compounds, such as vinegars and fragrances.

Practice

Understanding Concepts

2. Explain the phrase "the rich get richer" as it applies to Markovnikov's rule.
3. Draw structural diagrams to represent addition reactions to produce each of the following compounds:
   (a) 2,3-dichlorohexane
   (b) 2-bromobutane
   (c) 2-hydroxy-3-methylpentane
   (d) 3-hydroxy-3-methylpentane

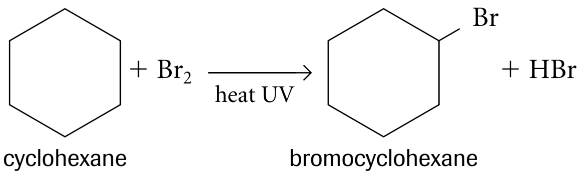
Reactions of Aromatic Hydrocarbons

Since aromatic hydrocarbons are unsaturated, one might expect that they would readily undergo addition reactions, as alkenes do. Experiments show, however, that the benzene ring does not undergo addition reactions except under extreme conditions of temperature and pressure. They are less reactive than alkenes.

Aromatic hydrocarbons do undergo substitution reactions, however, as alkanes do. In fact, the hydrogen atoms in the benzene ring are more easily replaced than those in alkanes. When benzene is reacted with bromine in the presence of a catalyst, bromobenzene is produced.

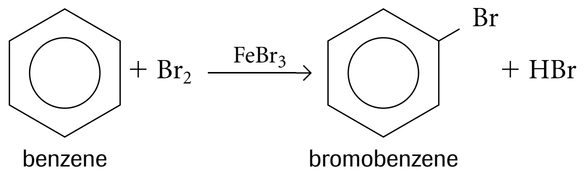
Overall, the reactivity of aromatic hydrocarbons appears to be intermediate between that of alkanes and alkenes.

(a) cyclohexane + Br_2 → bromocyclohexane



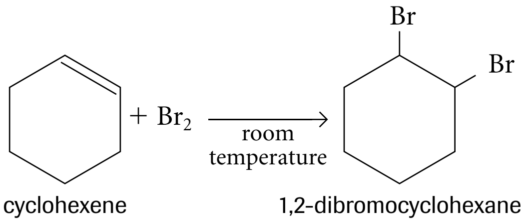
(substitution reaction)

(b) benzene + Br_2 → bromobenzene



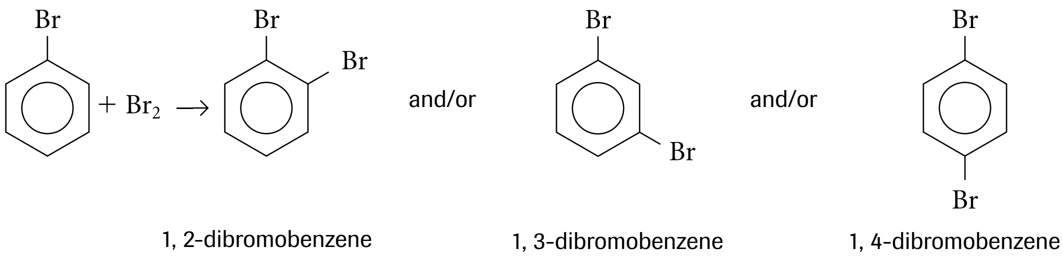
(substitution reaction; addition does not occur)

(c) cyclohexene + Br_2 → bromocyclohexane



(addition reaction)

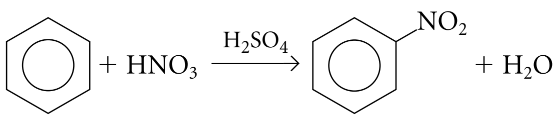
Further reaction of bromobenzene with Br_2 results in the substitution of another Br on the ring. In theory, this second Br atom may substitute for an H atom on any of the other C atoms, resulting in three possible isomers of dibromobenzene.



In practice, the 1,3 isomer appears to be favoured.

