CHAPTER

27

Basic Organic Chemistry

WHY CHEMICAL REACTION TAKE PLACE ?

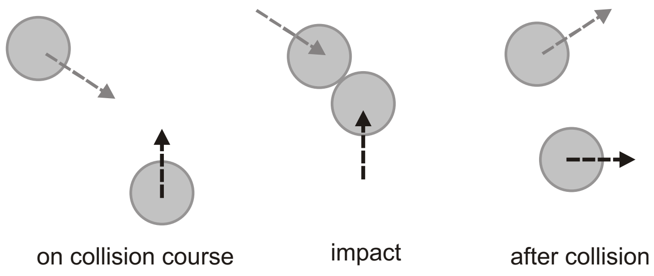
Chemical reactions

Most molecules are at peace with themselves. Bottles of water, or acetone (propanone, $Me_2C=O$), or methyl iodide (iodomethane CH_3I) can be stored for years without any change in the chemical composition of the molecules inside. Yet when we add chemical reagents, say, HCl to water, sodium cyanide (NaCN) to acetone, or sodium hydroxide to methyl iodide, chemical reactions occur. This chapter is an introduction to the reactivity of organic molecules: why they don't and why they do react; how we can understand reactivity in terms of charges and orbitals and the movement of electrons; how we can represent the detailed movement of electrons—the mechanism of the reaction—by a special device called the curly arrow.

Molecules react because they move. When two molecules bump into each other, they may combine with the formation of a new bond, and a chemical reaction occurs. We are first going to think about collisions between molecules.

Not all collisions between molecules lead to chemical change

All organic molecules have an outer layer of many electrons, which occupy filled orbitals, bonding and nonbonding. Charge–charge repulsion between these electrons ensures that all molecules repel each other. Reaction will occur only if the molecules are given enough energy (the activation energy for the reaction) for the molecules to pass the repulsion and get close enough to each other. If two molecules lack the required activation energy, they will simply collide, each bouncing off the electrons on the surface of the other and exchanging energy as they do so, but remain chemically unchanged. This is rather like a collision in snooker or pool. Both balls are unchanged afterwards but are moving in different directions at new velocities.



Electron flow is the key to reactivity

The vast majority of organic reactions are polar in nature. That is to say, electrons flow from one molecule to another as the reaction proceeds. The electron donor is called a nucleophile (nucleus loving) while the electron acceptor is called the electrophile (electron-loving). These terms come from the idea of charge attraction as a dominating force in reactions. The nucleophile likes nuclei because nucleus is positively charged and the electrophile likes electrons because electrons are negatively charged. Though we no longer regard reactions as controlled only by charge interactions, these names have stuck.

► **Molecules repel each other because of their outer coatings of electrons.**
Molecules attract each other because of :
- attraction of opposite charges
- overlap of high-energy filled orbitals with low-energy empty orbitals

For reaction, molecules must approach each other so that they have :
- enough energy to overcome the repulsion
- the right orientation to use any attraction

CURVED ARROWS

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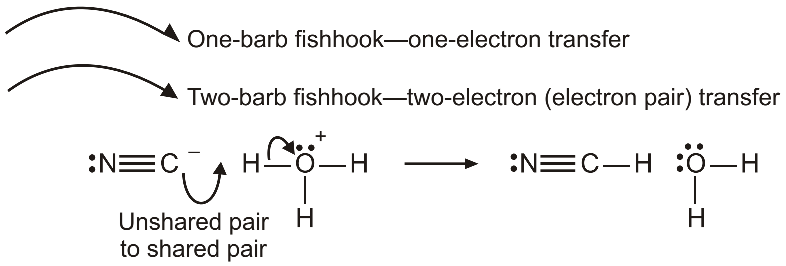


Mechanisms are your key to success in this course. If you can master the mechanisms, you will do very well in this class. If you don't master mechanisms, you will do poorly in this class. What are mechanisms and why are they so important?

When two compounds react with each other to form new and different products, we try to understand how the reaction occurred. Every reaction involves the flow of electron density—electrons move to break bonds and form new bonds. Mechanisms illustrate how the electrons move during a reaction. The flow of electrons is shown with curved arrows.

These arrows show us how the reaction took place. For most of the reactions that you will see this semester, the mechanisms are well understood (although there are some reactions whose mechanisms are still being debated today). You should think of a mechanism as ''bookkeeping of electrons.'' Just as an accountant will do the bookkeeping of a company's cash flow (money coming in and money going out), the mechanism of a reaction is the bookkeeping of the flow of electrons.

When you understand a mechanism, you will understand why the reaction took place, why the stereocenters turned out the way they did, and so on. If you do not understand the mechanism, then you will find yourself memorizing the exact details of every single reaction.

In this chapter, we will not learn every mechanism that you need to know. Rather, we will focus on the tools that you need to properly read a mechanism and abstract the important information. You will learn some of the basic ideas behind arrow pushing in mechanisms, and these ideas will help you conquer the early mechanisms that you will learn.

CURVED ARROWS

We have already gotten quite a bit of experience with curved arrows in chapter 2 (Resonance). The curved arrows that we use in mechanisms refer to the actual movement of electrons. Electrons are moving to break and form bonds (hence the term chemical reaction).

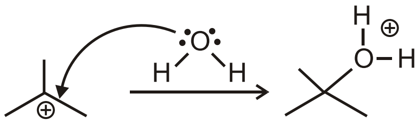
Let's just have a quick review of curved arrows, and the different types of arrows that you can draw. Every curved arrow has a head and a tail. It is essential that the head and tail of every arrow be drawn in the proper place. The tail shows where the electrons are coming from, and the head shows where the electrons are going :

Therefore, there are only two things that you have to get right when drawing each arrow. The tail needs to be in the right place and the head needs to be in the right place. Remember that electrons exist in orbitals, either as lone pairs or as bonds. So the tail of an arrow can only come from a bond or from a lone pair: The head of an arrow can only be drawn to make a bond or to make a lone pair: In total, this gives us four possibilities :

1. Lone pair bond
2. Bond lone pair
3. Bond bond
4. Lone pair lone pair

From a Lone Pair to a Bond

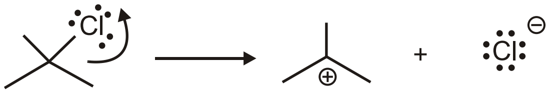
Consider the step below, where we are forming a single bond :



The tail of the arrow is coming from a lone pair on the oxygen atom, and the head of the arrow is going to form a bond between oxygen and carbon. Since the head of the arrow is placed on an atom, it might seem like the electrons are going from a lone pair to a lone pair, but they are not. The electrons are going from the oxygen lone pair to form a bond to the carbon atom. If this makes you unhappy, there is an alternative way of drawing the arrow that shows it more clearly:

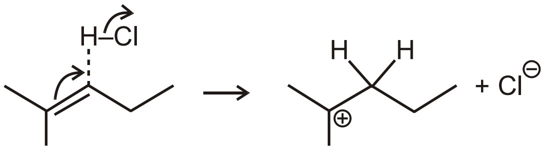
From a Bond to a Lone Pair

Consider the step below, where we are breaking a single bond :



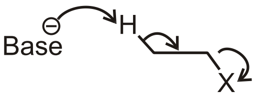
The tail of the arrow is on a bond, and the head of an arrow is forming a lone pair on the chlorine atom. The two electrons of the bond used to be shared between the carbon and the chlorine atoms. But now, both electrons are going on the chlorine. So the carbon has lost an electron, and the chlorine has gained one. This is why the carbon ends up with a positive charge, and the chlorine gets a negative charge.

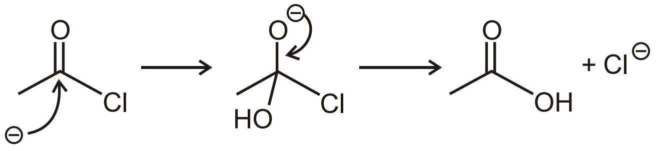
By the way, a chlorine atom with a negative charge is called a chloride ion (-ide- implies the negative charge). So in this reaction chloride is popping off of the molecule to form a carbocation (a carbon with a positive charge). Where we are using the electrons of the pi bond to attack a proton (H), and kicking off Cl in the process:



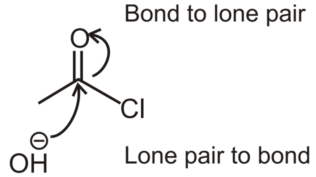
The first arrow has its tail on the pi bond and the head is being used to form a bond between a carbon atom and the proton.

