Chapter 1

Chains, Long and Short

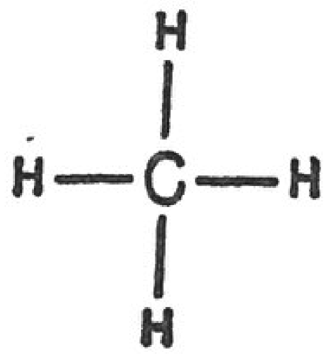
The Simplest Organic Compound

IT IS A good idea, I think, to start with something simple. There are compounds with molecules made up of only carbon atoms and hydrogen atoms. These are the two kinds of atoms that occur most frequently in organic compounds, so they're the logical ones to start with. Compounds made up of carbon atoms and hydrogen atoms only are called *hydrocarbons.*

The simplest hydrocarbon, naturally, is one with a molecule containing only a single carbon atom. A carbon atom is capable of hooking on to four other atoms. A hydrogen atom is capable of hooking on to only one other atom.

This means that one carbon atom can be connected with four hydrogen atoms. So we write a C for carbon, surround it by four H's for hydrogen, and connect each H to the C by little lines called *bonds.* thus:

Figure 1—Methane



This compound is *methane,* and it is the simplest organic molecule of all.

Methane is a gas, colorless and odorless, like the air about us. Like all gases, it can be turned into a liquid if it is made cold enough. However, the temperature required to liquefy methane can be reached only in specially equipped laboratories. Even the coldest winters in Antarctica wouldn't be nearly cold enough.

An important characteristic (or *property*) of methane is that it will burn. That is, when methane is heated in air, the carbon and hydrogen atoms in the molecule break away from one another and combine with the oxygen present in the air. Each atom of carbon combines with two atoms of oxygen to form a molecule of carbon dioxide. Each pair of hydrogen atoms combines with one oxygen atom to form a molecule of water. In the process, light is produced and heat is given off.

This is a very useful property. Methane can be led through pipes into houses (together with other inflammable gases, such as hydrogen or carbon monoxide). By setting fire to this gas in ranges and furnaces we can cook food and heat houses.

In general, almost any organic compound, if heated enough, will burn. The majority of inorganic compounds, on the other hand, will not burn.

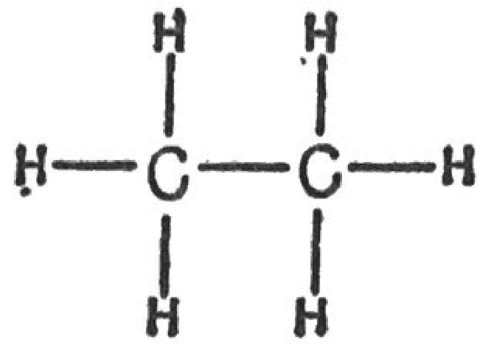
Methane sometimes forms when once-living matter decays and decomposes under water or underground. In marshy areas, the decay of tree stumps and of other vegetable matter under water produces bubbles of gas that consist mostly of methane. For this reason, methane is sometimes called *marsh gas*.

Methane also occurs in tiny pockets in coal beds. Coal (which is made up mostly of carbon atoms) is formed from once-living matter that has slowly decayed underground. Small quantities of methane are also formed and are trapped in the coal. As the miners break up the seams of coal, enough methane can seep into the air of the mines to become dangerous. If enough methane mixes with the air, the smallest spark may cause its molecules to combine with the oxygen of the air so suddenly that an explosion results. Miners call methane, *fire-damp* ("damp" being an old-fashioned word for "gas") and must guard against its presence.

Building up the Chains

Suppose, now, we place a bond between two carbon atoms. Each carbon atom has thus used up one bond but still has the ability to form bonds with three other atoms. If all those other atoms are hydrogen, this is what the molecule will look like:

Figure 2—Ethane



Molecules like these make up the compound *ethane.* Ethane is a gas with properties similar to those of methane.

You can build the chain further. Three carbons bonded together and surrounded by hydrogens make up the molecule of *propane.* Four carbons and the necessary hydrogen make up *butane.*

Propane and butane are also gases. However, as the molecules get larger, it becomes easier to liquefy them. (This is a general rule among organic compounds.) An Antarctic winter is sufficient to liquefy propane and even a New York winter will liquefy butane.

Propane and butane will burn like methane. Quantities of these more complicated gases can be forced, under pressure into metal cylinders. These cylinders can be attached to ranges and the gas allowed to feed slowly into the jets and burn. This can be very handy in isolated regions where cooking-gas is not supplied through pipes by large gas companies.

