

# Organic reactions

## Connections

### ➡ Building on

- Drawing molecules realistically **ch2**
- Ascertaining molecular structure spectroscopically **ch3**
- What determines molecular shape and structure **ch4**

### Arriving at

- Why molecules generally *don't* react with each other
- Why sometimes molecules do react with each other
- How molecular shape and structure determine reactivity
- In chemical reactions electrons move from full to empty orbitals
- Identifying nucleophiles and electrophiles
- Representing the movement of electrons in reactions by curly arrows

### ➡ Looking forward to

- Reactions of the carbonyl group **ch6**
- The rest of the chapters in this book

## Chemical reactions

Most molecules are at peace with themselves. Bottles of sulfuric acid, sodium hydroxide, water, or acetone can be safely stored in a laboratory cupboard for years without any change in the chemical composition of the molecules inside. Yet if these compounds are mixed, chemical reactions, in some cases vigorous ones, will occur. This chapter is an introduction to the behaviour of organic molecules: why some react together and some don't, and how to understand reactivity in terms of charges, orbitals, and the movement of electrons. We shall also be introducing a device for representing the detailed movement of electrons—the mechanism of the reaction—called the *curly arrow*.

To understand organic chemistry you need to be fluent in two languages. The first is the language of **structure**: of atoms, bonds, and orbitals. This language was the concern of the last three chapters: in Chapter 2 we looked at how to draw structures, in Chapter 3 how to find out what those structures are, and in Chapter 4 how to explain structure using electrons in orbitals.

But now we need to take up a second language: that of **reactivity**. Chemistry is first and foremost about the *dynamic* features of molecules—how to create new molecules from old ones, for example. To understand this we need new terminology and tools for explaining, predicting, and talking about **reactions**.

Molecules react because they move. Atoms have (limited) movement within molecules—you saw in Chapter 3 how the stretching and bending of bonds can be detected by infrared spectroscopy, and we explained in Chapter 4 how the  $\sigma$  bonds of alkanes (but not the  $\pi$  bonds of alkenes) rotate freely. On top of that, in a liquid or a gas whole molecules move around continuously. They bump into each other, into the walls of the container, maybe into solvent

Marcellin Berthelot (1827–1907) pointed out in 1860 that 'chemistry's creative capability, resembling that of art itself, distinguishes it from the natural and historical sciences'.

in a solution. It is all this incessant motion which drives reactions, and we first need to look at what happens when molecules collide.

### Not all collisions between molecules lead to chemical change

➡ We'll discuss this more in Chapter 12.

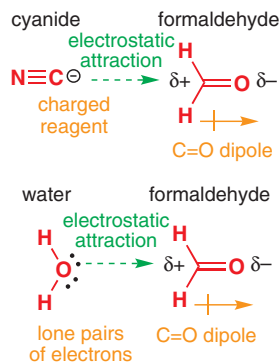
Molecules are coated with a layer of electrons which occupy bonding and maybe non-bonding orbitals. As a result the surface of each molecule is negatively charged and by and large molecules repel each other. Reactions can occur only if a pair of molecules have enough energy to overcome this superficial repulsion. If they don't, they will simply bounce off one another like two balls in pool or snooker, exchanging energy and moving off with new velocities, but remaining chemically unchanged. That minimum energy requirement for reaction—a barrier over which molecules must pass if they are to react—is known as the **activation energy**. In any sample of a compound, the molecules will have a range of energies, but at least some must have more than the activation energy if they are to react.

### Charge attraction brings molecules together

If you mix a solution of sodium chloride with a solution of silver nitrate, electrostatic attraction between the  $\text{Ag}^+$  cations and  $\text{Cl}^-$  anions is enough to bring them together into a stable, crystalline ionic lattice of silver chloride, which precipitates from solution. Both ions are of course surrounded by electrons, but the deficit of negative charge in the  $\text{Ag}^+$  cation (one electron short of the full Ag complement of 47) is enough to overcome the repulsion between the rest of the electrons.

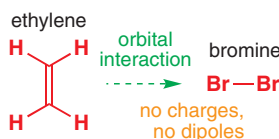
Direct reaction of a cation and an anion is rare with organic molecules because there are relatively few stable organic anions, and even fewer stable organic cations. A more common cause of organic reactions is attraction between a charged reagent (a cation or anion) and an organic compound that both possess a **dipole**. An example that we shall explore in this chapter (and which decorates the cover of this book) is the reaction between a carbonyl compound such as formaldehyde (methanal) and one of those few stable organic anions, cyanide ( $\text{CN}^-$ , in the form of its salt  $\text{NaCN}$ ). The carbonyl group of formaldehyde is polarized because oxygen is more electronegative than carbon (see p. 103). The negative cyanide ion is attracted to the positive end of the carbonyl group dipole.

Actually, it isn't necessary for *either* reagent to be charged. Water also reacts with formaldehyde and this time it is the **lone pair** of electrons—the non-bonding pair of electrons located on the oxygen atom of the uncharged water molecule—that is attracted to the positive end of the carbonyl dipole.



### Orbital overlap brings molecules together

Charges and dipoles can help bring molecules together for reaction, helping them to overcome their electronic repulsion and lowering their activation energy. But reactions can still take place even between completely uncharged molecules with no dipole, provided their molecular orbitals can interact. One of the old 'tests' for unsaturation was to treat a compound with bromine water. If the brown colour disappeared, the molecule was unsaturated (contained double bonds). Spectroscopy means we rarely need to use such tests now, but the reaction is still an important one. An alkene reacts with bromine, even though the alkene and the bromine molecule have neither charge nor dipole. The attraction between these molecules is not electrostatic; instead, their electronic repulsion is overcome because the bromine molecule has an empty orbital available—the  $\sigma^*$  orbital of the  $\text{Br}-\text{Br}$  bond—which can accept electrons from the alkene. Unlike the repulsive interaction between filled orbitals, the interaction between a filled and an unfilled orbital can lead to attraction and reaction.



In fact, orbital interactions are also involved in the other two reactions on this page, but in those cases the orbital interactions are augmented by electrostatic attraction.

● **To summarize the situation:**

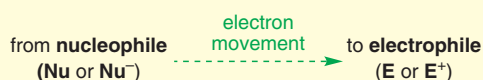
- In general, molecules repel each other, and need to overcome a barrier with a minimum amount of *activation energy* in order to react.
- Most organic reactions involve interactions between full and empty orbitals.
- Many, but not all, also involve charge interactions, which help overcome electronic repulsion.
- Some ionic reactions involve nothing but charge attraction.

We don't need to analyse whether *charge* or *orbital interaction* is the most important factor in bringing molecules together, but you do need to be aware that both may be involved to varying degrees.

## Reactions happen when electrons flow between molecules

When, as a result of these interactions, a pair of molecules find themselves close together, a reaction can take place provided electrons move from one molecule to another. This is what we call the **mechanism of the reaction**—the detailed description of the pathway the electrons take. In most organic reactions, the electrons start in one molecule and move towards another. We call the molecule that accepts the electrons the **electrophile** (electron-lover) for obvious reasons. The molecule that donates the electrons is called the **nucleophile**.

● **A bond forms when electrons move from a nucleophile to an electrophile:**



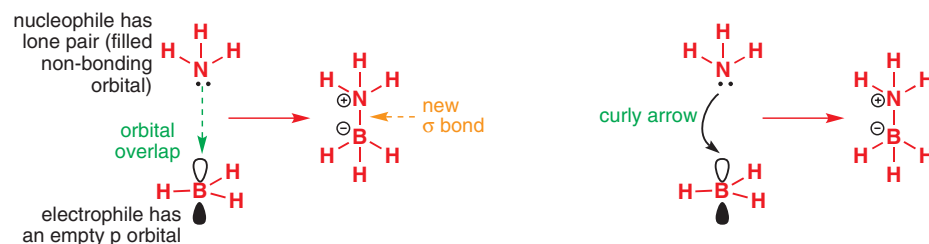
The nucleophile donates electrons.

