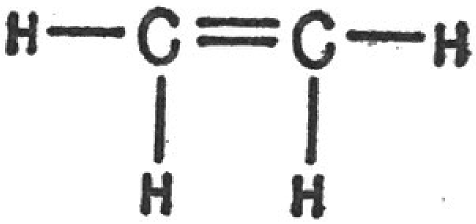
Chapter 2

A Shortage of Hydrogen

Two Bonds are Livelier than One

THERE ARE still a few variations left in the ways in which carbon atoms may be put together. In the structural formulas shown in Chapter 1, neighboring atoms were connected by single lines. Neighboring carbon atoms devoted just one of their four bonds to each other and saved their remaining three bonds for other atoms.

It is possible, however, that neighboring carbon atoms might be connected by two of their four bonds. This will leave each carbon atom with only two bonds to be used in other ways. The simplest such molecule is this:



$$H-\underset{H}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-H$$

Figure 5—Ethylene

This is *ethylene.* Its molecule contains a *double bond.*

Compare the structural formula of ethylene with that of ethane in Chapter 1. The ethane molecule is made up of two carbon atoms and six hydrogen atoms. The ethylene molecule is made up of two carbon atoms and only four hydrogen atoms. The ethane molecule has all the hydrogen atoms it can hold. It is a *saturated hydrocarbon.* In ethylene there is a hydrogen shortage because an extra bond that might otherwise be used for hydrogen atoms is used to hold the carbon atoms together. Ethylene is an *unsaturated hydrocarbon.*

A long carbon chain can have a double bond anywhere along the line. If the chain is branched, the double bond might be in the branch. There can be more than one double bond in a molecule. Important compounds are known with a dozen or more double bonds in their molecules. Every different arrangement, every different location, means a different compound. (More isomers! More trillions of organic molecules!)

The carbon atom is most at ease when its four bonds stick out comfortably in four different directions. There is a certain amount of strain when two bonds are forced to line up between the same two carbon atoms. The result is that the double bond represents a kind of weak spot in the carbon chain. The chain is livelier at that point. Other chemicals will attack it just at the double bond. If the action is vigorous enough, the double bond may be broken completely and the chain will fall apart.

By noticing what happens when certain chemicals are added to an organic compound, chemists can tell whether a double bond is present or not. By breaking the chain and studying the pieces, they can tell just where in the chain the double bond was located.

Catalysts and Plastics

If a compound with a double bond is treated with hydrogen gas under the proper conditions, hydrogen atoms will add on to the double bond. That is, one of the two bonds between the carbon atoms will be broken. Each carbon atom will then use its newly available bond to hook on to a hydrogen atom. In this way, an unsaturated compound will become saturated. As I shall explain later, such *hydrogenations* are sometimes of importance to the housewife.

The reaction between an unsaturated compound and hydrogen gas is a very slow process if those two subtsances are left to themselves. The chemist can hasten it, however, by adding to the mixture a small quantity of certain finely divided metals. The metal doesn't take part in the hydrogenation itself. It's just that the surface of the tiny metal particles seems to be an ideal place for the unsaturated compound and the hydrogen to combine. In the presence of the metal, therefore, the hydrogenation proceeds millions of times as rapidly as in its absence.

Any substance that hastens a reaction just by its presence, without getting used up in the process, is called a *catalyst*. Over the years, chemists have discovered numerous substances that can be used as catalysts for one type of chemical reaction or another. Without catalysts, our chemical industries would be stopped in their tracks.

The presence of the double bond can lead to other interesting results, too. If ethylene is heated to a high temperature and put under high pressure, two things happen. First, the high temperature breaks one of the two bonds between the carbon atoms. Then, because the ethylene molecules are pushed so closely together by the pressure, the newly available bonds can be easily used to link neighboring ethylene molecules. The result is a very long chain of thousands of carbon atoms all connected by single bonds. This compound is called *polyethylene* or *polythene.* (The prefix "poly" comes from a Greek word meaning "many" and is often used in chemical names.)

The polyethylene molecule is like a wax molecule except that its carbon chain is longer than that of a wax molecule. It is a cloudy white solid with a slippery feel. Polyethylene is not brittle, like wax, but is flexible and tough. And it is just as chemically inert as wax.