We needn't stop at butane. Five carbons can be bound together; or six, or seven, or eight, or, for that matter, even seventy or ninety. Chemists do not try to think up different names for each new string of carbon atoms. Once they get to hydrocarbons with more than four carbons in the molecule, they generally use numbers. There is one catch, alas. They use Greek numbers.

For instance, a hydrocarbon with five carbons is called *pentane.* The prefix, "pent," comes from a Greek word meaning "five." In the same way, the next three hydrocarbons are called *hexane, heptane,* and *octane.* "Hex," "hept" and "oct" are from Greek words meaning "six," "seven," and "eight."

The word "octane" may ring a bell with you. Perhaps you have heard of the word in connection with *gasoline*. If you have, it is not surprising. Gasoline is a mixture of various hydrocarbon molecules such as heptane and octane.

But gasoline, as you know, is a liquid. Remember, that as the hydrocarbon molecule becomes larger, it also becomes easier to liquefy. The hydrocarbon molecules in gasoline are so large they need not be cooled at all to form a liquid. They are liquid at ordinary temperatures.

The mixture of liquid hydrocarbons in gasoline is *volatile.* That is, the liquids tend to vaporize easily. It is those vapors you smell when a gas-station attendant fills an automobile's gas-tank. (Incidentally, gasoline is often spoken of as simply "gas." This is not a good nickname, because the word "gas" means any vapor.) Gasoline vapors, if mixed with air, will explode just as methane will. It is for that reason that gasoline is a fire hazard.

Inside the automobile motor, the explosion of gasoline vapors is made useful. The vapors are mixed with air in the carburetor and the mixture is fed into the cylinders. There it is exploded by means of an electric spark from the spark-plug. These explosions drive the pistons which in turn supply the force that moves the car.

Cigarette-lighter fluid, by the way, consists of a mixture of liquid hydrocarbons very similar to that in gasoline.

Branches in the Chain

Some kinds of gasolines are more expensive than others. We must return to our structural formulas to understand why.

When you imagine a hydrocarbon with seven or eight carbon atoms, it is a pretty safe bet that you think of the carbon atoms strung out in a straight line. It doesn't have to be that way, though. You can put the carbon atoms together in just about any way you wish.

Take butane, the four-carbon hydrocarbon, as an example. It can be put together in two different ways, as follows:

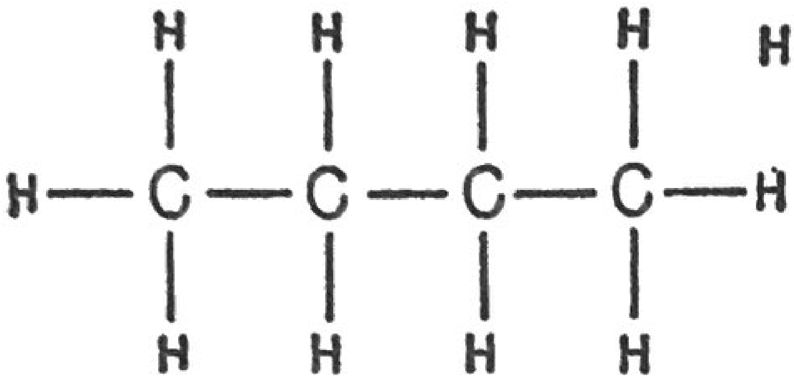


Figure 3—Normal Butane

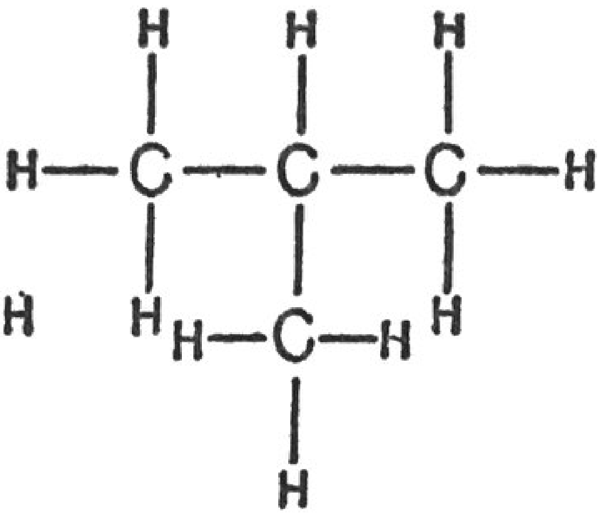


Figure 4—Isobutane

If you count the atoms in each molecule, you'll find that each has four carbon atoms and ten hydrogen atoms. The two molecules have somewhat different properties despite this, because the atoms are arranged differently. Molecules which have the same number and kinds of atoms, but have them arranged differently, are called *isomers.* A molecule with four carbon atoms in a straight line (a straight-chain compound) is called *normal butane.* One with four carbons not in a straight line (a branched-chain compound) is called *isobutane.*[1]

For a four-carbon compound, only two arrangements of the carbon atoms are possible. With more carbon atoms in the molecule, the number of possible arrangements increases rapidly. After all, you can branch the chain at different points; you can have more than one branch; you can have branches of different lengths; you can have branches on the branches.