The electrophile accepts electrons.

Here's a very simple example where the nucleophile is an anion (Cl<sup>-</sup>) and the electrophile is a cation (H<sup>+</sup>). The two are brought together by charge attraction, and the new bond is formed by electrons donated by the nucleophile. Since we are representing the formation of a new bond by the movement of electrons, it's natural to use an arrow to show the way the electrons flow. Arrows used to show electron flow are always curved: we call them 'curly arrows'. The arrow showing the reaction itself is straight.



In the next example, neither the nucleophile (ammonia, NH<sub>3</sub>) nor the electrophile (borane, BH<sub>3</sub>) are charged, but they are drawn together by the interaction between the electrons of the non-bonding lone pair at N and the empty p orbital on B. Electrons flow from the nucleophile (NH<sub>3</sub>) to the electrophile (BH<sub>3</sub>) and a new bond is formed.



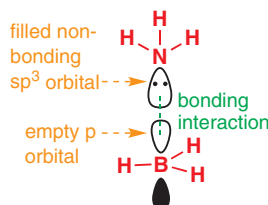
➡ Bonding in BH<sub>3</sub> and NH<sub>3</sub> was discussed on p. 103.

A 'dative covalent bond' is just an ordinary  $\sigma$  bond whose electrons happen to come from one atom. Most bonds are formed by electron donation from one atom to another and a classification that makes it necessary to know the history of the molecule is not useful. The only important distinction you need to make between types of covalent bonds is between  $\sigma$  bonds and  $\pi$  bonds.

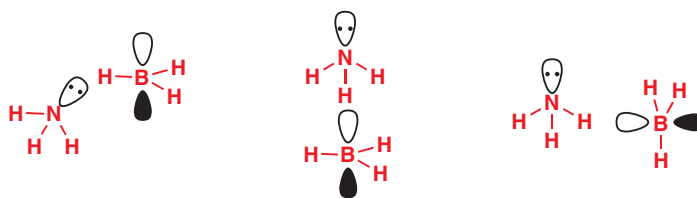
The charges on the B and the N are necessary simply to account correctly for the electrons. Usually, we think of the pair of electrons in a bond as coming one from each of the bonded atoms. But here, since nitrogen donates both electrons (such bonds used to be called 'dative bonds') we have to account for the fact that boron ends up with one electron extra, and nitrogen one electron too few. The bond that forms is just a normal  $\sigma$  bond.

### Orbital overlap is essential for successful reaction

In the reaction of ammonia with borane, not only do the molecules have to collide with enough energy to react, but they must also collide with the orbitals aligned correctly for them to interact. As you saw in Chapter 3, the lone pair of the nitrogen atom resides in a filled, non-bonding  $sp^3$  orbital. This orbital has to overlap with the empty p orbital on B to form a bond. So, a collision like this



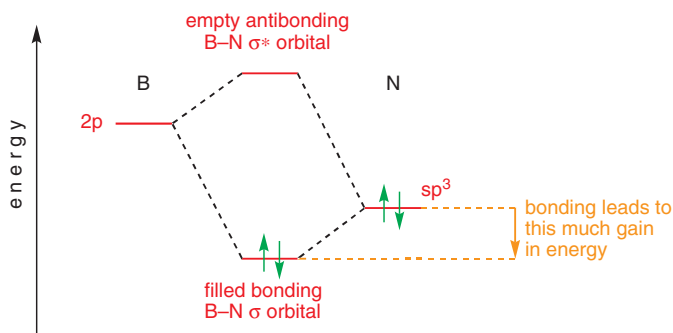
will do just fine for making a bond, but collisions like these



will not do at all.

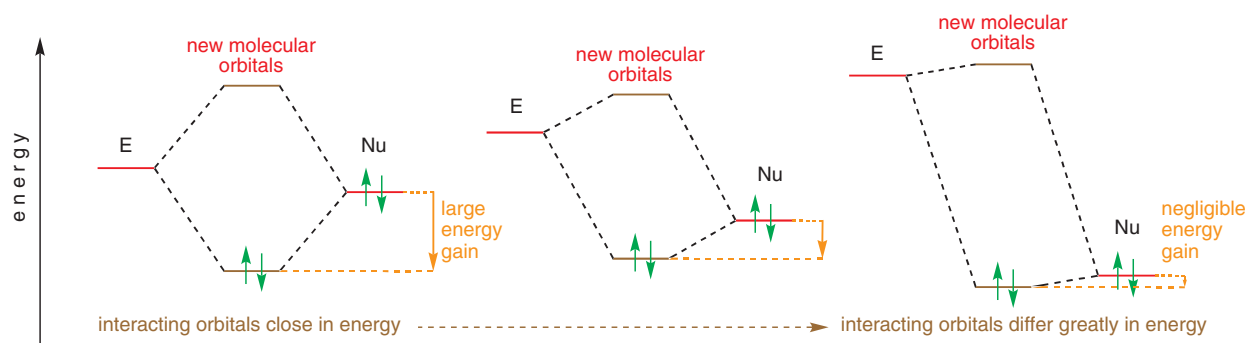
Of course we can also draw a molecular orbital energy level diagram for the constructive, end-on interaction of the orbitals: look back to Chapter 4 to remind yourself of how to do this. Here, we need the filled  $sp^3$  orbital on N to interact with the empty p orbital on B to give a new  $\sigma$  bonding orbital and an empty  $\sigma^*$  antibonding orbital. Finally, putting in the two electrons from the N's lone pair gives us a full picture of the new B–N bond.

■ We've ignored the N–H and B–H bonds as they are not involved in the reaction. The  $sp^3$  orbital on N is lower in energy than the p orbital on B for two reasons—firstly it has more s-character and secondly N is more electronegative than B.



The energy level diagram makes it clear why bonding is favourable too: the electrons have dropped down from the non-bonding  $sp^3$  orbital to the new lower energy bonding  $\sigma$  orbital. We don't need to consider what has happened to the energy of the unfilled orbitals because they're empty and don't contribute to the energy of the molecule as a whole.

We can generalize this idea to work out what makes a good nucleophile and a good electrophile. We'll use an imaginary, generic nucleophile Nu, with a pair of electrons in some sort of filled orbital (it doesn't matter what this orbital is) which it can donate to the empty orbital of a generic electrophile E. Here are three versions of the molecular orbital energy level diagram:



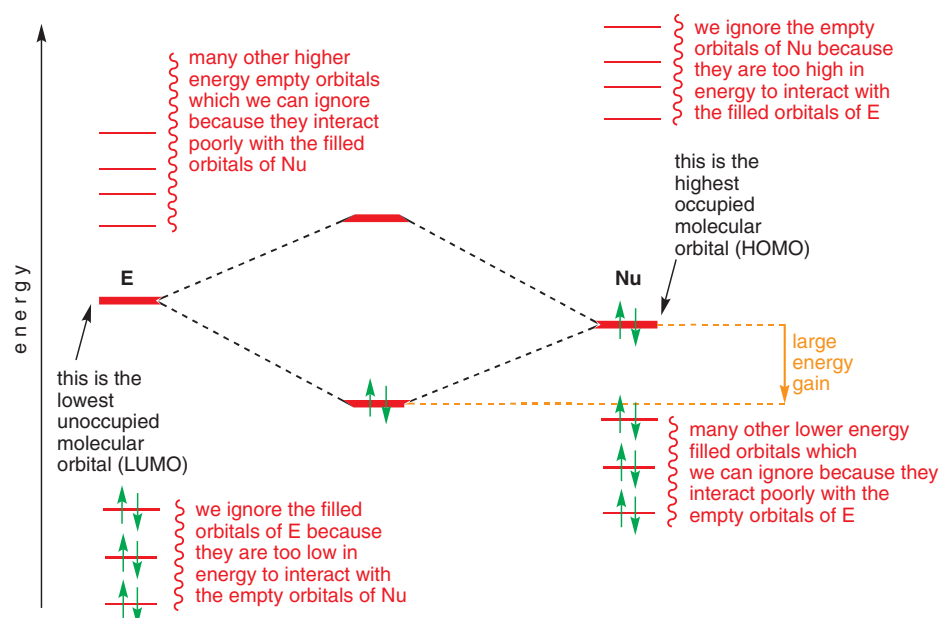
On the left, the energies of the filled Nu orbital and the empty E orbital are almost the same. There is a significant gain in energy when the new bond forms between them. On the right, there is a large difference between the energies of the filled Nu orbital and the empty E orbital, and the energy gain is negligible. This tells us something: **the best reactions are ones in which the energies of the interacting orbitals are similar in energy.**

● **For a reaction to take place, molecules must:**

- overcome their electronic repulsion by charge attraction and/or orbital overlap
- have orbitals of appropriate energy to interact—a filled orbital on the nucleophile and an empty orbital on the electrophile
- approach each other such that these orbitals can overlap to form a bonding interaction.

