

Lecture 1A • 09/26/11

What is organic chemistry? Typical question that a textbook starts out with. A lot of instructors start with it. I thought ok, I'll start with it as well. Just so we have an idea what it is we are going to be covering these three quarters of o-chem. Anybody have an idea, an answer? The study of carbon, essentially. Organic chemistry at one point was classified as the chemistry of things that were made by living objects. However, in the 1800s it was discovered that we could synthesize our own selves those very same compounds. And so the definition grew to include and incorporate nearly anything that is carbon-containing. So this is going to be the chemistry of carbon which, since we are carbon-based that is probably why we are so concerned about it. For organic chemistry, there's going to be several layers of topics that we are going to study. The first part of the quarter, you'll see that we are going to cover a lot of topics that we had in the Chem 1 sequence. In fact, much to everyone's joy I'm sure, we're going to go back and do a little bitty baby version of quantum, because the only way we can truly get at the structure of organic molecules is if we have at least a working understanding of what an orbital is, what an energy level is, we have to know how does bonding work, the distinction between the sigma and the pi bond for example. Makes a huge structural difference in the way that organic molecules tick. Once we spend some time studying first a little bit about atomic theory and then molecular theory, we're going to cover some of the big topics of general chemistry: kinetics, thermodynamics, and equilibrium. Because we have to be able to predict, is it likely that a reaction is going to happen. Is it going to release or require energy? Even if it releases energy, it doesn't mean the reaction is going to occur quickly, so that is why we need to know something about kinetics. Or, as many organic reactions are reversible reactions, that's why we need to know something about equilibrium. As we cover those topics, it is not going to be the same type of presentation as you got in general chemistry because you have already had general chemistry. So, I'm going to be used some organic examples to reteach these topics to the level that we need just for this course. We will then start branching out. And along the way, we'll start getting more into areas that we haven't studied back in general chemistry. So, you might have learned about stereoisomers, but we're going to learn a lot more about stereoisomers and other forms of isomers - molecules that are related molecules: same formula but different connectivity, different structure. Once we bring those principles under control, then we're really going to leap into organic chemistry. We'll start worrying about synthesis: how is it that we take one kind of molecule and transform it into another. What is its mechanism? What is the way that electrons flow during a chemical reactions. Do these reactions happen in one step or do they happen in multiple steps? Are there special conditions that they must be run other. Can they have water in them? Is it possible that multiple products can be made, which often will be the case. We'll learn how to predict what the most likely products are. This is for, again, transforming from one type of molecule into another. Then, once we learn how to do single transformations, we're going to put them together because the overall goal is to learn how to take a small set of common inexpensive starting materials and be able to join them together in some way to make complex molecules cause that's modern organic synthesis. So again, starting over with some review: atomic and molecular structure; going through the framework of chemistry: kinetics, thermodynamics, equilibrium. Getting into some more organic-related topics. From there, synthesis; the different aspects of synthesis; and then finally wrapping up with multi-step synthesis: how to do multiple reactions strung together.

With that overview, what I wanted to do today is to do some of the machinery of o-chem. How do we write molecules down? How do we show that a chemical reactions is going on? What are the general ideas as far as how these transformations occur. So, we're going to start, in fact, with line structures.

Now before I address the topic of line structures, one question that's the most commonly-asked question in the class: is it on the exam? The answer is: yes. If I write it down in here, or if I say it in class, it's on the exam. If it's something that's in the textbook but it's in one of those little info boxes that I don't even refer to it, then it may most likely not be on the exam. There will be a few times during the quarter where I will lecture to material that is not in the textbook: not very frequently, but it will happen on occasion. So, no matter what the circumstances, no matter what we're going over, you never actually need to ask the question "what's on the exam". Now, I know that's not very satisfying to some of you, so those of you that have not had me as an instructor before, the 3rd, 4th, 10th, 10000th time that you hear me say the same thing, that's a big hint that something related to that topic is going to show up on the exam. I will also be generating a list of topics each that I want to make sure that we get through. So, the topics today, in fact, are to write line structures, to review the principles of mechanism: how do we write down that a chemical reaction is going on; we're going to be covering functional groups: common characteristic patterns of atoms that, no matter what molecule they are on, tend to have the same kind of reactivity - that's what makes modern organic chemistry possible: that we don't, for each molecule, have a unique reaction. We have features on a molecule that we target. Then I want to go over these aspects of what synthesis is, and then touch briefly on stereochemistry - the fact that we can have mirror-image molecules that are identical except for the fact that they are mirror images. And there is something known as regiochemistry - that if you have a large molecule, that if you put an -OH group, an alcohol, over here, versus here, versus here, how can you accomplish putting it on different places on the molecule. Or, what are the consequences of it being on different places on the molecule.