In fact, it is possible to have all three types of arrows in one step of a mechanism. Consider the example below :

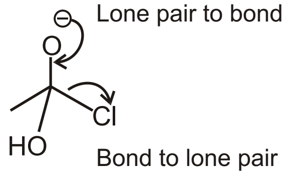




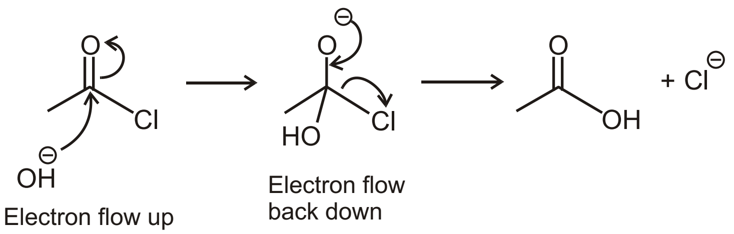
This type of reaction will be covered much later on in your course, but let’s use it now as an example. Notice that there are two steps to this mechanism. In the first step, we have two arrows: from a lone pair to form a bond, and then from a bond to form a lone pair:



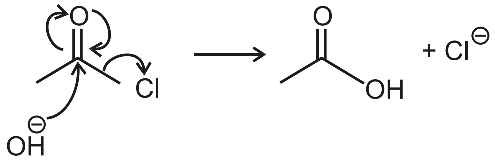
In the second step of the mechanism, we also have two arrows: from a lone pair to form a bond, and then from a bond to form a lone pair:



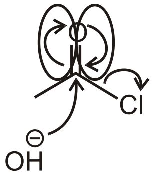
If we consider the overall reaction, we notice that the OH is replacing the Cl. If we look at how the electrons flowed, we see that it all started at the negative charge of the attacking OH . This charge flowed up temporarily on to the oxygen atom of the C O in step I of the mechanism, and then the charge flowed back down to kick off Cl :



When we consider how the charge flowed throughout the whole reaction, it might be tempting to draw it all in one step, like this :

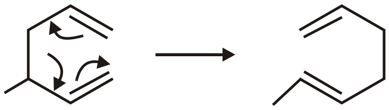


However, this is no good, because we have two arrows going in opposite directions:



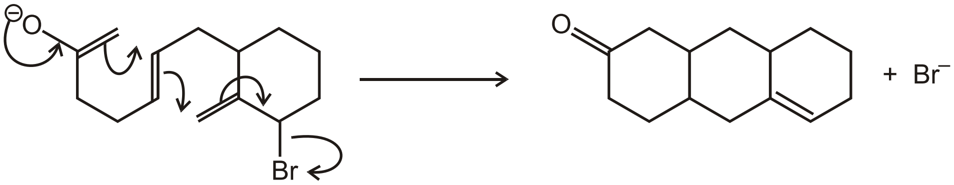
Never draw arrows in opposite directions. That would imply that the electrons were flowing in opposite directions at the same time. That is not possible. In this reaction,

INTRODUCTION



- Illustration of arrow pushing applied to the Cope rearrangement.
- Application of arrow pushing to homolytic cleavage using single-barbed arrows.
- Application of arrow pushing to heterolytic cleavage using double-barbed arrows.

(a)



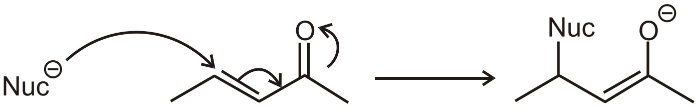
INTERMEDIATES

Drawing Intermediates

We have seen the different types of arrows and how to draw them. Now we need to get practice drawing intermediates when we are given the arrows. Intermediates are compounds that exist for a very short time before reacting further. Let's consider an analogy. Imagine that you are trying to climb a mountain and it is very cold (below freezing). You are wearing a hat that keeps your ears warm, but it is loose and keeps slipping off. Your friend offers you a spare hat that he brought, and you borrow it. Now you need to take your old hat off to replace it with the new hat. If someone were to take a picture of you while you have nothing on your head, the picture would look very strange. There you are, in the freezing cold, with no hat on. You were only like that for 3 seconds, but it was long enough for someone to take a picture. Intermediates of reactions are similar.

Intermediates are intermediate structures in going from the starting material to the product. They do not live for very long, and it is rare that you can isolate one and store it in a bottle, but they do exist for very short periods of time. Their structures are often critical in understanding the next step of the reaction. Going back to the analogy, if I saw the picture of you without your hat on, and I knew how cold it was on that mountain, then I would have been able to predict that you put on a hat right after the picture was taken. I would have known this because I would have been able to immediately identify an uncomfortable situation, and I could have predicted what resolution must have taken place to alleviate the problem. The same is true of intermediates. If we can look at an intermediate and determine which part of the intermediate is unstable, and we also know what options are available to alleviate the instability, then we can predict the products of the reaction based on an analysis of the intermediate. That's why they are so important.

Let's read the arrows. The first arrow is from a lone pair to form a bond. The arrow shows electrons in a lone pair on a nucleophile (anything that is electron rich) forming a bond with a carbon atom. The second arrow is from a bond to a bond. The third arrow goes from a bond to form a lone pair. All in all, these arrows serve as a road map for drawing the intermediate:



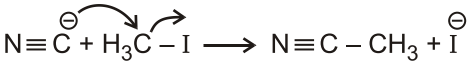
Solved Example

- Use arrow pushing to explain the following reactions :

  When drawing arrows to illustrate movement of electrons, it is important to remember that electrons form the bonds that join atoms. The following represent heterolytic-type reaction mechanisms:

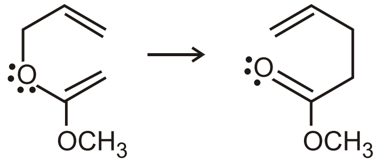
  (a) $N\equiv C^{\ominus} + H_3C - I \longrightarrow N\equiv C - CH_3 + I^{\ominus}$

Sol. This is an example of an S_N2 reaction mechanism converting an alkyl iodide (iodomethane) to an alkyl nitrile (acetonitrile). Arrow pushing is illustrated below :

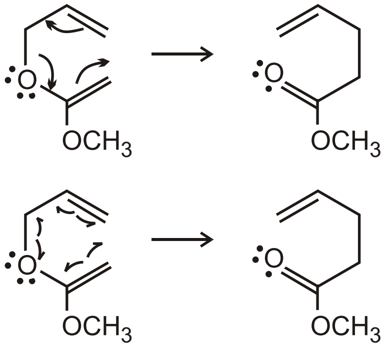


$$N\equiv\overset{\ominus}{C} + H_3C-I \longrightarrow N\equiv C-CH_3 + \overset{\ominus}{I}$$

(b)

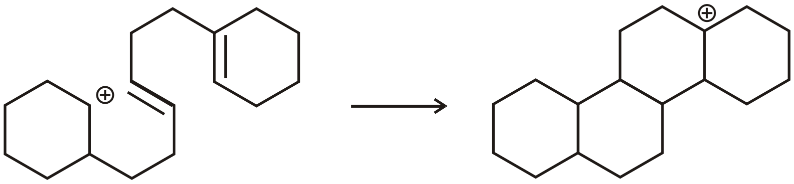


Sol. This is an example of a Claisen rearrangement and occurs through a concerted reaction mechanism. As illustrated, concerted mechanisms can be described either by movement of electron pairs or by movement of single electrons. However, these mechanisms are generally represented by movement of electron pairs using double-barbed arrows as is done for heterolytic reaction mechanisms. Although, mechanistically, the movement of electron pairs is preferred over the movement of single electrons, both processes are illustrated below using arrow pushing :

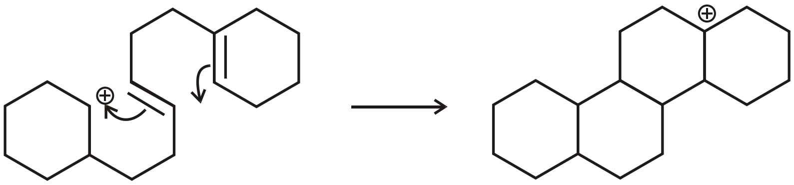


The following represents a heterolytic-type reaction mechanism:

(c)



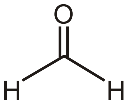
Sol. This is an example of a cation-*p* cyclization. Note that unlike the previously described heterolytic reaction mechanisms, this reaction is influenced by a positive charge. Also, please note that this reaction shares some characteristics with concerted mechanisms in that formation of the new bonds occurs almost simultaneously. Arrow pushing is illustrated below :



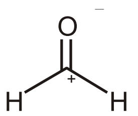
Solved Example

- Place the partial charges on the following molecules.