## Nucleophiles and electrophiles

What does this mean for nucleophiles and electrophiles? Well, in general, filled orbitals tend to be low in energy—that is after all why they are filled! Conversely, empty orbitals tend to be high in energy. So the best interaction (the one that gains the new molecule the most energy) is likely to be between the highest in energy of all the filled orbitals—an orbital we can term the ‘highest occupied molecular orbital’ or HOMO for short—and the lowest in energy of all of the unfiled orbitals—the ‘lowest unoccupied molecular orbital’ or LUMO for short. This diagram may help clarify this idea—it’s a repeat of the best interaction above (the one on the left), but with other orbitals sketched in.



Remember, we can ignore all interactions between pairs of filled orbitals (bonding and antibonding cancel out, see p. 94) and pairs of unfilled orbitals (they don't contain electrons so don't contribute to the stability of the molecule). Of the interactions that are left, the one that gains the molecule the most energy is between the LUMO of the electrophile and the HOMO of the nucleophile. To make these orbitals as close as possible in energy, we want the nucleophile to have a high-energy HOMO and the electrophile to have a low-energy LUMO.

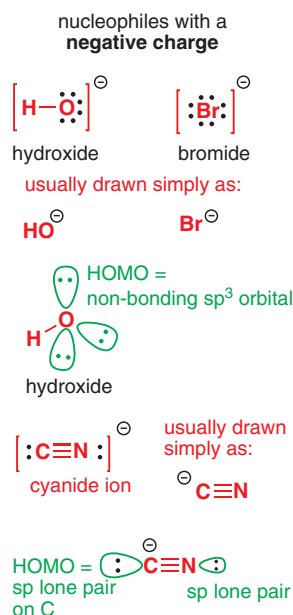
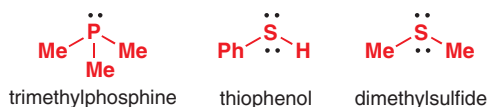
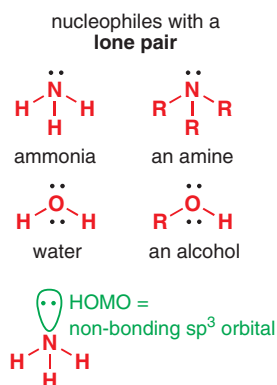
- The best nucleophiles have high-energy occupied molecular orbitals (HOMOs).
- The best electrophiles have low-energy unoccupied molecular orbitals (LUMOs).

The very first stage in understanding any reaction is to work out which of the reacting molecules is the nucleophile and which is the electrophile. It is impossible to stress too much how important it is to be able to identify nucleophiles and electrophiles correctly. For this reason we'll now conduct an identity parade of each class. We'll show you some of the top performing nucleophiles and top performing electrophiles, with a few comments on why they are so good at what they do, before we move on to see them in action.

### Identifying a nucleophile

Nucleophiles are either negatively charged or neutral species with a pair of electrons in a high-energy orbital (the HOMO). The most common type of nucleophile has a non-bonding **lone pair of electrons**. Non-bonding electrons are typically high in energy because they do not benefit from the stabilization bonding electrons get from being shared between two nuclei. Typical neutral nucleophiles with lone pairs are ammonia, amines, water, and alcohols, all of which have lone pairs (one for N, two of equal energy for O) occupying  $sp^3$  orbitals.

Other atoms later in the periodic table which carry lone pairs, such as phosphines, thiols, and sulfides, also make good nucleophiles, especially since their lone pairs are of even higher energy occupying orbitals made up of 3s and 3p atomic orbitals.



**Anions which have lone pairs** are often good nucleophiles too, partly because they can be attracted electrostatically by positively charged electrophiles. The anionic centre is usually O, S, or halogen, each of which can have several identical lone pairs. For example, hydroxide has three lone pairs—the negative charge cannot be assigned to one of them in particular. It's convenient just to draw the negative charge, and not the lone pairs as well. Negative charges like this actually represent a pair of electrons—both the 'extra' electron and its partner in the lone pair—so we normally write mechanisms with an arrow starting on the negative charge.

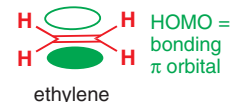
The most important *carbon* nucleophile with a lone pair of electrons is the cyanide ion. Although linear cyanide (which is isoelectronic with  $N_2$ ) has a lone pair on nitrogen and a lone pair on carbon, the nucleophilic atom is usually anionic carbon rather than neutral nitrogen as the  $sp$  orbital on carbon is of higher energy than that on the more electronegative nitrogen, and therefore constitutes the HOMO.

Molecules can still be nucleophilic without non-bonding lone pairs. The next highest set of orbitals are **bonding  $\pi$  orbitals**, especially **C=C double bonds**, since they are higher in energy than  $\sigma$  orbitals (see p. 93). Simple alkenes are weakly nucleophilic and react with strong electrophiles such as bromine. Note, however, that molecules with  $\pi$  bonds can also be electrophiles, particularly when the  $\pi$  bond involves an electronegative atom. The only common  $\pi$  nucleophiles are alkenes and aromatic rings.

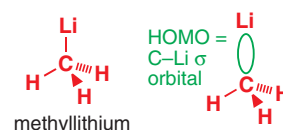
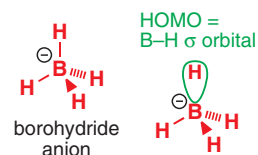
Finally, it is possible for the  $\sigma$  bond of a nucleophile to donate electrons, provided it is a  $\sigma$  **bond associated with electropositive atoms** such as B, Si, or the metals, along with C or H. You saw on p. 97 how the weak hold these atoms have over their electrons means that their atomic orbitals (and hence the molecular orbitals they contribute to) are high in energy. You met the borohydride anion  $\text{BH}_4^-$  in Chapter 4. Borohydride is a good nucleophile—it attacks electrophilic carbonyl compounds, as you will see shortly. It donates electrons from its HOMO, the B–H  $\sigma$  bond. Notice that in this case the negative charge does *not* represent a pair of electrons: you cannot start a curly arrow from it.

In later chapters you will see organometallics—compounds with carbon–metal bonds, for example methyl lithium—acting as nucleophiles. They do so because the  $\sigma$  orbital generated from electropositive C and even more electropositive Li is high in energy.