Octane, with eight carbon atoms, shows eighteen possible arrangements of the carbon atoms of the chain. That means that eighteen different octanes, each with eight carbon atoms and eighteen hydrogen atoms in the molecule can exist. Each one of the eighteen octanes behaves a little differently.

[1] Isomers often differ only slightly in their properties. Isobutane is a little harder to liquefy than normal butane, for instance, but not much. You may wonder if small differences are worth worrying about. The answer is, yes—and sometimes the differences aren't so small. There are many compounds that are vital to the body's workings, but become useless to it if the arrangement of atoms in the molecule is ever so slightly altered.

Each has to be studied separately if it is to be understood thoroughly.[2]

The various hydrocarbons in gasoline all burn if heated. All will explode if their vapor is mixed with air and a spark is set to the mixture. However, they don't all burn in quite the same way. Here is where isomer differences become quite important. Straight-chain hydrocarbons burn a little faster than branched-chain hydrocarbons do.

If the vapor of *normal heptane* (with seven carbon atoms in a straight line) is set burning within an automobile cylinder, explosion is too rapid. There is the sound of a "pop" inside the cylinder. The piston is jarred and its in-and-out rhythm is upset. This is called *engine knock.* It represents wasted power and possible engine damage.

Other hydrocarbons behave better. In particular, there is an isomer of octane with three small branches in its carbon chain, that behaves very well. This isomer is called *isooctane.* When the spark sets off a mixture of isooctane and air, the explosion takes place more slowly than in the case of heptane. First the molecules of isooctane near the spark explode, then those a little further away, then those still further away and so on. There is no "pop" and no jar. The piston is allowed a full, rhythmic stroke and power is delivered efficiently.

A particular type of gasoline is given an *octane rating,* depending on the amount of engine knock that is produced. Normal heptane by itself would have a zero-octane rating. Isooctane would have a hundred-octane rating. By comparing the way in which a particular gasoline burns with the way different mixtures of normal heptane and isooctane burn, the octane rating of that gasoline can be determined. The higher the octane rating of a gasoline, the more efficient it is, and the more expensive.

Chemists have found ways of decreasing knock by adding

[2] It has been calculated that a forty-carbon compound would show more than sixty trillion possible arrangements. Each of them would be a different compound. Naturally, chemists don't bother about all those different isomers or try to locate each one. There are more important problems to tackle. Still, it shows why there are so many different organic compounds.

certain anti-knock compounds to gasoline. The best known of these is a compound which contains a lead atom in its molecule and which is known as *tetraethyl lead*. Gasoline needs less than a tenth of a percent of it for good results. Such gasoline is known as ethyl gasoline or leaded gasoline. Leaded gasoline is deliberately colored because its lead content makes is more poisonous than ordinary gasoline, and it must be handled more carefully.

The octane rating of gasoline for sale to the public has improved continuously. In 1937, most makes of gasoline had octane ratings of 73 to 80. Now, premium gasolines have octane ratings of 95 or more. In fact, special gasolines with octane ratings higher than 100 have been prepared, particularly for use in aircraft. These "super-premium" gasolines are now in use for the specially powerful engines in late model cars.

Where Hydrocarbons Come From

There is a kind of oil that exists underground in some regions of the earth. Until about a hundred years ago, it was nothing more than a nuisance in those places where it happened to seep to the surface. Now it is one of the most precious things on earth and wars are fought over it. The oil is called *petroleum*, from two Latin words meaning "rock oil."