So line structures. Organic molecules take a awful long time to write down on paper, if you try to do it the way that you might have done it in general chemistry. For example, if you have oleic acid - it's a common constituent of olive oil - oleo related to oil. It is an eighteen-carbon compound. And if that took a while to write, that does not even the whole main point, because, carbon normally is what is known as tetravalent - meaning it has four connections to it, either in terms of single bonds, double bonds, triple bonds. Or you can have unusual situations: reactive intermediates that maybe don't have that four number of connections. But, almost always, on carbon-based molecules, if you don't find carbons or other non-hydrogen atoms, if a carbon does not have four connections, you can almost almost always assume it will have enough hydrogens to bring that number up to four. That means for this molecule, I could spend another minute or two writing in all the different hydrogens that go on here. Incredibly time-wasting. In fact, I won't complete it, because I'll just show you the way that we normally do it, is like this. That is the entire structure. Organic chemists would see that and would know exactly how many hydrogens there are. This is what is known as a line structure.

So let me point out a few features of these line structures and the rules for generating line structures because this will be the only type of structure we operate in this quarter. There will be a few times it is better practice to go ahead and write the entire structure out. But 95-98% of the time we'll be writing these line structure. So let me address the two rules for writing line structures.

Each of these atomic labels – the same atomic labels you learned about back in Chem 1A – if you have carbon, you leave those labels out. If you have hydrogens attached to carbon, you leave those labels out as well. Everything else is left in place. So for line structures, carbon atom labels and atom labels for hydrogens connected to carbons are omitted. Now that means in reverse when you're reading these structures, you always presume that carbon is tetravalent. So if you look at something like the end of this molecule, where it's just a point, that point having one line back in the other directions means there is a single connection, a single bond. That means there's three other connections that should be there at that position but by convention are not being shown. So you would have to automatically know and assume therefore there are the three hydrogens there. So, when reading a line structure, a carbon is assumed to be tetravalent unless otherwise notated. As we get into this course, we will learn how to write the exceptions. And again, the way that we assume tetravalency is that for whatever's missing we assume that hydrogen's there.

Now we have some more details for me to fill in. A little more terminology. There is this term heteroatom. Hetero, a prefix meaning different, an atom is, of course, an atom. So a pure hydrocarbon is a molecule that only contains, as it sounds like, carbon and hydrogen. But there are a select number of elements that are commonly found in organic molecules: oxygen being one of the main ones; sulfur; phosphorus; nitrogen; some of the halogens, chlorine, bromine, principally those two. So, atoms that are not carbon or hydrogen, those are heteroatoms, those that are different atoms.

So one statement I could make about writing line structures is that heteroatoms are always explicitly written. If you look again, even though I didn't complete the oleic acid I was starting to write out you can see over on the right-hand side that we have a carbon attached to an oxygen, another oxygen, and then a hydrogen. Notice that the two oxygens are both in the final line structure, and notice also that there's this hydrogen that, since it was attached to oxygen, we don't make the same assumptions that we would for carbon. So anytime that we have something attached not to carbon, usually you go ahead and write it in. So, heteroatoms, and, to be explicit about it, hydrogens attached to heteroatoms are always written in line structures.

The last detail about this structure I wrote: might be hard to see, but there are these little dots floating around the oxygen. What are those? Lone electrons; lone pairs. Some textbooks will not always show lone pairs. Because once you get some experience reading organic structures, you can know just by looking at a structure, oh yeah, it's got one lone pair, oh yeah, it's got two lone pairs. Because you're beginning students, I don't want you to make that assumption. So, all charges and lone electrons must always, always, always, always, without exception, be shown.