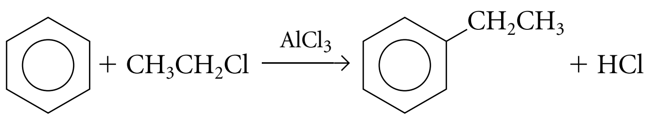
The relatively low reactivity of aromatic hydrocarbons indicates that the benzene structure is particularly stable. It seems that the bonds in a benzene ring are unlike the double or triple bonds in alkenes or alkynes. In 1865, the German architect and chemist Friedrich August Kekulé (1829–1896) proposed a cyclic structure for benzene, C_6H_6. With 6 C atoms in the ring, and one H atom on each C atom, it appears that there might be 3 double bonds within the ring, each alternating with a single bond. As carbon—carbon double bonds are shorter than single bonds, we would predict that the bonds in the benzene ring would be of different lengths. Experimental evidence, however, shows otherwise. The technique of X-ray diffraction indicates that all the C—C bonds in benzene are identical in length and in strength (intermediate between that of single and double bonds). Therefore, rather than having 3 double bonds and 3 single bonds, an acceptable model for benzene would require that the valence electrons be shared *equally* among all 6 C atoms, making 6 identical bonds. A model of benzene is shown in **Figure 3**. In this model, the 18 valence electrons are shared equally, in a *delocalized* arrangement; there is no specific location for the shared electrons, and all bond strengths are intermediate between that of single and double bonds. This explains why benzene rings do not undergo addition reactions as double bonds do, and why they do undergo substitution reactions as single bonds do, and do so more readily. In Chapter 4, you will examine in more detail the unique bonding that is present in the benzene ring.

In another substitution reaction, benzene reacts with nitric acid in the presence of H_2SO_4 to form nitrobenzene. Benzene also reacts with alkyl halides (R—X) in the presence of an aluminum halide catalyst (AlX_3); the alkyl group attaches to the benzene ring, displacing an H atom on the ring. These products can undergo further reactions, enabling the design and synthesis of aromatic compounds with desired groups attached in specific positions.



(substitution reaction)

nitrobenzene



(substitution reaction)

ethylbenzene

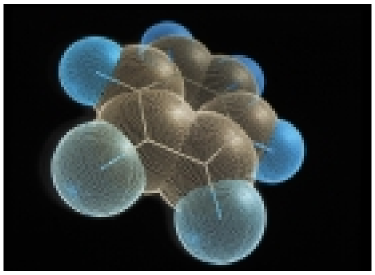


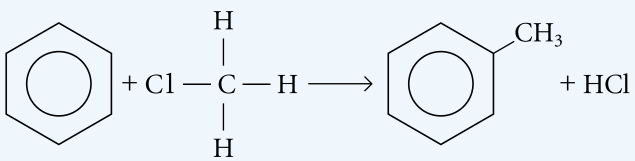
Figure 3
Kekulé wrote the following diary entry about a dream he had, in which he gained a clue to the structure of benzene: "Again the atoms gambolled before my eyes. This time the smaller groups kept modestly to the background. My mind's eyes, rendered more acute by repeated visions of a similar kind, could now distinguish larger structures, of various shapes; long rows, sometimes more closely fitted together; all twining and twisting in snakelike motion. But look! What was that? One of the snakes grabbed its own tail, and the form whirled mockingly before my eyes. As if struck by lightning I awoke; ... I spent the rest of the night in working out the consequences of the hypothesis.... If we learn to dream we shall perhaps discover the truth."

Predicting Reactions of Aromatic Hydrocarbons

SAMPLE problem

Predict the product or products formed when benzene is reacted with 2-chlorobutane, in the presence of a catalyst ($AlCl_3$). Draw structural diagrams of the reactants and products.

The methyl group of chloromethane substitutes for one of the H atoms on the benzene ring, forming methylbenzene and releasing the chloride to react with the displaced hydrogen.



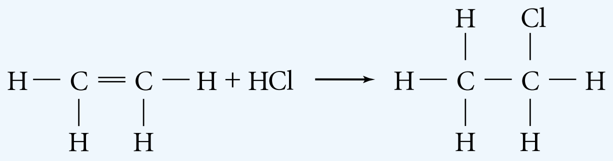
The products formed are methylbenzene (toluene) and hydrogen chloride.

Example

Draw balanced chemical equations (including structural diagrams) to represent a series of reactions that would take place to synthesize ethylbenzene from benzene and ethene. Classify each reaction.