Petroleum contains hundreds of different hydrocarbons. If it is to be useful, it must be refined. That is, it must be separated into different groups of hydrocarbons, each with its own special use. For instance, gasoline would be no good if it contained molecules with a fifteen-carbon chain. Such molecules would not evaporate easily and they would burn far too slowly. They would just choke the engine with gummy soot. So gasoline must consist of only a fraction of the whole petroleum mixture.[3]

The chief trick in petroleum refining depends on the fact that different hydrocarbons vaporize differently. The longer the carbon chain of a molecule, the harder it is to vaporize;

[3] The English refer to gasoline as *petrol*, which is, of course, short for petroleum. This is a poor name because gasoline and petroleum are not the same thing, but it is no poorer than our nickname "gas" which is short for gasoline.

more heat is required to turn it completely to vapor. A hydrocarbon with a long carbon chain, in other words, has a higher *boiling point* than one with a short carbon chain.

If just a little heat is applied to petroleum, the vapors of those molecules with very short carbon chains are produced. These vapors can be drawn off and allowed to cool into a liquid again. If more heat is applied, vapors with longer chains come off; the more heat, the longer the chain that is vaporized. The vapors are drawn off as they form and are then cooled until they liquefy. Each liquid is a different fraction of the original petroleum. This process is known as *fractional distillation.*[4]

The first fraction of petroleum to boil off is made up chiefly of pentanes and hexanes and is called *petroleum ether.* After that comes gasoline, which I've just been talking about. The next fraction is *kerosene.*

Fifty years ago or more, kerosene was quite an important substance because it was used to light the houses at night. Even today, in country districts (or in a city, when a hurricane or some other disaster has knocked out the power lines) kerosene lamps may be used. Petroleum was once important chiefly for its kerosene content. With the development of the electric light, kerosene went out, and with the development of the automobile, gasoline came in.

Today kerosene is cheaper than gasoline and special engines have been designed which can get along on kerosene. The Diesel engine does this. It is used in trucks, buses, locomotives, and ships. Efforts are being made these days to adapt such engines for use in ordinary automobiles, so kerosene may make a comeback yet.

The fraction after kerosene is *fuel oil.* This is being used more and more commonly to heat houses. As the hydrocarbon molecules get longer, less vapor is formed, and there is less danger of explosion. Fuel oil is much safer than gaso-

[4] Petroleum often contains hydrocarbons with very short chains that are gases to begin with. These are dissolved in the liquid portion of the oil, but when petroleum is drawn out of the earth, the gases come bubbling out. This is called *natural gas* and is made up mostly of methane. As I said earlier, this can be used in cooking food and in heating houses.

line to handle; yet it will burn easily enough in oil furnaces.

Nowadays, in refining petroleum, chemists are not content with its natural gasoline content. The petroleum is subjected to special processes designed to break up the long carbon-chain molecules into shorter pieces. In this way, molecules which would ordinarily be in the kerosene or fuel oil fractions end up in gasoline. This process is known as *cracking*. In one way or another, about half of each gallon of petroleum can be made into gasoline.

It is also possible to prepare gasoline from coal. Some grades of coal contain long-chain hydrocarbons which can be separated out. Their molecules can then be cracked down to the proper length. Even the solid coal itself, which is mostly carbon atoms, can be treated with hydrogen gas so as to form some gasoline.

More Fractions

It may seem that hydrocarbons are useful only because they will burn or explode to give heat, light, and power. This is not so. Hydrocarbons with molecules even larger than those in fuel oil burn with such difficulty that other uses become more important.

For instance, petroleum fractions with molecules larger than those in fuel oil are useful in cutting down friction. A film of such *lubricating oil,* placed between two moving surfaces, allows those surfaces to move past each other smoothly on a slippery cushion of hydrocarbon. A specially refined type of lubricating oil is *mineral oil*. This is sometimes taken internally so that a lubricating film may be formed on the walls of the intestines to ease the discomforts of constipation. Solids of various sort can be added to lubricating oil to thicken it to a blackish, semi-solid *lubricating grease*.

Petroleum fractions with molecules still more complicated than those of lubricating oils are no longer liquid at ordinary temperatures. They are solid or semi-solid. An example is *petrolatum* or *petroleum jelly*[5] which is used in ointments

[5] This may be more familiar to you under the name of *Vaseline*. The name, Vaseline, is an example of a *trade name*. This is a name given to a particular product by the company that manu-

or directly on the human skin for its softening and smoothing action.

The nature of the final fraction of petroleum depends on the particular oilfield from which the petroleum came. Sometimes, a remainder, made up mostly of carbon atoms, is left behind after refining. This is *petroleum coke.* Other times, a soft solid made up of very large hydrocarbon molecules (plus other types of molecules as well) is left behind. This is *petroleum asphalt.*

Asphalt is often used to surface roads. It was used for this purpose in ancient Babylon in 600 B.C. The first use in the United States was in 1870 in Newark, New Jersey. Now 800,000,000 miles of American streets and highways are so paved.