So, again, to review, when writing a line structure, if it's a carbon, we generally leave it out. I'll show you momentarily a couple of situations in which you don't leave it out. And, it's not a hard rule. If you want to show and highlight that you have a particular carbon that's doing something, then, it's ok for you to write it in. The general tendency is: leave the carbons out. Same thing with the hydrogens attached to carbons: we normally leave those out. Which, again, when you're going in the reverse direction, the way you read those structures is to assume that you're going to have four connections on those carbons. Heteroatoms, which are things besides carbon and hydrogen, are always left in, as well as hydrogens attached to those heteroatoms. And then any charges and lone electrons you must always show.

So let me put up an example molecule or two example molecules. I'd like you to convert a "regular" structure that I'm about to write into a line structure, and I'd like you to convert the line structure back into a "regular" structure. So this is the structure I'd like you convert into a line structure, and then now convert this line structure into "regular" structure.

One warning about the exams. It's not always going to be that the information on the exam is difficult. It is, though, that I'm going to expect a certain level of proficiency. So, for example, at some point, once you get used to it, and I realize that physically it takes a while to write these answers down, the first molecule you should be able to look at and, as you are looking at it, you should be immediately able to start drawing. So the first molecule should have needed no more than about 5 or 10 seconds. If you didn't do that now, that's fine, you're learning the system, but by the time we get to our first quiz, it should only take you those few seconds to do it. So it's not just that you know something, it's have you practiced it.

Let's go ahead and write down these answers. The main ring of this first molecule: does anyone recognize what it looks like? Benzene, that's right. Following the rules, the six carbons, we would leave them out, so we would just have a hexagon. The double bonds, we do write to show the multiple connections. So there's our benzene unit. Can we just use a circle? It is commonly encountered that you will write benzene with just a circle. I strongly recommend against it. The reason that the circle there is actually a good reason, because there are no double and single bonds in that portion of the molecule. That is a resonance structure, which there is no such thing as a resonance structure. A resonance structure means that there is an inadequacy in this writing system. These line structure that are based on Lewis dot structures are based on a classical picture of bonding in which a bond only occurs between two atoms, which is not always the case. There is, in fact, a bond orbital that goes all the way around benzene, which means in real life benzene has six bonds – the ones between carbons – that are between a single and double bond in length. And that's why the circle is written. However, the one usefulness about writing the double bonds that aren't really there in is you can better count electrons. So at this stage, don't use the little circles; do use the bonds so you can count electrons.

Now, the five hydrogens on the outside of that benzene ring you would not include, because they are directly connected to carbon. But we do have an oxygen. Oxygen is a heteroatom, so we write it in, along with the hydrogen that is attached to that heteroatom. Does it matter if the bonds for the double bonds are written on the inside or the outside [of the ring]? It's purely aesthetics, different people have different ways they like to do it, so for my class, any way you would like to do it is fine. So that H on the O, it's ok if you just write OH? That's a condensed structure; it would be understood that there is a single bond there.

In fact, that leads me into another topic we were going to get to, which I might as well address it here. Lots and lots and lots of molecules have these OH groups. Realize that this line structure system is based on Lewis structures which is based on covalent bonding. So when you see OH in o-chem, it does not mean hydroxide; most of the time it does not mean hydroxide. It is a carbon that's covalently bound to an oxygen, which means it will not dissociate. You will not generate a basic solution from this molecule. In fact, this molecule is very vaguely acidic. So just because you see OH, erase from your mind that it means hydroxide. Instead, we call that an alcohol. There is consumable alcohol, which is a kind of alcohol – a very popular kind of alcohol – but it is just one of the many molecules that has this particular functional group.

No matter what molecule it is found on, this characteristic pattern of atoms has predictable, repeatable behavior. So there in an alcohol in this first molecule. Let me back up to the first molecule because this is another extraordinarily common functional group – a carboxylic acid. So that the carbon that's part of the chain – that carbon is part of that functional group – and then the O, O, H.

So since that's a resonance structure you can put the OH anywhere? On this particular molecule, yes, because there is only one substituent. So, substitute, to replace something. Substituent, that which does the substituting. What it means is that I could take benzene and substitute an -OH group for one of the hydrogens, that's how this particular molecule is produced, which has the name phenol, which is one of the active ingredients of chloroseptic. A substituent could be more than just a small group. It could be several carbons bound together.

A substituent is a group of atoms that takes the place (substitutes) of, generally, hydrogen.