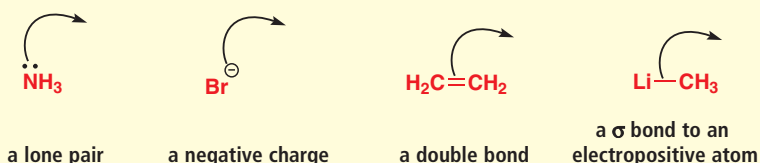
a nucleophile with a  
**C=C double bond**



nucleophiles with a  $\sigma$  **bond**  
between electropositive atoms



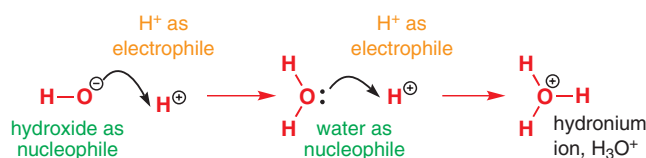
● **Nucleophiles donate electrons from available, high-energy orbitals represented by one of the following:**



The curly arrows in the box above represent electron movement away from the nucleophile. But the electrons have to go somewhere: they are donated to an **electrophile**.

## Identifying an electrophile

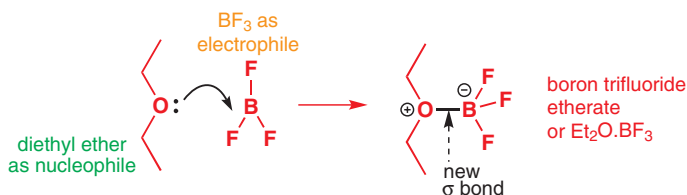
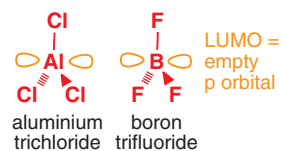
**Electrophiles** are neutral or positively charged species with an empty atomic orbital (such as the empty p orbital in borane) or a low-energy antibonding orbital that can easily accept electrons. The simplest electrophile is the hydrogen cation,  $\text{H}^+$ , usually named for what it is, a proton.  $\text{H}^+$  is a species without any electrons at all and a vacant, very low energy, 1s orbital. It is so reactive that it is hardly ever found and almost any nucleophile will react with it. Acid solutions containing  $\text{H}^+$  are neutralized by the nucleophile hydroxide, for example, and strong acid goes on to protonate water as well, the water acting as a nucleophile and the proton as the electrophile. The product is the hydronium ion,  $\text{H}_3\text{O}^+$ , the true acidic species in all aqueous strong acids. Here's the reaction between hydroxide and  $\text{H}^+$  with the electron movement from the nucleophile to the electrophile represented by curly arrows. The arrows start on the hydroxide's negative charge, which represents one of the oxygen's pairs of electrons:



Other electrophiles with **empty atomic orbitals** include borane, which you met on p. 103, and related compounds such as boron trifluoride and aluminium trichloride.  $\text{BF}_3$  reacts with ethers, as shown below, to form stable complexes. This time the arrow starts on the lone pair.

electrophiles with an  
**empty atomic orbital**

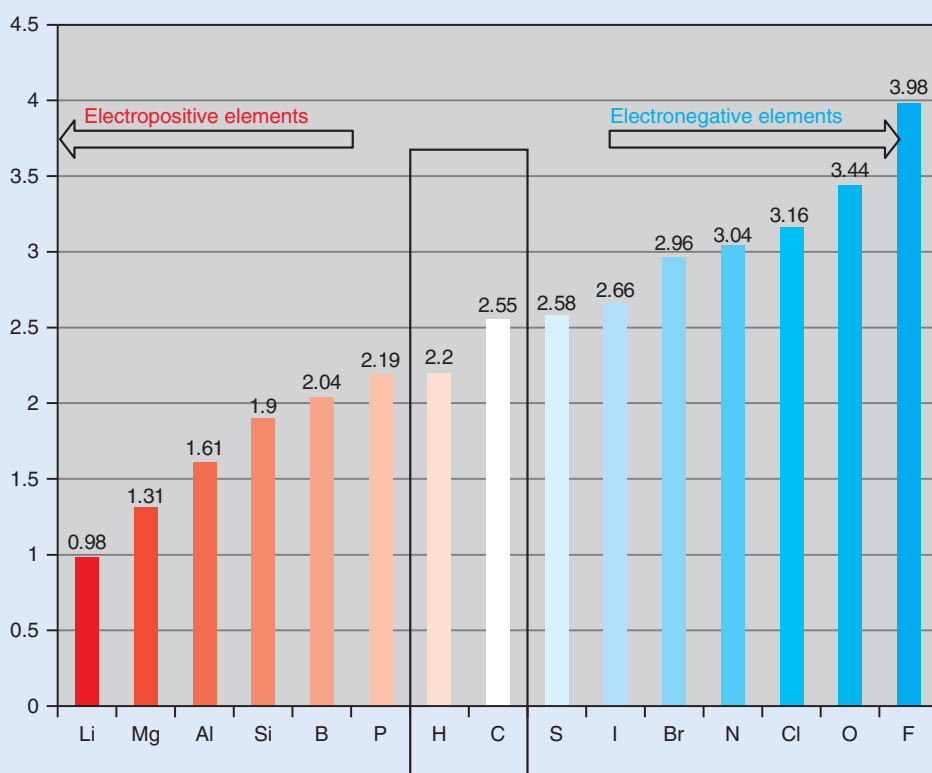




Few organic compounds have vacant atomic orbitals and in most organic electrophiles the LUMOs are instead **low-energy antibonding orbitals associated with electronegative atoms**. These antibonding orbitals can be either  $\pi^*$  orbitals or  $\sigma^*$  orbitals—in other words, molecules which make good electrophiles might have a double or a single bond to an electronegative atom such as O, N, Cl, or Br. It's important that an electronegative atom is involved in order to lower the energy of the orbital (see p. 96) and make it ready to accept electrons.

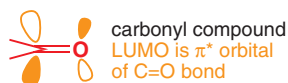
### Carbon's place in the electronegativity scale

Here is a summary of electronegativities for atoms commonly involved in organic reactions.



This bar chart makes it clear why carbon is just so special: it can form strong bonds to almost anything, especially itself. Elements at either end of the scale form weak bonds to similar elements (metal–metal bonds are weak, as are halogen–halogen or O–O bonds), but elements in the middle can form strong bonds to other elements at either end of the scale or elements in the middle. Being in the middle also gives C versatile reactivity: it is electrophilic when bonded to a more electronegative element and nucleophilic when bonded to a more nucleophilic element.

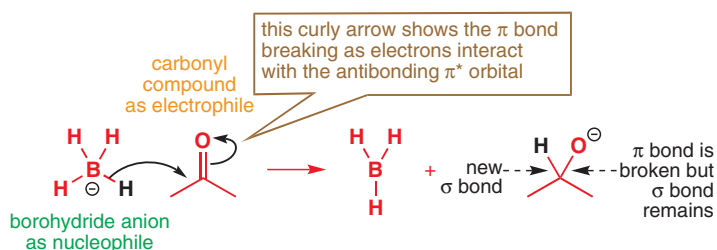
electrophiles with a  
**double-bonded  
electronegative atom**



The most important molecules with a **double bond to an electronegative atom** are carbonyl compounds. In fact carbonyl groups are the most important functional groups in organic chemistry. We looked at their orbitals on p. 103 and we devote the next chapter, Chapter 6, to a detailed study of their reactivity. The low-energy  $\pi^*$  orbital is available to accept electrons, and its electrophilicity is further enhanced by the partial positive charge at carbon which arises from the C=O dipole. Here's an example of a carbonyl compound, acetone, reacting with an anionic nucleophile—we'll choose borohydride in this case. Notice



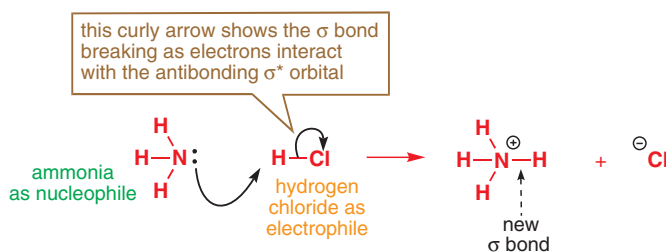
how the arrow does not start on the negative charge, as the charge does not represent a pair of electrons here.