Wax will become soft from the heat of our hands. Polyethylene must be heated above the temperature of boiling water before it begins to soften. Once softened, though, it can be molded into any desired shape. If it is then cooled, it will keep its new shape indefinitely.

Any substance which can be molded into a permanent shape (either with heat or under pressure) is called a *plastic.* Polyethylene is an example.

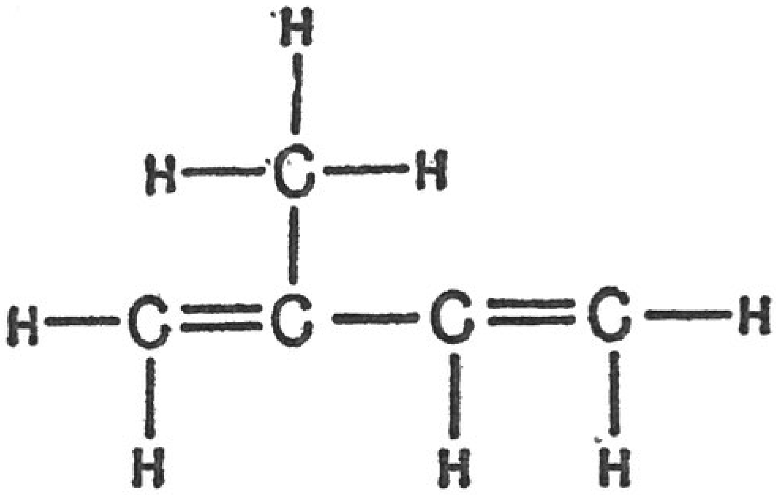
Polyethylene has come into general use only since World War II, but already it is everywhere. Objects can be wrapped in polyethylene bags which are heat-sealed at the edges. (Two sheets of polyethylene heated at the edges, will melt together and form an airtight, watertight seal.) Wastepaper baskets, laundry baskets, sink-mats, bags, containers, and many other objects are being made of it. Polyethylene is light, and is kept clean easily. It will not break, crack or chip. It is not affected by water or most of the other materials one is likely to find in the house. It is an example of a useful substance which did not exist until it was manufactured by chemists.

Many types of molecules, usually unsaturated, can be made to hook together into long chains in this way. Polystyrene, also called *distrene,* is another plastic, that starts with an unsaturated hydrocarbon, *styrene,* which is somewhat more complicated than ethylene. In general, the single molecule that one starts with is called a *monomer* (from Greek words meaning "one part"). The long chain built out of the monomer is a *polymer* (from Greek words meaning "many parts"). Ethylene, for instance, is said to *polymerize* to form polyethylene. Usually, a compound can be considered a polymer when its molecule contains at least 200 carbon atoms.

Natural Colors

One very important unsaturated hydrocarbon is *isoprene* and here is its structural formula:

Figure 6—Isoprene



Isoprene, as you see, is a five-carbon molecule with a branch in the chain. Also, it has two double bonds, with a single bond between them. This is very important. Whenever double bonds and single bonds take turns along a carbon chain, like this: —C=C—C=C—C=C—C=C—, the double bonds are said to be *conjugate.*

Conjugate double bond arrangements are more stable than double bonds arranged otherwise. Organic compounds that have long chains of carbon atoms with several double bonds included, usually have these double bonds arranged in conjugate form.

Like ethylene, isoprene molecules can be made to join together. In fact, many of the natural products found in plant tissues have molecules that look as if they were formed by joining together a number of isoprene molecules in various ways. The resulting molecules have ten carbon atoms, or fifteen, or twenty, or more, depending on the number of isoprene molecules that have been joined. Molecules built out of isoprene units in this way are called *terpenes,* because such compounds were first located in turpentine.

One of the most important terpens is *carotene,* which contains forty carbon atoms (eight isoprene units joined). Carotene was first found in carrots; hence its name.

Carotene contains eleven double bonds and these are conjugate. That brings up an interesting point. A compound with several conjugate double bonds is usually colored. Carotene is colored and is responsible for many of the colors in nature. Solid carotene is red, but when it is dissolved in fat, it can be orange or yellow depending on the amount dissolved. Carrots and sweet potatoes are orange-colored because of the carotene they contain. Carotene is also responsible for the yellow color of butter and egg yolk. Animal fat that contains carotene, such as chicken fat, is yellow. Animal fat without carotene, such as lard, is white.