So yes, since there is only one substituent on benzene, it does not matter where you wrote it. But if we had two of them, you would have to keep that relative distance between the two the same.

Back to the other line structure problem. How many carbons total are in this compound? 6? 5? How many people think 5? How many people think 6? How many people are too bored or tired to vote? It's the first day, you know. The part that often confuses people is this break that occurs. In fact, you'll see some people who don't even write the little space there. That's a triple bond, and a classical tripple bond only occurs between two atoms. So this is one connection point – one carbon – and this is another connection point – which means this corner has to be yet another carbon. So there are 3 carbons there, for 6 six total. Again, it's the triple bond that often throws people off.

Let's write in that carbon framework. There's the six carbons. Now let's go ahead and write the heteroatoms in, since we know we always have to write those in. Then after that we'll worry about the hydrogens involved. So at the fourth carbon from the left, we have a chlorine, the next carbon over there's a nitrogen, and it's fine if you wrote your bonds out or if you wrote a condensed structure. But now let's fill in those other hydrogens. Starting from the very left how many hydrogens does the first carbon need? 1, since it already has a triple bond, so three plus one equals four. The second carbon over – how many hydrogens do we need on it? None, because we already have a triple bond and a single bond, so we don't put anything on there. Next position? 2. Next one? 1. Next one, zero – a single bond to carbon, a single bond to nitrogen, and a double bond, that's four connections, so nothing needed there. And then the end of the molecule? 2.

Nomenclature – the naming of molecules.

Imagine a simple molecule like this: four carbons and a chlorine. There's another molecule that you could have that also has four carbons and a chlorine. In fact, there's a couple of other molecules. So, there are names that we have to be able to distinguish these from one another. Just to show you a little about the naming system today.

There are common names for some molecules – historical names, names that don't have a system to them. And then there's a systematic nomenclature. Almost universally we follow the International Union of Pure and Applied Chemistry (IUPAC) rules. So, some carbon compounds have regular-sounding names like pentane, hexane, heptane, octane – which, if you remember those prefixes, are 5, 6, 7, and 8 carbons. That's what the numbers mean in these names. But some other smaller molecules have common names. You've probably heard of propane before, that you might use in a grill or something like that. Propane is a three-carbon molecule. Butane – in butane lighters – that's a four-carbon molecule. These first two molecules are called forms of butane, but they have a substituent on them that we need to name as well, and it matters whether that substituent is on the end of the molecule or somewhere in the interior.

We will be learning about a system in which we use location numbers to establish the position of substituents. In this simple case, whichever way of numbering the compound that gives you the lowest numbers, is the way that we number it. So, chlorine being on the right-hand side, we give the first carbon – not the chlorine – number one. In the second molecule, because chlorine is closer to right side, that's why we start numbering it here. The third molecule, we'll talk about later how we properly name it. To show where that substituent is, we have a prefix that shows there's a chlorine there. Then we tack on the carbon backbone name at the end. So that molecule is called 1-chlorobutane. That distinguishes it from 2-chlorobutane.

We are going to be jumping from section to section in the textbook. That's partly because of the way our curriculum for the course is designed. It doesn't 100% match the chapter order in the text. So by necessity I've got to go a little out of order. Then there's also the way that I've been teaching o-chem the last few years. I've got an order I like to present things in and that I feel is easier to learn that way. Again, that doesn't quite match 100% to the textbook. Don't be scared that we're only doing a couple of these sections then a few over here then a few over here. I'll make sure to very clearly indicate what's going on in lecture.

So the 1- and 2- show you where something is located. Chloro- as you probably figured out refers to the chlorine. Then butane, that but- part of it is a common name indicating four carbons.

Mechanism

Mechanism is one of the reasons we have such a highly-developed o-chem synthesis, because instead of just the old day of – oh! the molecule reacted this way when we put this reagent in and memorized that. You memorized that it does this thing with this molecule and memorized that it does this thing with that compound. We now have the ability to figure out what physically is going on in a chemical reaction. So instead of just learning reagents and how they pair up with molecules, we learn what those reagents do in a step-by-step process. That step-by-step process is called a mechanism. A step-by-step flow of electrons in a chemical reaction. The abbreviation "rxn" is an extremely common shorthand for "reaction".