The arrows showing electron movement are a little more involved this time, but the explanation is straightforward. The first arrow shows the electrons moving from the nucleophile's HOMO (the B–H  $\sigma$  orbital) to the electrophile's LUMO (the C=O  $\pi^*$  orbital). The new feature in this mechanism is a second arrow showing the electrons moving from the double bond onto the oxygen atom. This is easy to explain. Since the reaction is putting electrons into an *antibonding* orbital (the  $\pi^*$ ), a bond has to break. That breaking bond is the C=O  $\pi$  bond (the  $\sigma$  bond remains intact). The electrons in the bond have to go somewhere and they end up as an extra lone pair (represented by the negative charge) on oxygen. The product has a new C–H  $\sigma$  bond in place of the C=O  $\pi$  bond.

Molecules with a single bond to electronegative atoms can also make good electrophiles. In compounds such as HCl or CH<sub>3</sub>Br, the  $\sigma^*$  orbital is low in energy because of the electronegative Cl or Br (see p. 95) and the dipole attracts the electrons of the nucleophile to the H or C atom.

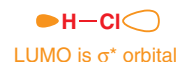
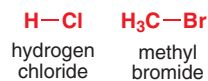
Here's an example of hydrogen chloride acting as an electrophile with ammonia as the nucleophile. As with the carbonyl example above, we are putting electrons into an antibonding orbital, so a bond must break. This time the antibonding orbital is the H–Cl  $\sigma^*$ , so the bond which breaks is the H–Cl  $\sigma$  bond.



➔ We shall come back to this very important reaction at the beginning of Chapter 6.

■ In the carbonyl group, the C=O  $\pi$  bond breaks, rather than the  $\sigma$  bond, because the  $\pi^*$  is lower in energy than the  $\sigma^*$  orbital.

electrophiles with a **single bond to an electronegative atom**

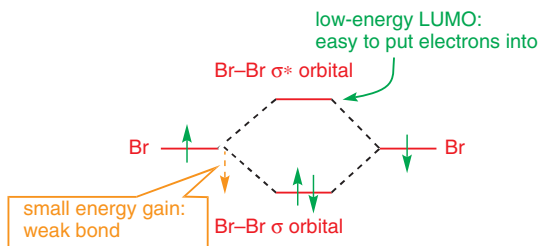
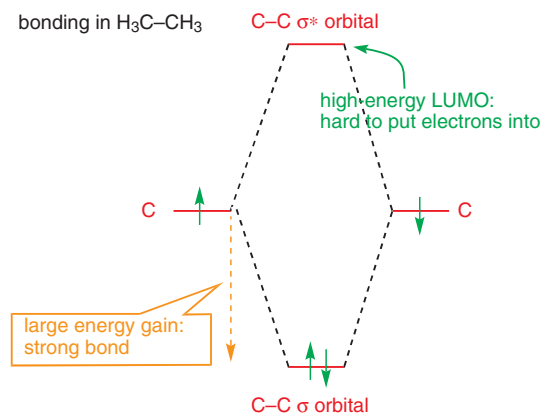


You may recognize this reaction, and the one on p. 113, as the reaction between a base and an acid. All acid–base reactions are reactions between a nucleophile (the base) and an electrophile (the acid). We call an electrophile an acid if it has an X–H bond (X being any atom) that loses H<sup>+</sup> in its reactions. We call a nucleophile a base when it uses a lone pair to donate electrons to the X–H bond.

There is a little more to the definition of an acid, which we shall discuss in Chapter 8, where you will meet the term 'Lewis acid'.

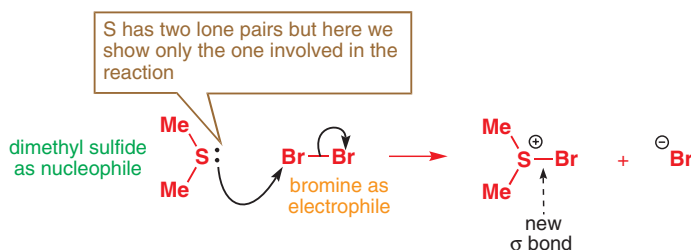
Some  $\sigma$  bonds are electrophilic even though they have no dipole at all. The bonds in the halogens I<sub>2</sub>, Br<sub>2</sub>, and Cl<sub>2</sub> are a case in point. Bromine, for example, is strongly electrophilic because it has a weak Br–Br bond with a low energy  $\sigma^*$  orbital. Why is the  $\sigma^*$  low in energy? Well, bromine is slightly electronegative, but it is also large: it has to use 4s and 4p atomic orbitals for bonding, but these orbitals are large and diffuse, and overlap poorly, meaning the  $\sigma^*$  molecular orbital is not raised far in energy and can easily accept electrons. How different the situation is with a C–C bond: C–C single bonds are almost never electrophilic.

bonding in Br–Br

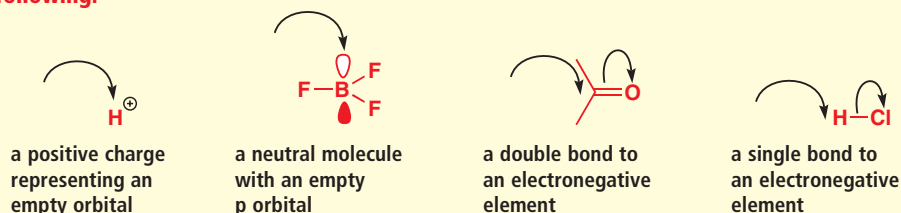
bonding in  $\text{H}_3\text{C}-\text{CH}_3$ 

The unreactivity of C–C bonds is why we think of structures in terms of a hydrocarbon skeleton and functional groups: the hydrocarbon framework is made up of strong C–C bonds with unreactive low-energy filled and high-energy empty orbitals, while the functional groups tend to involve electronegative and electropositive atoms, which react because they contribute to more accessible low-energy LUMOs or high-energy HOMOs.

Bromine reacts with many nucleophiles, for example in the reaction shown below between a sulfide and bromine. Lone pair electrons are donated from sulfur into the Br–Br  $\sigma^*$  orbital, which makes a new bond between S and Br, and breaks the old Br–Br bond.



● Electrophiles accept electrons into empty low-energy orbitals represented by one of the following:



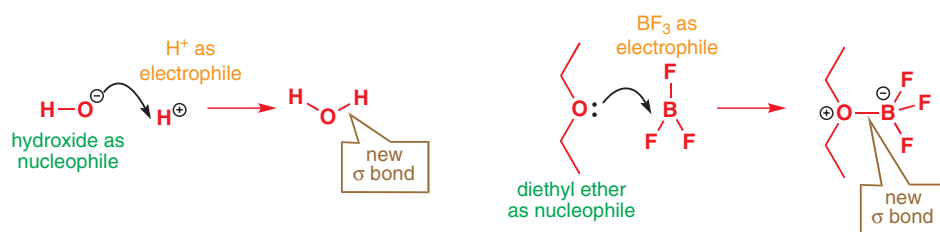
## Curly arrows represent reaction mechanisms

You have now seen several examples of curly arrows representing the movement of electrons during a reaction, and it is time to discuss them in detail. It is no exaggeration to say that this simple device is the one most powerful tool chemists have for explaining simply and accurately how reactions work—in other words the mechanisms of reactions. Curly arrows are to reactions what structural diagrams are to molecules. We discussed the guidelines for drawing structures in Chapter 2, explaining that although the structure of a molecule may be very complex, a good structural diagram will represent all of its important features without unnecessary detail. Curly arrows are similar: you have seen how reactions involve the overlap and summation of molecular orbitals to make new molecular orbitals, and the movement of electrons within those orbitals. Curly arrows allow us to represent all the important features of those interactions and electron movements very simply, without being concerned with unnecessary detail. It's now time to outline some guidelines for writing mechanisms with curly arrows.