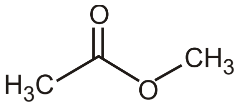
(a)



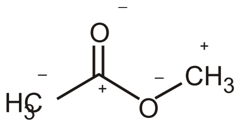
Sol. Carbonyls are polarized such that a partial negative charge resides on the oxygen and a partial positive charge resides on the carbon.



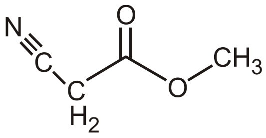
(b)



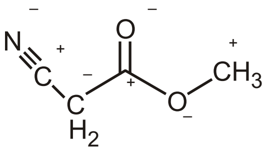
Sol. Because of the polarity of the carbonyl, adjacent groups are also polarized. In general, where a partial positive charge rests, an adjacent atom will bear a partial negative charge. This can occur on more than one adjacent atom or heteroatom.



(c)

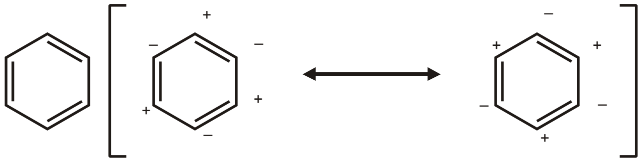


Sol. Nitriles, like carbonyls, are polarized with the nitrogen bearing a partial negative charge and the carbon possessing a partial positive charge.

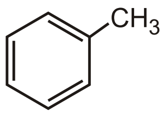


(d)

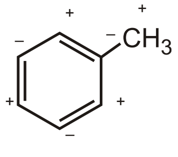
Sol. Benzene has no localized positive or negative charges because of its symmetry. The two illustrated resonance forms are equivalent, rendering benzene a nonpolar molecule.



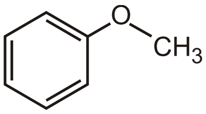
(e)



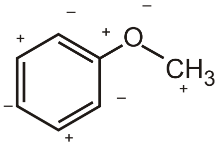
Sol. Methyl groups are electron donating. This is not due to any defined positive charges on the carbon atom and is more the result of hyperconjugation. Hyperconjugation, in this case, relates to the ability of the carbon-hydrogen s bonds of the methyl group to donate electrons into the conjugated system of benzene. While this effect will be discussed in more detail later, let us, for now, define methyl groups as possessing a formal partial positive charge. This resulting positive charge thus polarizes each double bond in the ring.

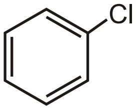


❑ **NOTE :** This is not a hybrid.

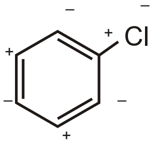
(f) 

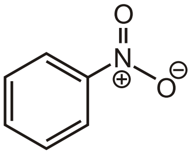
Sol. As with the previous example, groups possessing partial negative charge characteristics donate electrons into conjugated systems and polarize the double bonds. This effect is generally noted with heteroatoms such as oxygen. Also, while in the previous example a methyl group was argued to possess a partial negative charge, the partial positive charge illustrated here is due to the overriding partial negative characteristics of the oxygen atom.



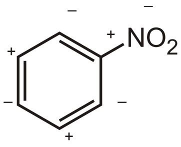
(g) 

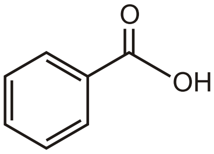
Sol. As with the previous example, heteroatoms such as chlorine possess partial negative charge characteristics and donate electrons into conjugated systems polarizing the double bonds.



(h) 

Sol. As with groups possessing negative charge characteristics, when a positive charge is present on an atom connected to a conjugated system, the double bonds are polarized. This polarization is opposite of that observed for negatively charged groups.



(i) 

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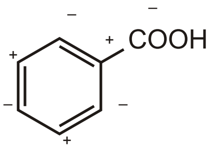
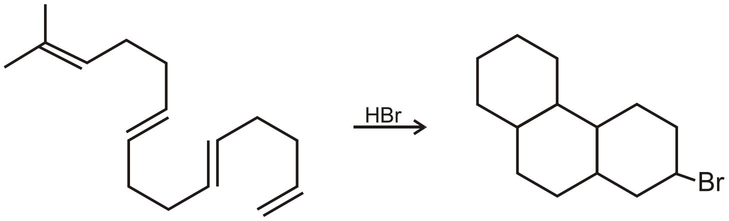


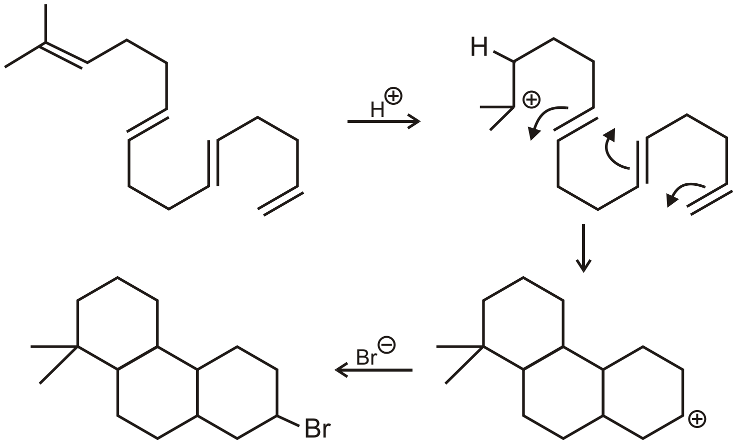
Solved Example

- Explain the following reactions in mechanistic terms. Show arrow pushing.

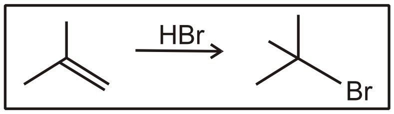
(a)



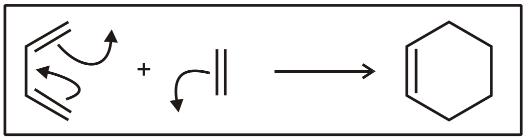
Sol. As presented in this chapter, olefins can become protonated under acidic conditions, leading to the formation of electrophilic and cationic carbon atoms. Furthermore, because olefins have nucleophilic character, they can add to sites of positive charge. The cascading of this mechanism, illustrated below, generates polycyclic systems through the cation- cyclization.



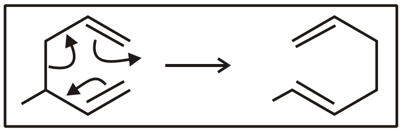
MOVING FORWARD



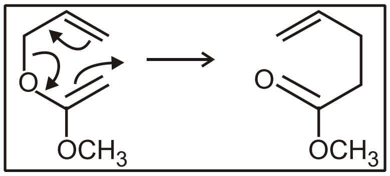
Markovnikov addition of hydrobromic acid across a double bond.