I'll show you a very simple reaction mechanism: an acid-base neutralization. So let's take that molecule phenol that we had earlier and let's say that we reacted with sodium hydroxide. Notice the way I wrote hydroxide. I've got my minus sign in a little circle. That's done because an older way of writing lone pairs was just to write a line. And so to distinguish a line meaning a lone pair versus a line meaning a negative charge, way back when I learned chemistry I was told to put circles around my charges. It's actually a common convention.

Phenol has a pKa of 10. What does a pKa of 10 signify? pKa is the negative log(10) of Ka which is the equilibrium constant for the auto-ionization of this molecule. So in other words, if you just put it in a solution, will the proton come off; that's what Ka tells you. Big Ka means small pKa, cause it's a negative log. So a pKa of 10 is actually a pretty large number. It means a Ka that's ten to the negative 10, which means this thing doesn't want to dissociate. If it doesn't want to dissociate, which means it doesn't want to give off its hydrogen, then we say it is a what?

Not a base, because the lack of a hydrogen coming off does not mean it wants to grab hydrogen. So it means it's just not very acidic. It's a weak acid.

So we have a weak acid – phenol – and a relatively strong base – hydroxide. I say relatively because in organic land hydroxide can actually be a very weak base. Organic molecules, if you rip their protons off of them, can be so basic that they'll ignite in open atmosphere because they so desperately want to grab protons from anything including the surrounding air. Long story made short, an acid-base reaction is going to happen.

The hydroxide is going to get the hydrogen, and then the hydrogen can only have one bond at a time (normally), so it's going to lose the bond that it has with phenol. This is the way that we show this. In any mechanistic arrow, here where the start of the arrow is is where electrons come from. The other end, the point, is where the electrons go to. The tail of the arrow, the base of the arrow, is where the electrons come from, and the head of the arrow, the point of the arrow, is where the electrons go to. It is not which way atoms move. Mechanism arrows always show the flow of electrons, not atoms.

There may be cases where the molecule moves the same way as the electron. For example, you could argue that yes, that hydroxide is going to reach out and grab that hydrogen. But the arrow is not showing that. It's showing that the electrons are reacting with the hydrogen. So that's a bond-forming event, because a lone pair is attacking something and making a new bond.

Similarly, we could have a bond-breaking event. Heterogenesis and heterolysis – the fact that we are generating a bond by a lone pair of electrons, two electrons moving to make that bond. And when that -OH bond breaks, it only breaks one way, which means the hydrogen, if it was by itself, would be positively charged. The oxygen would be negatively charged. That is two contrasting charges which is why we call it heterolysis – uneven breaking. The arrowhead itself means that an electron pair moves. To show you what the other arrow would look like. If you were to write only a hook, a half of a head, then that is showing that a single electron moves.

So what's the end result? Well, the oxygen-hydrogen bond broke. There were two lone pairs on oxygen to start with, but because the bond broke, it leaves a third lone pair, which means you're now going to have a negative charge. You're going to generate the ion phenoxide, -oxide indicating something that is charged, phen- coming from phenol. We'll also have water as our other product.

Synthesis

One of the most common types of problems is something like this, where you start off with something like an alcohol that's one type of functional group. You react it with some reagent that has some kind of predictable reactivity with alcohols. If you knew this reagent, you would know that, in the place of an -OH group, at the end of the chemical reaction, you're going to have a bromine instead. I'm going to write the mechanism to show you what a mechanism looks like.

If you look at the structure of PBr_3 , it's an electrophile, it's electron poor. In fact, if you look at it, it does not have a complete octet, which means it's going to be fairly reactive. What can happen, in fact, is that the oxygen from the alcohol can provide some electron density to that phosphorous. If it does so, you first temporarily have a positive charge on that oxygen because you made a new bond. At the same time that's happening, a bromine gets kicked off. Sometimes only one arrow might be in a step, then another one in a step after that, then another one, then another one. So you have what is called a stepwise mechanism. Here, we have two arrows at the same time; that's what's known as a concerted mechanism. Think of the word concert. After that occurs, this intermediate is acidic, so a hydrogen drops off. Notice the arrow does not go to hydrogen, because the arrow shows where the electrons go, not where the hydrogen goes. Then that bromine that got kicked off earlier, which is now bromide, the ion, comes back later and substitutes.