There is a famous asphalt "lake" in the Caribbean island of Trinidad, covering 115 acres, at least 285 feet deep in spots, and containing perhaps as much as 15 million tons of asphalt. This was probably once an ordinary petroleum deposit which was exposed to the open air through some unusual set of geological processes. All the liquid portions have been lost with the ages and only the asphalt is left.

Large hydrocarbon molecules, containing eighteen or more carbon atoms, can be separated from the solid fractions of petroleum. These are white solids, slippery to the touch, and easily melted. A mixture of these is called *paraffin wax.* Paraffin wax is a mind-its-own-business kind of substance. It is affected by very few chemicals and it bothers very few. It is *chemically inert.* The very word "paraffin" comes from two Latin words which can be roughly translated as "slight tendency to mix."

This standoffishness is useful. Paper coated with wax

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factures it. Such a name is protected by law so that only one company may use it. Other companies, that may be marketing the identical product, must use a different name. Sometimes such a trade name becomes so well known that even chemists use it instead of the official chemical name of the product. Trade names should always be capitalized. Lately, it is even becoming customary to follow trade names with a special symbol ®, which means Registered.

(*wax-paper*) is often used as a wrapping for various kinds of food. Wax-paper is waterproof. It can't be penetrated by water; and water won't even wet it. If a drop of water touches it, it stays on the surface and can be easily wiped off. The containers in which milk is often sold are made of waxed cardboard.

Parraffin wax is used in the home preparation of fruit preserves or jellies. Melted paraffin is poured over the surface of the jelly in the jar. When it cools and hardens, it acts as a seal to keep out air and prevent molding and crystallization. Candles are often made of paraffin wax. Melted wax is allowed to solidify in a long column around a cotton cord called a wick. The end of the wick is then set on fire. The heat of the burning wick melts some of the wax near it and then cracks the long carbon-chains of the molecules in the melted wax into shorter chains. These shorter-chain molecules vaporize and burn. The heat of this burning melts more of the wax and supplies more vapor. In this way, little by little, the whole candle burns.

Oil and Water

I mentioned a while ago that paraffin wax is waterproof. Let's look into that a little bit.

As you know, substances like salt or sugar will *dissolve* and appear to vanish if placed in water. What happens is that the solid salt or sugar breaks up into single molecules (or parts of molecules) which then mix completely with the water. Salt and sugar are, for that reason, said to be *soluble* in water.

Hydrocarbons are *insoluble* in water. If gasoline and water are shaken together, for instance, and allowed to stand, they will separate again and form two layers. (The gasoline layer will be on top because, like all hydrocarbons and hydrocarbon mixtures, it is lighter than water.)

Water molecules and hydrocarbon molecules have different electrical properties. These properties depend upon the *electrons* in the various atoms that make up the molecule. Electrons are particles that are much smaller than atoms and occur within atoms. If the electrons are evenly distributed through the molecule, the electrical properties are like those in hydrocarbon. If they are unevenly distributed, the electrical properties are like those in water.

Substances with molecules that have electrical properties like those of water will dissolve in water, but not in hydrocarbon. Substances with molecules that have electrical properties like those of hydrocarbon will dissolve in hydrocarbon, but not in water. Like clings to like in this particular case. Opposites don't attract.

Salt and sugar have electrical properties like water. They dissolve in water.

The fats and oils we find in food are among the compounds that have molecules with the electrical properties of hydrocarbons. They dissolve in hydrocarbons.

All too frequently, clothing, tablecloths, or other fabrics are accidentally spotted by grease. Dabbing at the spots with water will have no effect. Hydrocarbon or some similar compound must be used. Moreover, the hydrocarbon to be used must not itself remain behind as a spot (and a smelly one, to boot). The trick then is to use a petroleum fraction with molecules made up of the shortest possible carbon chains. Then, when the spot is gone, the hydrocarbon molecules still in the fabric quickly turn to vapor and blow away, leaving nothing behind.

The liquid petroleum fraction with the smallest molecules is, as I mentioned earlier, petroleum ether. (This may be more familiar to you as "benzine." That, however, is an undesirable name. There is another, and much more important, substance called "benzene" and the two should not be confused.) This substance is quite commonly used in the home as a spot-remover.

Since this method of cleaning does not involve water, petroleum ether is an example of a *dry cleaner*. The main danger involved in its use is that it is even more inflammable than gasoline. There is always the risk of fire and explosion. When you use a petroleum ether dry cleaner, make sure there are no gas flames about—and don't smoke!