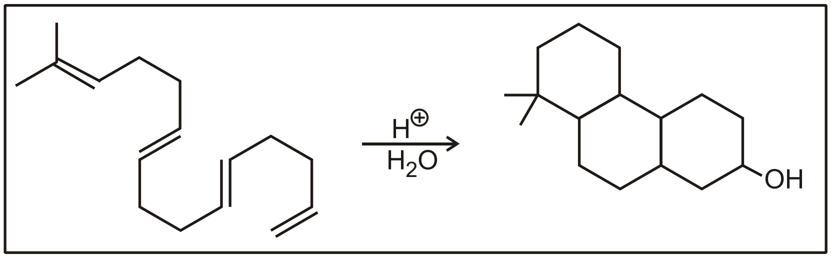
Diels-Alder reaction



Diels-Alder reaction

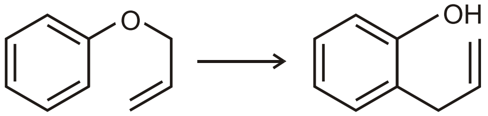


Diels-Alder reaction

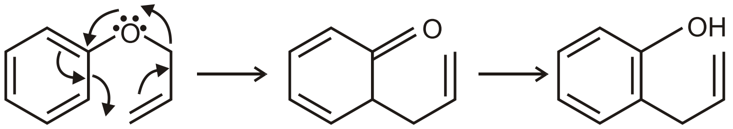


Cation- cyclization

Solved Example



Sol. This is an example of a Claisen rearrangement which is an electrocyclic reaction where no charges are involved. While no charges are involved, like the Diels-Alder reaction, electron pairs do move and their movement can be illustrated using arrow pushing. The mechanism, illustrated below, involves moving a lone pair of electrons from the oxygen into the aromatic ring. The aromatic ring then adds electrons to the double bond. The double bond then migrates and the carbon-oxygen bond is cleaved. While the expected product may be the illustrated ketone, spontaneous conversion to the enol form is facilitated by the stability of the resulting aromatic ring. Thus the illustrated product is formed.

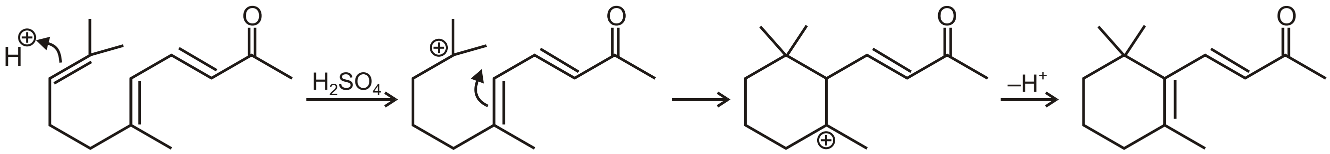


When considering the above mechanistic description, it is important to recognize that all of these steps occur concurrently. Furthermore, like the Diels-Alder reaction (and all electrocyclic reactions), there is no net loss or gain of bonds.

Protonation to favourable tertiary carbocation

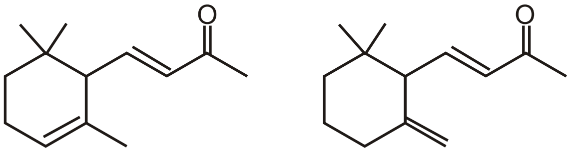
electrophilic addition to give favourable tertiary carbocation

proton loss generates more substituted double bond and favourable conjugated system



6,10-dimethyl-
undeca-3,5,9-triene-2-one

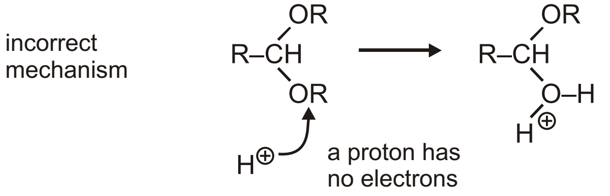
-ionone

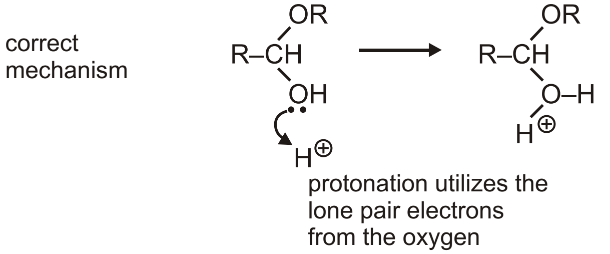


alternative products not favoured
less-substituted double bond; not conjugated

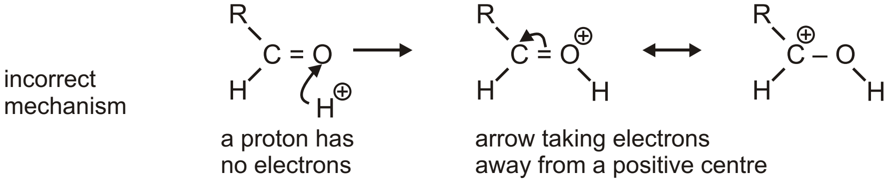
SOME COMMON MISTAKES IN DRAWING MECHANISMS

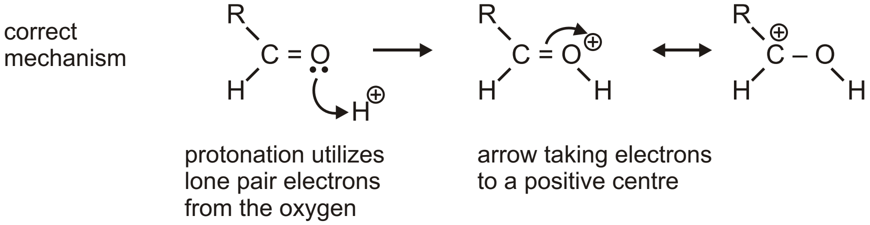
Arrows from protons Ask yourself how many electrons are there in a proton ? We trust the answer is none, and you will thus realize that arrows representing movement of electrons can never ever start from a proton. It seems that this mistake is usually made because, if one thinks of protonation as addition of a proton, it is tempting to show the proton being put on via an arrow. With curly arrows, we must always think in terms of electons.



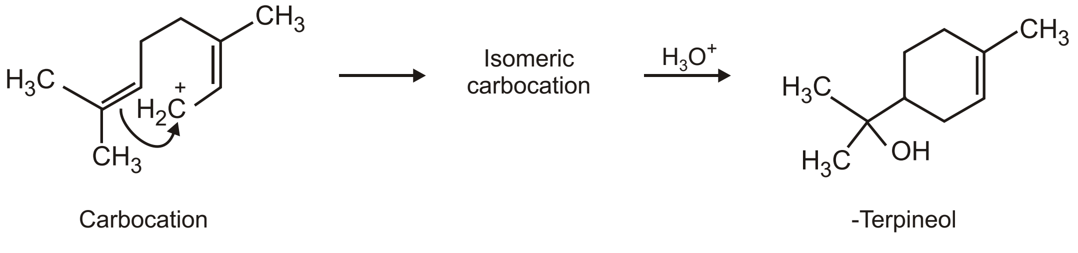


We were even less keen on the second example, where, in the resonance delocalization step, an arrow is shown taking electrons away from a positive charge and creating a new positive centre.



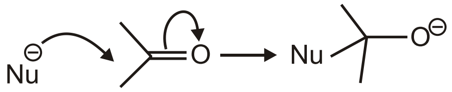


- The naturally occurring molecule a-terpineol is biosynthesized by a route that includes the following step :



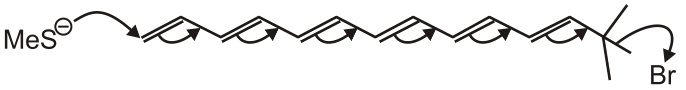
Curly arrows also show movement of electrons within molecules

So far all the mechanisms we have drawn have used only one or two

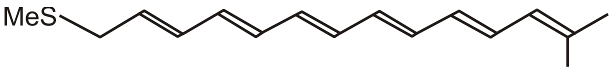


arrows in each step. In fact, there is no limit to the number of arrows that might be involved and we need to look at some mechanisms with three arrows. The third arrow in such mechanismsusually represents movement of electrons inside of the reacting molecules. Some pages back we drew out the addition of a nucleophile to a carbonyl compound.

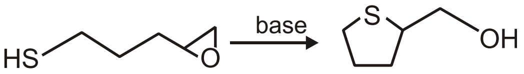
Mostly for entertainment value we shall end this section with a mechanism involving no fewer than eight arrows. See if you can draw the product of this reaction without looking at the result.



The first arrow forms a new C — S bond and the last arrow breaks a C — Br bond but all the rest just move bonds along the molecule. The product is therefore:



Now for a real test: can you draw a mechanism for this reaction?