### Curly arrows show the movement of electrons

A curly arrow represents the *movement of a pair of electrons* from a filled orbital into an empty orbital. You can think of the curly arrow as representing a pair of electrons thrown, like a

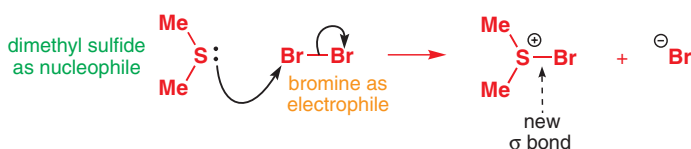
climber's grappling hook, across from where he is standing to where he wants to go. In the simplest cases, the result of this movement is to form a bond between a nucleophile and an electrophile. Here are two examples we have already seen in which lone pair electrons are transferred to empty atomic orbitals.



A curly arrow always starts with its tail resting on the symbol representing a pair of electrons in a filled orbital—in this case the lone pair or the negative charge (which actually represents a lone pair). The head of the arrow indicates the final destination of the pair of electrons—the new bond between oxygen and hydrogen or oxygen and boron in these examples. As we are forming a new bond, the head of the arrow should be drawn to a point somewhere on the line between the two atoms.

Why does a curly arrow represent two electrons? Well, as you saw in Chapter 4, it takes two electrons to make a bond, and in these two cases those electrons come from a lone pair. We use a different sort of arrow for movements of one electron, as you will see in Chapters 24 and 37.

When the nucleophile attacks an antibonding orbital, such as the weak Br–Br bond we have just been discussing, we need two arrows, one to make the new bond and one to break the old.



The bond-making arrow is the same as before—it starts on the nucleophile's lone pair and ends near the electrophile—but the bond-breaking arrow is new. This arrow shows that the two electrons in the bond move to one end (a bromine atom) and turn it into an anion. As always the arrow starts on something representing a pair of electrons in a filled orbital—the Br–Br  $\sigma$  bond. It should start in the centre of the bond and its head should rest on the atom (Br in this case) the electrons are heading for.

Another example is the attack of a base on the strong acid HBr.



It is not important how much curvature you put into the arrows—as long as they curl enough to distinguish them from straight reaction arrows, they can be as curly as you like. Neither does it matter whether they go to the left or the right, or whether they curve up or down as long as they begin and end in the right places. The mechanism below is just as correct:



Some chemists prefer to place this point halfway between the atoms but we think it is clearer and more informative if the arrowhead is closer to the atom to which the new bond is forming. For these examples the difference is minimal and either method is completely clear, but in more complex situations our method prevents ambiguity, as we shall see later. We shall adopt this convention throughout this book: that the arrow ends close to the electrophile.

Notice that the final arrow ends up delivering the electrons to an electronegative atom, satisfying its desire for electron density. This is part of the reason why double or single bonds to electronegative atoms are often a feature of good electrophiles.

● **Curly arrows always start on something representing a pair of electrons:**

- a negative charge
- a lone pair
- or a bond

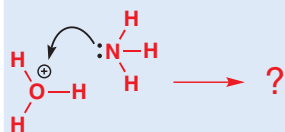
and end at the point those electrons are moving to.

### Charge is conserved in each step of a reaction

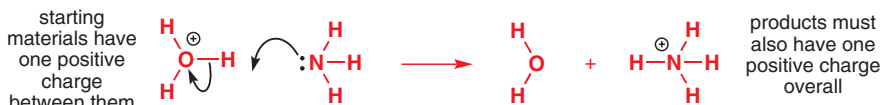
Charge cannot be created or destroyed. If the starting materials have no overall charge, then neither must the products. In the last example above, it is obvious why the bromine becomes negatively charged—it takes both electrons from the bond even though only one of them formally ‘belongs’ to it. It may be less obvious to you why the ammonium cation has to have a positive charge, but it must, in order to maintain overall neutrality. One way to think about it is to note that both of the electrons in the new N–H bond come from N, so N is one electron down on the deal.

If the starting materials are charged, then the products must have, overall, the same charge. Here’s ammonia being protonated by  $\text{H}_3\text{O}^+$ —both starting materials and products must have overall charge 1+.

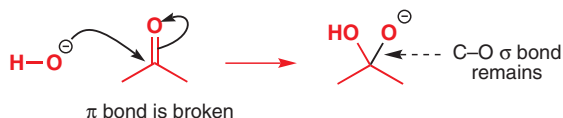
$\text{H}_3\text{O}^+$  (the hydronium ion) is of course the electrophile here: it accepts electrons into the  $\text{H}-\text{O}$   $\sigma^*$ . Why doesn’t this reaction happen though?



The answer is that the oxygen atom already has eight electrons—six from the three bonds to H and two from the other lone pair. It can’t receive any more unless one of those bonds breaks. The positive charge here does not represent an empty orbital in the way that  $\text{H}^+$  has an empty orbital.  $\text{H}_3\text{O}^+$  is electrophilic at H and not electrophilic at O.



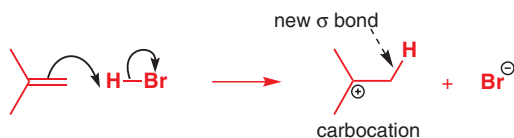
When it is a  $\pi$  bond that is being broken rather than a  $\sigma$  bond, only the  $\pi$  bond is broken and the  $\sigma$  bond should be left in place. This is what commonly happens when an electrophilic carbonyl group is attacked by a nucleophile. Just as in the breaking of a  $\sigma$  bond, start the arrow in the middle of the  $\pi$  bond and end by putting the arrowhead on the more electronegative atom, in this case oxygen rather than carbon.



In this case the starting materials had an overall negative charge and this is preserved in the anionic product. The charge disappears from the hydroxide ion because it is now sharing a pair of electrons with what was the carbonyl carbon atom and a charge appears on what was the carbonyl oxygen atom because it now has one of the electrons in the old  $\pi$  bond.

### $\pi$ bonds as nucleophiles

As you saw above, alkenes can be nucleophiles. The reaction of an alkene with  $\text{HBr}$  is a simple example: the  $\text{C}-\text{C}$   $\pi$  bond is the HOMO of the nucleophile. The first arrow therefore starts in the middle of the  $\pi$  bond and goes into the gap between one of the carbon atoms and the hydrogen atom of  $\text{HBr}$ . The second arrow takes the electrons out of the  $\text{H}-\text{Br}$   $\sigma$  bond and puts them onto the bromine atom to make bromide ion. Overall charge is conserved, so we must generate a positively charged species called a carbocation. The carbocation has a positive charge and an empty p orbital (you can count the electrons to make sure).



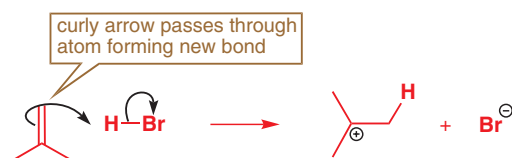
➡ We discussed the simplest carbocation,  $\text{CH}_3^+$ , on p. 103.

■ We’ve drawn in the new  $\text{C}-\text{H}$  bond in the product to make it clear what has happened in the reaction: there are also two other  $\text{C}-\text{H}$  bonds at this C atom, which as usual we haven’t drawn in.

Notice that it was important to draw the two reagents in the right orientation since we need the arrow to show which end of the alkene reacts with which end of HBr. If we had aligned them differently we would have had trouble drawing the mechanism. Here is a less satisfactory representation, in which the H doesn't seem to transfer to the correct end of the alkene:



If you find yourself making an ambiguous drawing like this, it is worth having another go to see if you can be clearer. When the nucleophile is a  $\pi$  (or  $\sigma$ ) bond rather than a lone pair or a charge there is always the question of which end of the bond actually reacts. One way to make this clear is to draw an *atom-specific* curly arrow *actually passing through* the atom that reacts. Something like this will do:



This reaction does not, in fact, stop here as the two ions produced now react with each other to form the product of the reaction. The anion is the nucleophile and the carbocation, with its empty p orbital, is the electrophile.