In this one reaction, we have the substrate, the starting molecule. We have certain reagents that are used. Then we have the product. We're going to start learning: what do all of these different reagents do to alcohols? What is the mechanism? If I gave you an alcohol and a reagent, can you predict its product? If I gave you a product and I show you the starting material, the substrate, can you figure out the appropriate reagent that's going to go there?

Rules for writing line structures

- Atom labels for carbons and atom labels for hydrogens attached to carbons are omitted.
- When reading a line structure, carbon is assumed to be tetravalent (unless otherwise notated), meaning it has a total of four bonds. If fewer than four bonds are explicitly shown, the "missing" bonds are assumed to be towards hydrogens.

hydrocarbon – a compound that contains only carbon and hydrogen.

heteroatoms – "different" atoms – atoms other than carbon or hydrogen (such as O, N, P, S, Cl)

- In line structures, heteroatoms and hydrogens attached to heteroatoms are always explicitly shown.
- Lone electrons and charges should always be explicitly shown.

functional group – a characteristic pattern of atoms that has predictable reactivity regardless of the molecule it is found on.

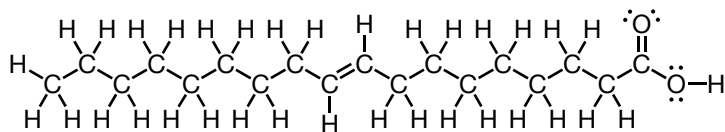
Nomenclature – the naming of molecules

substituent – a group of atoms that takes the place of hydrogen on a larger molecule

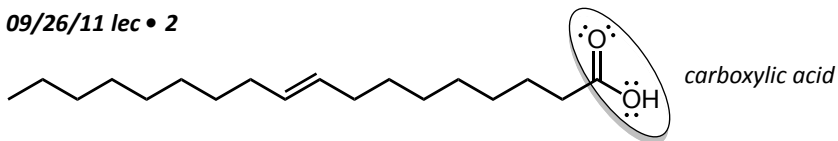
Mechanism - the step-by-step flow electrons during a chemical reaction (rxn)

Structures

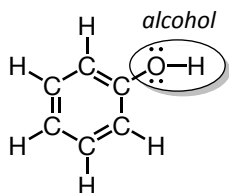
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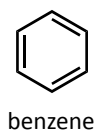
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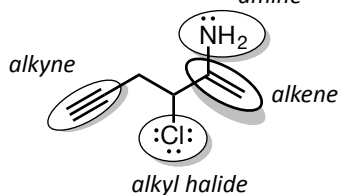
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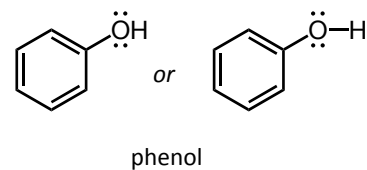
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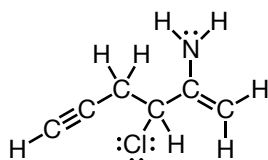
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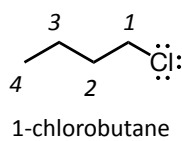
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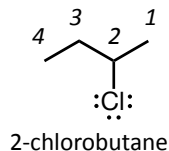
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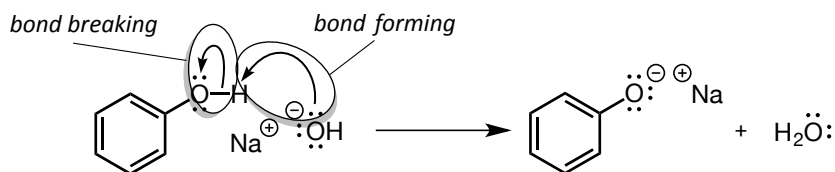
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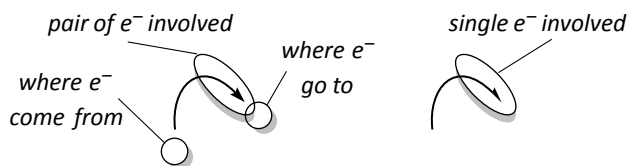
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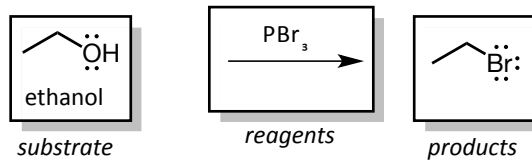
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