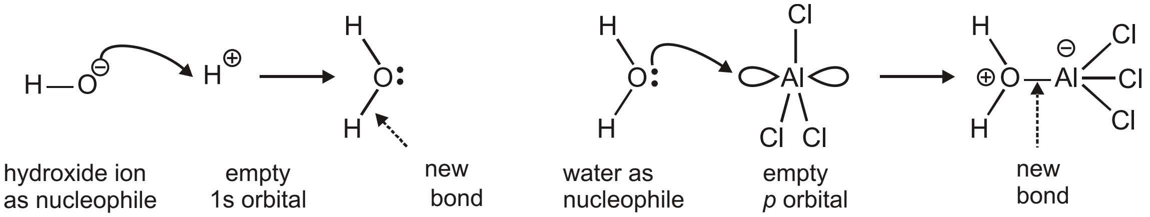


ELECTROPHILE AND NUCLEOPHILE

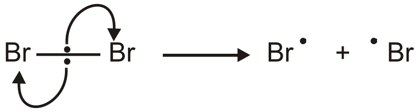
Organic chemists use curly arrows to represent reaction mechanisms

You have seen several examples of curly arrows so far and you may already have a general idea of what they mean. The representation of organic reaction mechanisms by this means is so important that we must now make quite sure that you do indeed understand exactly what is meant by a curly arrow, how to use it, and how to interpret mechanistic diagrams as well as structural diagrams.

A curly arrow represents the *actual 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.



These three examples all have the leaving group taking both electrons from the old s bond. This type of decomposition is sometimes called **heterolytic fission** or simply heterolysis and is the most common in organic chemistry. There is another way that a bond can break. Rather than a pair of electrons moving to one of the atoms, one electron can go in either direction. This is known as **homolytic fission** as two species of the same charge (neutral) will be formed. It normally occurs when similar or

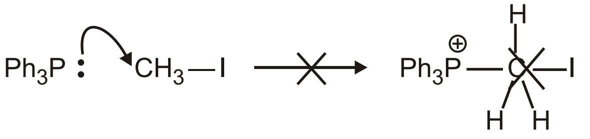


indeed identical atoms are at each end of the bond to be broken. Both fragments have an unpaired electron and are known as radicals. This type of reaction occurs when bromine gas is subjected to sunlight.

The weak Br–Br bond breaks to form two bromine **radicals**. This can be represented by two single-headed curly arrows, **fish hooks**, to indicate that only one electron is moving. This is virtually all you will see of this special type of curly arrow until we consider the reactions of radicals in more detail. When you meet a new reaction you should assume that it is an ionic reaction and use two-electron arrows unless you have a good reason to suppose otherwise.

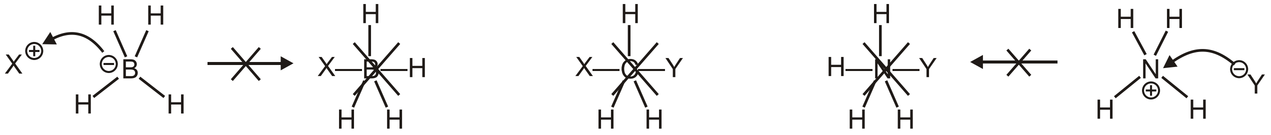
☞ **Warning! Eight electrons is the maximum for B, C, N, or O**

We now ought to spell out one thing that we have never stated but rather assumed. Most organic atoms, if they are not positively charged, have their 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' Ph_3P to MeI in this last example without breaking the C — I bond: what would happen?



wrong mechanism

impossible structure
carbon has five bonds



impossible reaction

impossible structure
boron has five bonds

impossible structure
carbon has five bonds

impossible structure
nitrogen has five bonds

impossible reaction

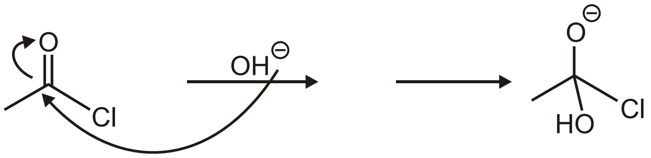
Nucleophiles and Electrophiles

Whenever one compound uses its electrons to attack another compound, we call the attacker a nucleophile, and we call the compound being attacked an electrophile. It is very simple to tell the difference between an electrophile and a nucleophile. You just look at the arrows and see which compound is attacking the other. A nucleophile will always use a region of high electron density (either a lone pair or a bond) to attack the electrophile (which, by definition, has a region of low electron density that can be attacked). These are important terms, so let's make sure we know how to identify nucleophiles and electrophiles.

Solved Example

- Look at the arrows below, and draw the intermediate that you get after pushing the arrows:

Ans. We need to read the arrows like a road map: the first arrow is going from a lone pair on HO to form a bond with the carbon of the C O. The second arrow goes from the C O bond to form a lone pair on oxygen. We use this info to draw the products :



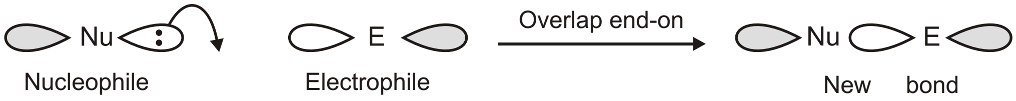
The hard part was assigning formal charges. Notice that we had two arrows moving in a flow. We had a negative charge in the beginning, so we must have a negative charge in the end. It started off on the first atom in the flow of arrows, and it ended on the last atom of the flow (the oxygen).

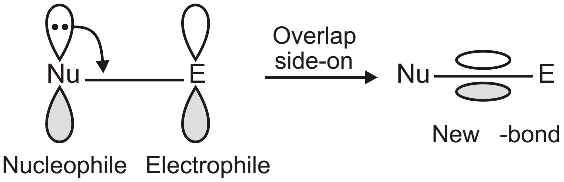
Orbital overlap and energy

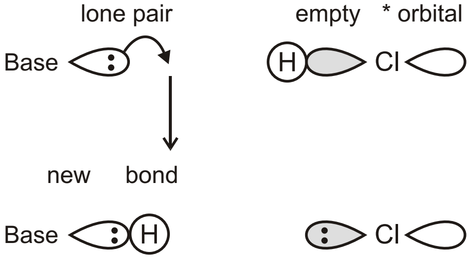
Two atomic orbitals can combine to give two molecular orbitals – one bonding molecular orbital (lower in energy than the atomic orbitals) and one antibonding molecular orbital (higher in energy than the atomic orbitals). Orbitals that combine in-phase form a bonding molecular orbital and for best orbital overlap, the orbitals should be of the same size.

The orbitals can overlap end-on (as for s-bonds) or side-on (as for -bonds). The empty orbital of an electrophile (which accepts electrons) and the filled orbital of a nucleophile (which donates electrons) will point in certain directions in space. For the two to react, the filled and empty orbital must be correctly aligned; for end on overlap, the filled orbital should point directly at the empty orbital.

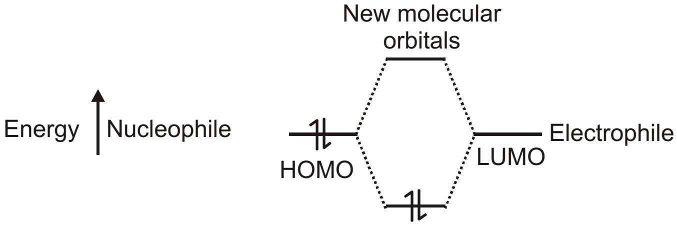
Molecules must approach one another so that the filled orbital of the nucleophile can overlap with the empty orbital of the electrophile







The orbitals must also have a similar energy. For the greatest interaction, the two orbitals should have the same energy. Only the highest-energy occupied orbitals (or HOMOs) of the nucleophile are likely to be similar in energy to only the lowest-energy unoccupied orbitals (or LUMOs) of the electrophile.

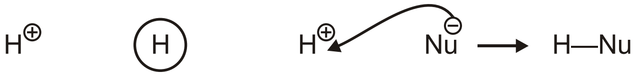


The two electrons enter a lower energy molecular orbital.
There is therefore a gain in energy and a new bond is formed.
The further apart the HOMO and LUMO, the lower the gain in energy.