## $\sigma$ bonds as nucleophiles

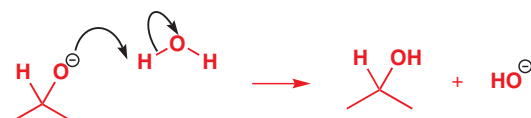
When  $\sigma$  bonds act as nucleophiles, the electrons also have to go to one end of the  $\sigma$  bond as they form a new bond to the electrophile. We can return to an earlier example, the reaction of sodium borohydride ( $\text{NaBH}_4$ ) with a carbonyl compound, and complete the mechanism. In this example, one of the atoms (the hydrogen atom) moves away from the rest of the  $\text{BH}_4^-$  anion and becomes bonded to the carbonyl compound. The LUMO of the electrophile is, of course, the  $\pi^*$  orbital of the  $\text{C}=\text{O}$  double bond.



The arrow from the nucleophile should start in the middle of the bond that breaks and show which atom is transferred to the electrophile. You could use an atom-specific arrow if you wanted to make it absolutely clear that the electrons in the  $\sigma$  bond act as a nucleophile through the hydrogen and not through the boron atom:



The anion which forms is an intermediate, not the final product. The reaction is often carried out in water and the anion acts as a nucleophile to remove a proton from water. Water is the electrophile: its LUMO is the  $\text{O}-\text{H}$   $\sigma^*$ .



■ In Chapter 19 we will explain why the new  $\text{C}-\text{H}$  bond forms at this end of the alkene.

■ Notice the contrast with the reaction of  $\text{H}_3\text{O}^+$  above: unlike the O atom in  $\text{H}_3\text{O}^+$ , the C atom in the carbocation has only six electrons and so can accept two more.

■ Remember (p. 115) you can't start a curly arrow on the negative charge of  $\text{BH}_4^-$  because it does not represent a lone pair: all eight electrons around the B atom are shown as the four  $\text{B}-\text{H}$  bonds. This negative charge is conceptually similar to the positive charge of  $\text{H}_3\text{O}^+$ , which does not represent an empty orbital. Contrast them with the negative charge of  $\text{HO}^-$  (representing an  $\text{sp}^3$  lone pair) or the positive charge of  $\text{H}^+$  (representing the empty 1s orbital).

■ In common with some other molecules, water can be either a nucleophile or an electrophile. In cases like this you can work out which it must be by looking at the other reagent: here, the anion *has* to be a nucleophile. Negatively charged molecules are *never* electrophiles.

### ● Summary: Curly arrow health check

- A curly arrow shows the movement of a pair of electrons.
- The tail of the arrow shows the source of the electron pair, which will be a filled orbital (HOMO) and can be represented by:
  - a lone pair
  - or a negative charge
  - or a  $\pi$  bond
  - or a  $\sigma$  bond.
- The head of the arrow indicates the destination of the electron pair, which will be:
  - an empty atomic orbital where a new bond will be formed
  - or a  $\pi^*$  or  $\sigma^*$  antibonding orbital where a new bond will be formed *and* an old bond will break
  - or an electronegative atom that can support a negative charge.
- Overall charge is always conserved in a reaction.

## Drawing your own mechanisms with curly arrows

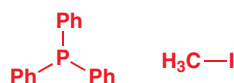
When you meet a new reaction, you must do two things:

1. identify which bonds have been formed and broken, and
2. decide which molecule is the nucleophile and which is the electrophile.

Once you have done that, you are well on the way to writing a reasonable mechanism using curly arrows. We'll take as an example the reaction of triphenylphosphine with methyl iodide.



First observe what has happened: a new bond has been formed between the phosphorus atom and the methyl group, and the carbon–iodine bond has been broken. So we need to draw the two reagents in such a way that a curly arrow can be used to represent this new bond. You'll also need to make sure that you draw out all of the bonds that are actually involved in the reaction (too much detail is better than too little):



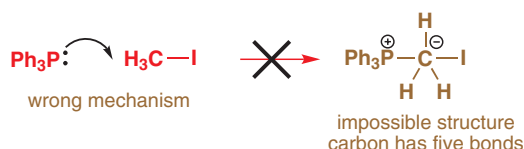
Now the all-important question: **which is the nucleophile and which is the electrophile?** For the nucleophile we are looking for a high-energy pair of electrons such as a lone pair, which the phosphorus has. Likewise, methyl iodide fits the bill as a plausible electrophile, with its bond between C and an electronegative element (I). All that remains is to draw the arrows. The first one starts on the source of the electrons, the phosphorus lone pair, and finishes near the C atom to indicate the new P–C bond. The second one breaks the old C–I bond and moves electrons onto the I atom.



Admittedly, that was quite an easy mechanism to draw but you should still be pleased if you succeeded at your first try.

## Watch out for five-valent carbons

We now ought to spell out one thing that we have never stated but rather assumed. Most atoms in stable organic molecules have a full complement of electrons (two in the case of hydrogen, eight in the cases of carbon, nitrogen, and oxygen) and so, if you make a new bond to one of those elements, *you must also break an existing bond*. Suppose you just 'added'  $\text{Ph}_3\text{P}$  to  $\text{MeI}$  in this last example without breaking the  $\text{C-I}$  bond: what would happen?



This structure must be wrong because carbon cannot have five bonds—if it did it would have ten electrons in the 2s and the three 2p orbitals. Four orbitals can contain only eight electrons.

- B, C, N, and O never have more than four bonds. If you make a new bond to uncharged H, C, N, or O you must also break one of the existing bonds in the same step.

## Mechanisms with several steps

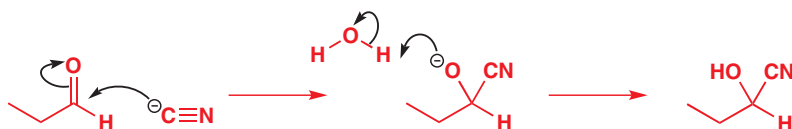
At the beginning of the chapter, we mentioned the fact that carbonyl compounds react with cyanide. We are now going to deduce a mechanism. This is the reaction:



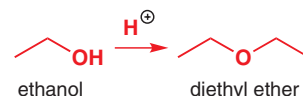
We must decide what happens.  $\text{NaCN}$  is an ionic solid so the true reagent must be cyanide ion, whose structure was discussed on p. 112. As it is an anion, it must be the nucleophile and the carbonyl group must be the electrophile. Starting the arrow on the nucleophile's negative charge and heading for the  $\text{C=O}$  group, and then using a second arrow to break the  $\text{C=O}$  bond gives us this:



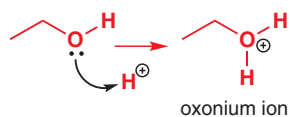
This is a good mechanism but it doesn't quite produce the product. There must be a second step in which the anionic oxygen picks up a proton from somewhere. The only source of protons is the solvent, water, so we can write the full mechanism in one sequence:



Try a more complicated example: primary alcohols can be converted into symmetrical ethers in acid solution. Suggest a mechanism for this acid-catalysed conversion of one functional group into another.

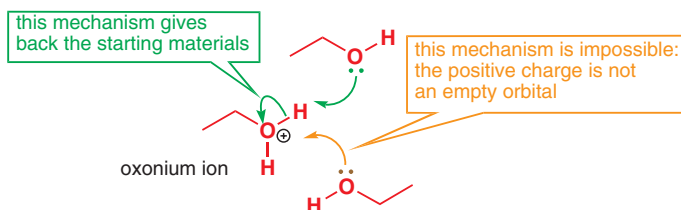


This reaction is presented in a style with which you will become familiar. The organic starting material is written first and then the reagent and solvent over and under the reaction arrow. We call this a *reaction scheme*. It is not an 'equation': it is not balanced, and we use a (straight) reaction arrow  $\longrightarrow$ , not an 'equals' sign.