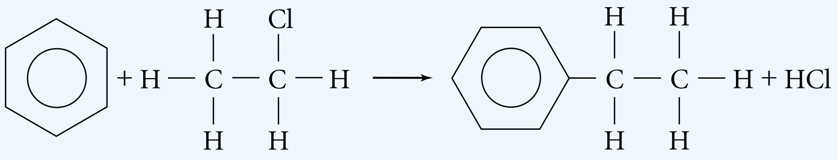
Solution

Reaction 1: Halogenation (by addition) of ethene by hydrogen chloride



ethene chloroethane

Reaction 2: Halogenation (by substitution) of benzene by chloroethane

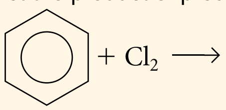


Practice

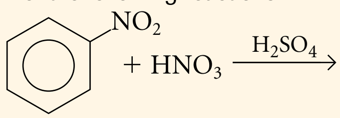
Understanding Concepts

4. Predict the product or products formed in each of the following reactions:

(a)



(b)



5. Propose a reaction series that would produce 2-phenylbutane, starting with benzene and 1-butene as reactants.

6. Which of the terms “addition,” “substitution,” or “halogenation” describes the reaction between benzene and bromine? Explain.

7. Describe the bonding structure in benzene, and explain the experimental evidence in support of this structure.

SUMMARY Reactions of Hydrocarbons

- All hydrocarbons undergo combustion reactions with oxygen to produce carbon dioxide and water.

Alkanes

- Primarily undergo **substitution** reactions, with heat or UV light:
  with halogens or hydrogen halides: halogenation
  with nitric acid

Alkenes and Alkynes

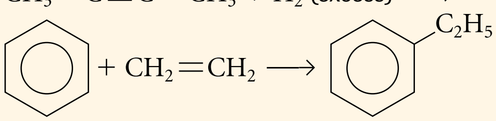
- Primarily undergo **addition** reactions:
  with H_2: hydrogenation
  with halogens or hydrogen halides: halogenation
  with water: hydration

Aromatics

- Primarily undergo **substitution** reactions:
  with X_2: halogenation, $\varnothing-X$
  with HNO_3: nitration, $\varnothing-NO_2$
  with RX: alkylation, $\varnothing-R$
- Do *not* undergo addition reactions.

Section 1.3 Questions

Understanding Concepts

1. Write a balanced equation for each of the following types of reactions of acetylene:
   (a) addition
   (b) hydrogenation
   (c) halogenation
   (d) hydration
2. Classify each of the following reactions as one of the following types: addition, substitution, hydrogenation, halogenation, or combustion. Write the names and the structures for all reactants and products.
   (a) methyl-2-butene + hydrogen →
   (b) ethyne + Cl_2 →
   (c) $CH_3-C\equiv C-CH_3 + H_2$ (excess) $\longrightarrow$
   (d)
   
   (e) $$CH_3-CH=\overset{\overset{\displaystyle C_2H_5}{|}}{C}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3 + O=O \longrightarrow$$
3. Classify and write structural formula equations for the following organic reactions:
   (a) 3-hexene + water $\xrightarrow{H_2SO_4}$
   (b) 2-butene + hydrogen → butane
   (c) 4,4-dimethyl-2-pentyne + hydrogen → 2,2-dimethylpentane
   (d) methylbenzene + oxygen → carbon dioxide + water
   (e) 2-butene → 3-methylpentane

Applying Inquiry Skills

4. To make each of the following products, select the reactants and describe the experimental conditions needed.
   (a) 2-hydroxypropane
   (b) 1, 3-dichlorocyclohexane from cyclohexane
   (c) 2-methyl-2-hydroxypentane from an alkene
   (d) chlorobenzene

Making Connections

5. If a certain volume of propane gas at SATP were completely combusted in oxygen, would the volume of gaseous product formed be greater or smaller than that of the reactant? By how much?
6. From your knowledge of intermolecular attractions, which of these organic compounds—2-chlorononane, 2-hydroxynonane, or nonane—would be the most effective solvent for removing oil stains? Give reasons for your answer.
7. TNT is an explosive with a colourful history (**Figure 5**). Research and report on who discovered it, and its development, synthesis, uses, and misuses.

Figure 5

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