- The HOMO of a nucleophile is usually a (non-bonding) lone pair or a (bonding)   -orbital. (These are higher in energy than a   -orbital).
- The LUMO of an electrophile is usually an (antibonding)   *-orbital. (This is lower in energy than a   * orbital.)
- In reaction mechanisms
- **Nucleophiles donate electrons**
- **Electrophiles accept electrons**

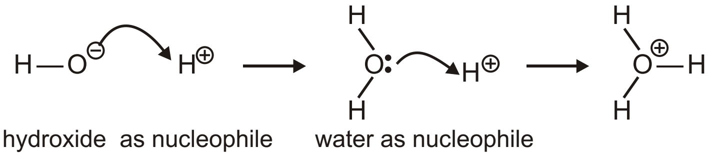
Electrophiles have a low-energy vacant orbital

Electrophiles are neutral or positively charged species with an empty atomic orbital (the opposite of a lone pair) or a low-energy antibonding orbital. The simplest electrophile is the proton, H , a species without any electrons at all and a vacant 1s orbital. It is so reactive that it is hardly ever found and almost any nucleophile will react with it.

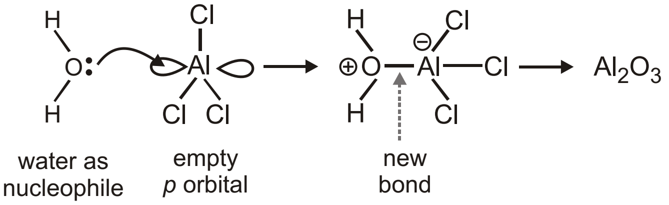


proton empty 1s orbital reaction with anionic nucleophile

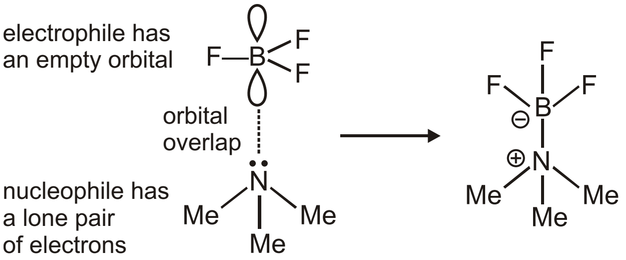
Each of the nucleophiles we saw in the previous section will react with the proton and we shall look at two of them together. Hydroxide ion combines with a proton to give water. This reaction is governed by charge control. Then water itself reacts with the proton to give H_3O , the true acidic species in all aqueous strong acids.



We normally think of protons as acidic rather than electrophilic but an acid is just a special kind of electrophile. In the same way, Lewis acids such as BF_3 or $AlCl_3$ are electrophiles too. They have empty orbitals that are usually metallic *p* orbitals. We saw above how BF_3 reacted with Me_3N. In that reaction BF_3 was the electrophile and Me_3N the nucleophile. Lewis acids such as $AlCl_3$ react violently with water and the first step in this process is nucleophilic attack by water on the empty *p* orbital of the aluminium atom. Eventually alumina (Al_2O_3) is formed.



More often, reaction occurs when electrons are transferred from a lone pair to an empty orbital as in the reaction between an amine and BF_3. The amine is the nucleophile because of the lone pair of electrons on nitrogen and BF_3 is the electrophile because of the empty *p* orbital on boron.



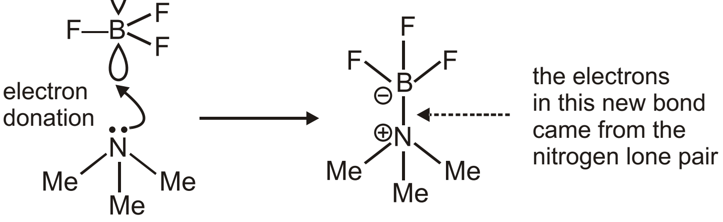
The kind of bond formed in these two reactions used to be called a 'dative Covalent bond' because both electrons in the bond were donated by the same atom. We no longer classify bonds in this way, but call them bonds or bonds as these are the fundamentally different types of bonds in organic compounds. Most new bonds are formed by donation of both electrons from one atom to another.

► A 'dative covalent bond' is just an ordinary 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. Forget 'dative bonds' and stick to bonds or bonds.

These simple charge or orbital interactions may be enough to explain simple inorganic reactions but we shall also be concerned with nucleophiles that supply electrons out of bonds and electrophiles that accept electrons into antibonding orbitals. For the moment accept that polar reactions usually involve electrons flowing from a nucleophile and towards an electrophile.

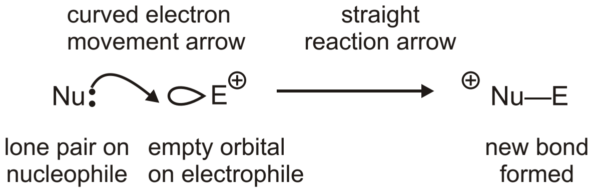
Since we are describing a dynamic process of electron movement from one molecule to another in this last reaction, it is natural to use some sort of arrow to represent the process. Organic chemists use a curved arrow (called a 'curly arrow') to show what is going on. It is a simple and eloquent symbol for chemical reactions.

The curly arrow shows the movement of a pair of electrons from nitrogen into the gap between nitrogen and boron to form a new bond between those two atoms. This representation, what it means, and how it can be developed into a language of chemical reactions is our main concern in this chapter.



The orbitals must also have about the right amount of energy to interact profitably. Electrons are to be passed from a full to an empty orbital. Full orbitals naturally tend to be of lower energy than empty orbitals—that is after all why they are filled! So when the electrons move into an empty orbital they have to go up in energy and this is part of the activation energy for the reaction. If the energy gap is too big, few molecules will have enough energy to climb it and reaction will be bad. The ideal would be to have a pair of electrons in a filled orbital on the nucleophile and an empty orbital on the electrophile of the same energy. There would be no gap and reaction would be easy. In real life, a small gap is the best we can hope for.

Now we shall discuss a generalized example of a neutral nucleophile, Nu, with a lone pair donating its electrons to a cationic electrophile, E, with an empty orbital. Notice the difference between the curly arrow for electron movement and the straight reaction arrow. Notice also that the nucleophile has given away electrons so it has become positively charged and that the electrophile has accepted electrons so it has become neutral.



REACTION REAGENTS

Organic reagents can be classified in two categories :

(a) **Electrophile :** Electron deficient species or electron acceptor is electrophile.

(b) **Nucleophile :** Electron rich species or electron or electron donor is nucleophile.

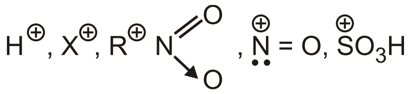
(a) **Electrophiles**

It can be classified into two categories :

(i) Charged electrophiles (E)

(ii) Neutral electrophiles (E)

(i) **Charged electrophiles :** Positively charged species in which central atom has incomplete octet is charged electrophile



$$H^{\oplus}, X^{\oplus}, R^{\oplus}\ N\overset{\displaystyle O}{\underset{\displaystyle O}{\lt}}, \underset{\cdot\cdot}{\overset{\oplus}{N}} = O, \overset{\oplus}{S}O_3H$$

Note : All cations are charged electrophiles except cations of IA, IIA group elements, Al and $\overset{\oplus}{N}H_4$.

(ii) **Neutral electrophiles :** It can be classified into three categories :

- Neutral covalent compound in which central atom has incomplete octet is neutral electrophile,

$$BrCl_2,\ BH_3,\ ZnCl,\ AlX_3,\ FeX_3,\ CH_3, CH_2, CX_2$$

- Neutral covalent compound in which central atom has complete or expended octet and central atom has unfilled -d-shell is neutral electrophile

$$SnCl_4, SiCl_4, PCl_5, SF_6, IF_7$$

- Neutral covalent compound in which central atom is bonded only with two or more than two electronegative atoms is neutral electrophile.

$$BeCl_2, BX_3, AlX_3, FeX_3, SnCl_4, PCl_3$$

$$PCl_5, NF_3, CX_2, CO_2, SO_3, CS_3, CX_4$$

❑ **NOTE :**

(i) Cl_2, Br_2 and I_2 also behave as neutral electrophiles.

(ii) Electrophiles are Lewis acids.