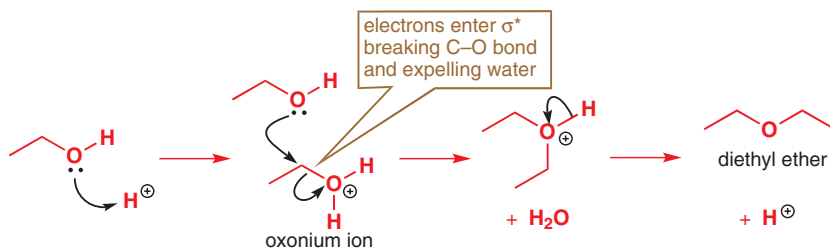


The acid must do something, so we need to start with the reaction between ethanol and  $\text{H}^+$ .  $\text{H}^+$  has to be an electrophile, so the nucleophile must be ethanol, using its HOMO, one of the O lone pairs, as the source of electrons. The first intermediate we get is called an oxonium ion.

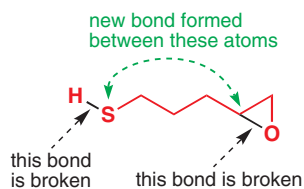
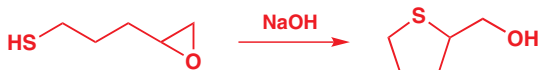
The positively charged oxonium ion has to be the electrophile in the second step of the reaction, and the only possible nucleophile is another molecule of ethanol. But how do they react? It's tempting to allow the ethanol's lone pair to attack the positively charged oxygen atom, but that would give us an oxygen atom with ten electrons—as with  $\text{H}_3\text{O}^+$  this positive charge is not an empty orbital. Attacking the H–O bond is a good alternative, but that just takes us back to where we started.



What we need is a new C–O bond, so the lone pair must attack at carbon, putting electrons into the C–O  $\sigma^*$  and expelling a molecule of water. Here's the full mechanism. The last step is loss of the proton to give the ether.



Now for something completely new: try drawing a mechanism for this reaction.



You might well protest that you don't know anything about the chemistry of either of the functional groups, the thiol or the cyclic ether. Be that as it may, you can still draw a mechanism. Ask first of all: which bonds have been formed and which broken? Clearly the S–H bond has been broken and a new S–C bond formed. The three-membered ring has gone by the cleavage of one of the C–O bonds. The main chain of carbon atoms is unchanged. All this is sketched in the diagram in the margin. We suggest you now cover the rest of this page and try to work out a mechanism yourself before reading further.

The hydroxide must do something, and since it is negatively charged, a reasonable starting point is going to be to use it as a nucleophile to break the S–H bond. Hydroxide is after all a base; it likes to remove protons. So here's the first step:



Now we have a negatively charged sulfur atom, which must be the nucleophile. We want to make a bond to carbon, so the C–O bond in the three-membered ring must be the electrophile. So ... just draw the arrows and see what happens. Here goes ...





That is not quite the product: we need to let this anion pick up a proton from somewhere. Where can the proton come from? It must be the proton originally removed by the hydroxide. The anion attacks water and the hydroxide is regenerated.



Your mechanism possibly didn't look as neat as the printed version, but if you got it roughly right, you should be proud. This is a three-step mechanism involving chemistry that is new to you and yet you could draw a mechanism for it.

### Curly arrows are vital for learning organic chemistry

Curly arrows can be used to explain the interaction between the structure of reactants and products, and their reactivity in the vast majority of organic reactions, regardless of their complexity. When used correctly they can even be used to predict possible outcomes of unknown processes and hence to design new synthetic reactions. They are a powerful tool for understanding and developing organic chemistry and it is vital that you become proficient in their use. They are the dynamic language of organic reaction mechanisms and they will appear in every chapter of the book from now on.

Another equally important reason for mastering curly arrows now, as we start the systematic study of different types of reactions, is that the seemingly vast number of 'different reactions' turn out not to be so vast after all. Most organic reactions involve the movement of pairs of electrons between nucleophiles and electrophiles. And with relatively few types of organic nucleophiles and electrophiles involved in all these reactions, the similarity between seemingly unrelated reactions will become immediately apparent if you understand and can draw mechanisms. Learning to draw mechanisms means you can understand groups of related reactions rather than having to learn them individually.

Drawing curly arrow mechanisms is a bit like riding a bike. Before you've mastered the skill, you keep falling off. Once you've mastered the skill, it seems so straightforward that you wonder how you ever did without it. You'll come across busy streets and complex traffic junctions, but with care you'll get through safely.

### Step-by-step guide to drawing mechanisms with curly arrows

If you still feel you are at the wobbly stage, and need a helping hand, this step-by-step guide may help you. You'll soon find you won't need to follow it through in detail.

1. Draw out the reagents as clear structures following the guidelines in Chapter 2. Check that you understand what the reagents and the solvent are under the conditions of the reaction, for example if the reaction is in a base, will one of the compounds exist as an anion?
2. Inspect the starting materials and the products, and assess what has happened in the reaction. What new bonds have been formed? What bonds have been broken? Has anything been added or removed? Have any bonds moved around the molecule?
3. Identify the nucleophilic centres in all the reactant molecules and decide which is the most nucleophilic. Then identify the electrophiles present and again decide which is the most electrophilic.
4. If the combination of these two centres appears to lead to the product, draw the reactants, complete with charges, so as to position the nucleophilic and electrophilic centres within bonding distance, ensuring that the angle of attack of the nucleophile is more or less consistent with the orbitals involved.
5. Draw a curly arrow from the nucleophile to the electrophile. It must start on a representation of electrons—a filled orbital or negative charge (show this clearly by just touching the bond or charge)—and finish where the electrons are heading for (show this clearly by the position of the head).

■ We will generally show mechanisms using black arrows on red diagrams but the only point of that is to make the arrows stand out. We suggest that when you write mechanisms you consider using a colour for your arrows that contrasts with the structures.

➡ The few reaction types that don't involve nucleophiles and electrophiles are discussed in Chapters 34, 35, 37, and 38.

➡ You will see a great example of this in Chapter 10: carboxylic acids, amides, esters, anhydrides ... many functional groups, but all the same mechanisms.

6. Consider whether any atom that has been changed now has too many bonds; if so one of them must be broken to avoid absurd structures. Select a bond to break. Draw a curly arrow from the centre of the chosen bond, the filled orbital, and terminate it in a suitable place, such as an electronegative atom.
7. Write out the structures of the products specified by the curly arrows. Break the bonds that are the sources of the arrows and make those that are the targets. Consider the effect on the charges on individual atoms and check that the overall charge is not changed. Once you have drawn the curly arrows, the structure of the products is already decided and there is no room for any further decisions. Just write what the curly arrows tell you. If the structure is wrong, then the curly arrows were wrong so go back and change them.
8. Repeat stages 5–7 as required to produce a stable product.

Now you have met the language of mechanism it's time to look in detail at the reactions of some functional groups, and we start with the most important functional group of all, the carbonyl group.

## Further reading

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S. Warren, *Chemistry of the Carbonyl Group: A Programmed Approach to Organic Reaction Mechanisms*, Wiley, Chichester, 1974. Our recommendation for the last chapter, *Molecular Orbitals and Organic Chemical Reactions: Student Edition* by Ian Fleming, Wiley, Chichester, 2009, also gives guidance on using orbitals in chemical reactions and drawing mechanisms.

For a theoretical/physical approach to the question of reactivity, see J. Keeler and P. Wothers, *Why Chemical Reactions Happen*, OUP, Oxford, 2003.

## Check your understanding

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To check that you have mastered the concepts presented in this chapter, attempt the problems that are available in the book's Online Resource Centre at <http://www.oxfordtextbooks.co.uk/orc/clayden2e/>