Carotene is sometimes even responsible for the color of human skin. Some of it is dissolved in the fatty layer under the skin. The people of East Asia have enough carotene under their skins to give it a yellowish cast.

There are other colors in nature for which compounds like carotene are responsible. The red color of tomatoes and of boiled lobster shells are caused by carotene-like compounds. The compound in tomatoes is called *lycopene* from the Latin name for the tomato plant.

Have you noticed that all the saturated hydrocarbons I mentioned in Chapter 1 had names that ended in "ane" while the unsaturated hydrocarbons mentioned in this chapter have names ending in "ene"? Chemists always try to make logical rules for naming organic compounds. Their most ambitious attempt in this direction was at an international meeting of chemists held in Geneva, Switzerland in 1892. A system called the *Geneva nomenclature* was set up. One of the rules was "ane" endings for saturated hydrocarbons and "ene" for hydrocarbons with double bonds. Every organic compound with a molecule of known structure has an official Geneva name. However, the names actually used are not always the official ones. For one thing, some organic chemicals were named well before 1892 and people got used to those old names and wouldn't change them. For another, the Geneva name is sometimes long and complicated so that chemists think of a shorter name for convenience and then stick to it.

The South American Toy

Certain tropical plants produce a kind of milky sap called *latex*. This will ooze out if the outer layers of the stem are cut. This latex is made up mostly of microscopic particles of polymerized isoprene floating in water. The latex can be treated with certain chemicals which cause the tiny particles to clump together and settle out as *raw rubber.* (Rubber is so called because one of the first uses to which it was put was to rub out pencil marks. The British call it *India rubber* because they got their first supplies from the West Indies.)

The rubber tree, which is the most important source of the substance, was originally native to Brazil. Indeed, rubber was unknown to Europe until Columbus discovered South American Indian children using pieces of rubber as bouncing toys. The French name for rubber, *caoutchouc,* comes from the original Indian word, which meant "weeping wood." Rubber trees were eventually transplanted to the Malayan peninsula in Southeast Asia and grown on plantations there. Malaya is now a much more important rubber-producing region than Brazil.

Raw rubber is soft and sticky, particularly in hot weather. In cold weather, it gets as stiff as a board. For this reason, early raincoats (called mackintoshes after the Scotsman—Charles Macintosh—who first smeared rubber on cloth to make it waterproof) were only useful part of the time.

In 1838, however, Charles Goodyear, an American, discovered, quite by accident, that if raw rubber were heated with a bit of sulfur, the product would resist heat and cold much better. It remained non-sticky and flexible in winter and summer alike. Rubber so treated is called *vulcanized rubber.* Almost all rubber in use to day is vulcanized. When enough sulfur is added, hard rubber (sometimes called *ebonite* or *vulcanite*) is formed. This was used quite a bit in the days before modern plastics became popular.

(Such an important discovery ought to have made Goodyear rich. It would certainly have done so in a story book. Unfortunately, things don't always work out so neatly. Goodyear was in debt all his life and ran his first experiments on rubber while in debtors' prison. After that, patent troubles of one sort or another kept him poor and when he died in 1860, he was in debt for $600,000.)

Rubber has really come into its own since the development of the automobile. It is a tough substance that takes much longer to wear out from rubbing against the road than any metal would. It is elastic and, used in tires, helps give a smooth ride. (Have you ever ridden in a wagon with metal-rimmed wooden wheels? Imagine one of those going sixty miles an hour.) Furthermore, rubber tires flatten against the road and, with the aid of gouges called "treads," grip the road and resist skidding.

The industrial nations have become more and more dependent on rubber for tires as well as for many other uses. Their main supplies come from far-away Malaya. This is, naturally, a ticklish situation, especially in war time, when the need for rubber is increased. (The first objects to be rationed in the United States during the World War II crisis were automobile tires.)

Many attempts have been made to produce an artificial rubber in order that nations might not find themselves cut off from their rubber supplies in time of war. You might think that the logical thing to do would be to take some isoprene and treat it in such a way as to polymerize it. Well, that was one of the first things tried but it didn't work.