(b) Nucleophiles

Nucleophiles can be classified into three categories :

(i) Charged nucleophiles : Negatively charged species are charged nucleophiles.

$$\overset{\ominus}{H}, \overset{\ominus}{OH}, R-\overset{\ominus}{O}, \overset{\ominus}{CH_3}, \overset{\ominus}{X}, \overset{\ominus}{SH}, R-\overset{\ominus}{S}$$

(ii) Neutral nucleophiles : It can be classified into two categories :

- Neutral covalent compound, in which central atom has complete octet, has at least one lone pair of electrons and all atoms present on central atom should not be electronegative, is neutral nucleophile.

$$NH_3, R-NH_2, R_2NH, R_3N, NH_2-NH_2$$

$$H-O-H, R-O-H, R-O-R$$

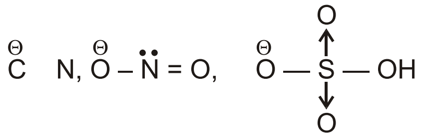
$$H-S-H, R-S-H, R-S-R$$

$$PH_3, RPH_2, R_2PH, R_3PH_3$$

- Organic compound containing carbon, carbon multiple bond/bonds behave as nucleophile.

  Alkenes, Alkynes, Benzene, Pyrole, Pyridine

(iii) Ambident nucleophile : Species having two nucleophilic centres, one is neutral (complete octet and has at least one lone pair of electrons) and other is charged (negative charge) behaves as ambident nucelophile.



$$\overset{\ominus}{C}\equiv N,\ \overset{\ominus}{O}-\ddot{N}=O,\quad \overset{\ominus}{O}-\underset{\downarrow}{\overset{\uparrow}{S}}-OH \text{ (S bonded to O above and O below)}$$

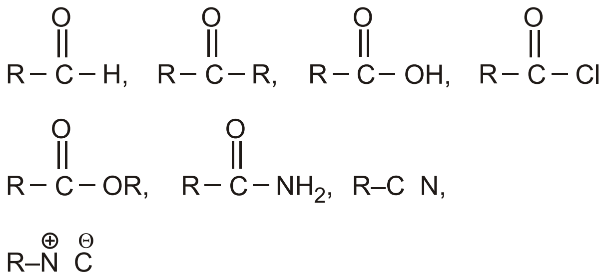
❑ **NOTE :**

(A) Organometallic compounds are nucleophiles.

(B) Nucleophiles are Lewis bases.

Organic compounds which behave as electrophile as well as nucleophile :

Organic compound in which carbon is bonded with electronegative atom (O, N, S) by multiple bond/bonds behaves as electrophile as well as nucleophile.



$$R-\overset{O}{\overset{\|}{C}}-H,\quad R-\overset{O}{\overset{\|}{C}}-R,\quad R-\overset{O}{\overset{\|}{C}}-OH,\quad R-\overset{O}{\overset{\|}{C}}-Cl$$

$$R-\overset{O}{\overset{\|}{C}}-OR,\quad R-\overset{O}{\overset{\|}{C}}-NH_2,\quad R-C\equiv N,$$

$$R-\overset{\oplus}{N}\equiv\overset{\ominus}{C}$$

❑ **NOTE :** During the course of chemical reaction electrophile reacts with nucleophile.

Orbitals of Nucleophiles and Electrophiles

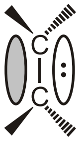
Nucleophiles

1. Filled nonbonding orbital

n

2. Filled bonding orbital

π

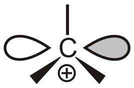


3. Filled bonding orbital

Electrophiles

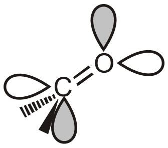
1. Empty nonbonding atomic orbital

a



2. Empty pi antibonding orbital

π^*

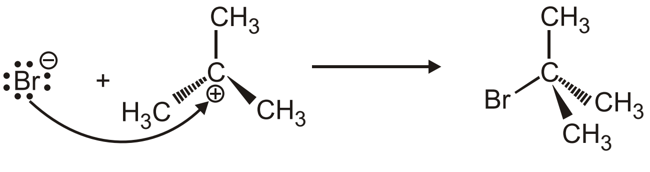


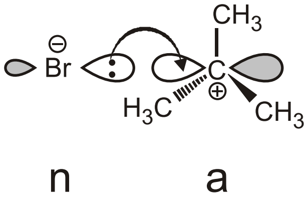
3. Empty sigma antibonding orbital

*

Filled Nonbonding + Empty Nonbonding

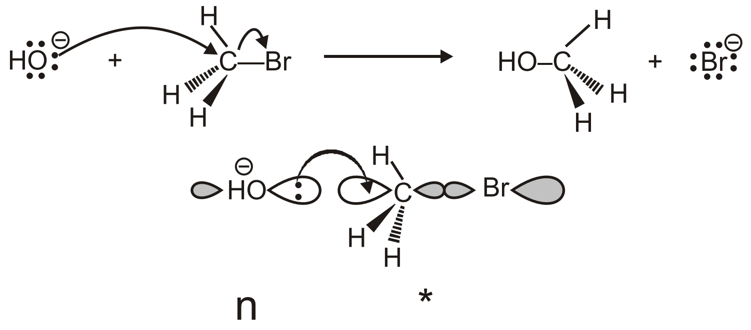
n + a





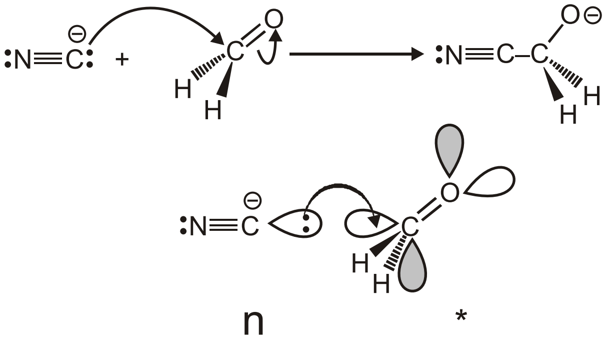
Filled Nonbonding + Sigma Antibonding

n + *



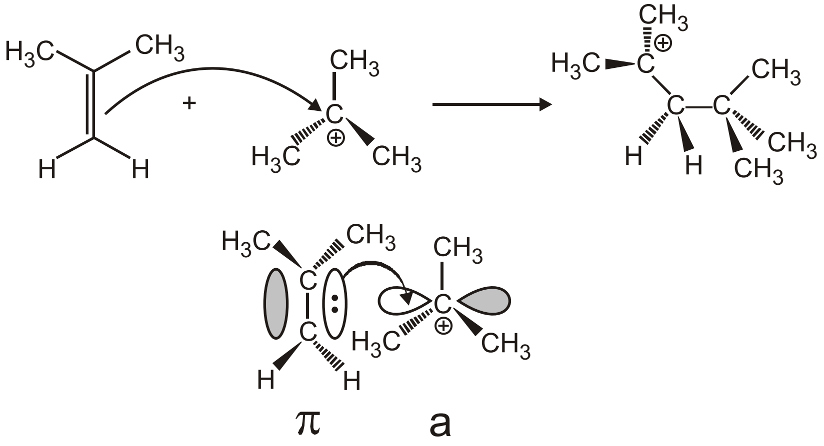
Filled Nonbonding + Pi Antibonding

n + *



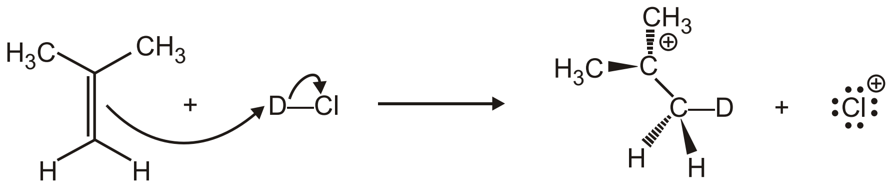
Pi Bonding + Empty Nonbonding

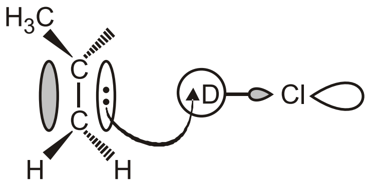
π + a



Pi Bonding + Sigma Antibonding

\+ *





*

Still Having Trouble Identifying Nu: and E +?