The isoprene molecules in rubber, you see, are joined in one particular way. For many years, chemists could get the isoprene molecules to join, but not in the right way. The artificial product turned out to be more like *gutta percha*. This is a substance produced by certain Malayan trees. It is also an isoprene polymer, but it is not elastic and so it is useless as a rubber substitute.

Other unsaturated hydrocarbons were used and elastic polymers (called *elastomers*) were obtained. An artificial rubber made from *butadiene* (which has a molecule like isoprene without the little one-carbon branch) has been used in Germany and the Soviet Union since the early 1930s, for instance. It goes under the trade name of *Buna.*

Organic compounds that are not hydrocarbons have also been built up into artificial rubbers. Most of them have their good points but none seem to have the all-round virtues of natural rubber.

Within the last year or so, finally, chemists have learned to duplicate rubber itself in the laboratory. It was a question of finding just the proper catalyst and this they have now done. (Brand-new useful polymers of all sorts may lie just ahead as the result of these new catalysts.)

Rubber, a hydrocarbon, will dissolve in kerosene and in similar liquids. Such solutions are the *rubber cements.*

Three Bonds Are Still Livelier

Two carbon atoms can be held together by three bonds, a so-called *triple bond.* If this happens, each carbon atom has only one bond left free for attachment to another atom. An example of a compound with a molecule that contains such an arrangement is this:

$$H-C\equiv C-H$$

Figure 7—Acetylene

This compound is called *acetylene.*[1]

Carbon chains with triple bonds are like carbon chains with double bonds, only more so. Acetylene has fewer hydrogen atoms than ethylene (only two of them) and is therefore more unsaturated.

The triple bond is under even more strain than the double bond. (A "quadruple bond," by the way, is completely impossible.) It takes considerable energy to hold the triple bond in place. When acetylene burns, the triple

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[1] Here is an example of a chemical name not based on the Geneva nomenclature. The Geneva congress agreed to have triple-bond hydrocarbons named with a "yne" ending. In most cases, this is done. Acetylene should be called "ethyne" but it isn't and it won't be and that's all there is to it.

bond is broken and all that energy is changed into heat. As a result, the flame of burning acetylene is hotter than the flame of burning ethane or burning ethylene.

This heat is made use of in the *oxyacetylene torch.* This device brings a stream of oxygen and one of acetylene together. When the mixture is set on fire, the resulting flame is used for welding and cutting metals. Such a torch will melt its way through steel as though it were so much butter.

The strain built up by triple bonds has another result. Compounds containing triple bonds will sometimes explode. Their molecules break at the triple bond and become simpler molecules without triple bonds. The energy released by the elimination of the triple bond causes the force of the explosion.

This is particularly true if the carbon of the triple bond is attached to a copper or silver atom rather than to a hydrogen atom. Such *metal acetylides* are more dangerous than explosives like methane. Methane will explode only if mixed with air or oxygen. Metal acetylides don't need the outside help of any other molecules. Even after mixture with air, methane won't explode unless it is heated. Metal acetylides don't need heat. Sometimes just the shock of a light blow is sufficient.

One metal acetylide that is not explosive is *calcium carbide.* Its molecule contains two carbon atoms held together by a triple bond and both connected by the spare bond to a single calcium atom. (Calcium is a silvery metal. Its atoms are found in limestone and in bones. Substances containing calcium atoms in their molecules are quite common in the soil about us.)

If calcium carbide makes contact with water, the water molecules combine with the calcium atom and leave hydrogen atoms in its place. In this way, acetylene is formed. Back in the days when bicycles were very popular, and before battery-powered electric lights came into popular use, canisters of calcium carbide were sometimes used for lighting purposes. Water was allowed to drip into the canister slowly and the acetylene which was produced fed a flame that acted as a bicycle headlight. It was also used in the headlights of the very early automobiles.

In building up complicated molecules for our uses, the chemist likes to begin with simple compounds that are as cheap and common as possbile. Acetylene is one of the most important of the chemist's starting materials. The fact that the triple bond is extra lively and allows the acetylene to react with a number of chemicals makes it all the more useful.