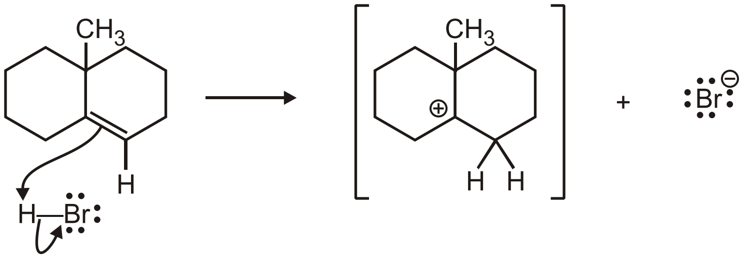
1. Look for regions of electron density and electron deficiency
2. Draw in all lone pairs
3. Draw as many resonance structures as you can

(Often, the 2nd best resonance structure shows the electrophilic and nucleophilic sites in a molecule)

The terms ‘‘nucleophile’’ and ‘‘electrophile’’ can mean the entire molecule or specific atoms and functional groups.

Don’t let the dual meaning confuse you!

A Few Notes About Electron Pushing

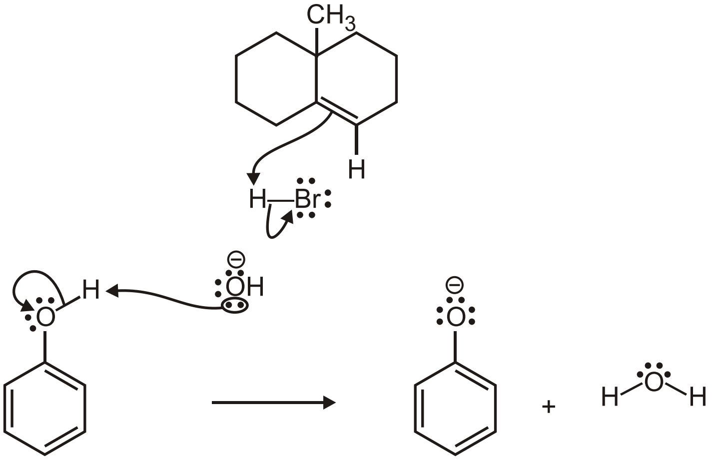


- A curved arrow show the **“movement”** of an electron pair.
- The tail of the arrow shows the **source** of the electron pair, which is a **filled** orbital. This will be a :
  - lone pair
  - -bond
  - -bond
- The head of the arrow indicates the **destination (sink)** of the electron pair which will be :
  - An **electronegative atom** able to support negative charge
  - An **empty** orbital when a new bond is formed
- Overall **charge is conserved.** Check that your products obey this rule.

Courtesy of Jefrey S. Moore, Department of Chemistry, University of Illinois at Urbana-Champaign Used with permission. Adapted by Kimberly Berkowski.

Electron Pushing to Uncharged C, H, N, or O

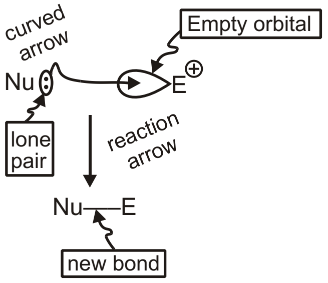
If you make a new bond by pushing an arrow to an uncharged C, H, N, or O, you must also break one of the existing bonds in the same step.



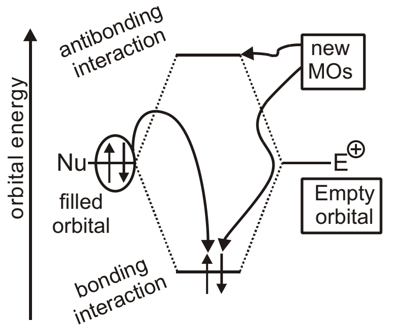
Courtesy of Jefrey S. Moore, Department of Chemistry, University of Illinois at Urbana-Champaign Used with permission. Adapted by Kimberly Berkowski.

Addition of Nucleophiles to Electrophiles

"Arrow Pushing" Description

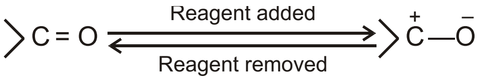


Molecular Orbital Description

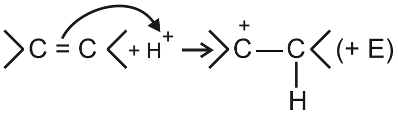


ELECTROMERIC EFFECT

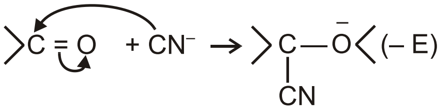
This involves a transfer of electrons of a multiple bond (double or triple) to one of the bonded atoms (usually more electronegative) in the presence of an attacking reagent. The effect is temporary and takes place only in the presence of a reagent. As soon as the reagent is removed, the molecule reverts back to its original position.



If the electrons are transferred to the atom of the double bond to which the reagent gets finally attached, it is +E effect. Consider addition of acid to alkenes.



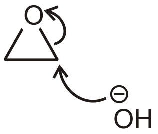
If, however, the electrons of the double bond are transferred to an atom of the double bond other than the one to which the reagent gets finally attached, the effect is called –E effect. Consider the addition of CN to the carbonyl group.



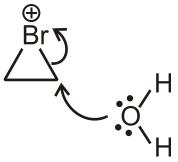
Solved Example

- In each of the reactions below, determine which compound is the nucleophile and which compound is the electrophile.

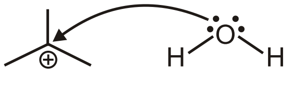
(a)



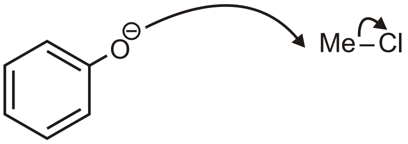
(b)



(c)

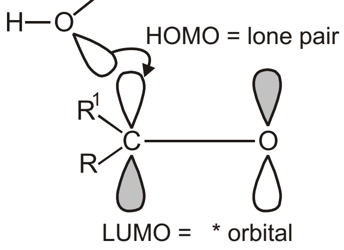


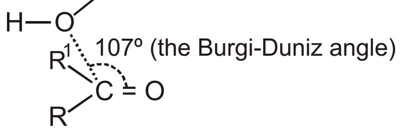
(d)



Solved Example

- Addition of water to a ketone

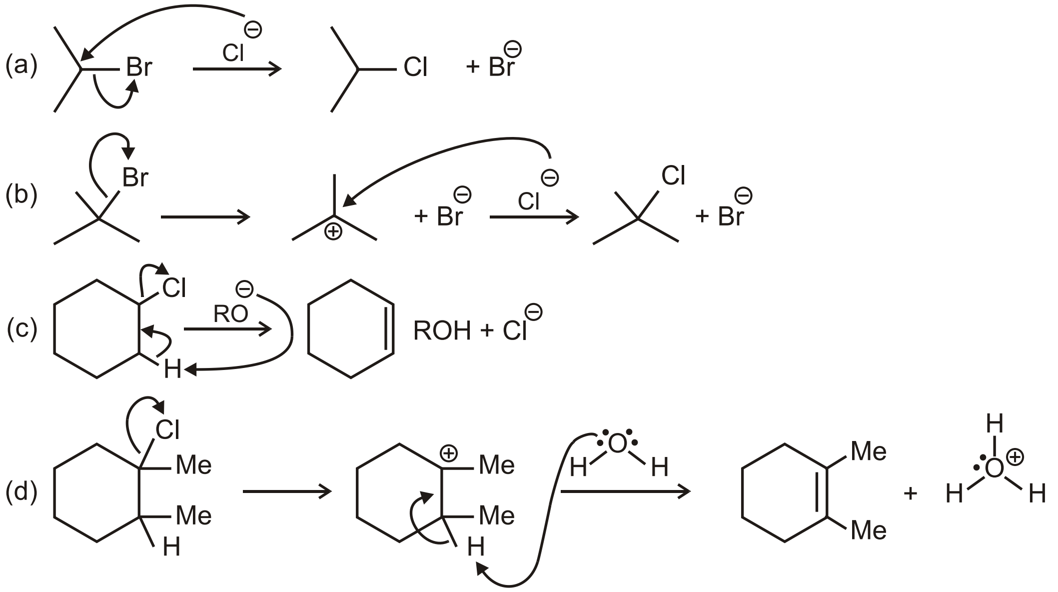


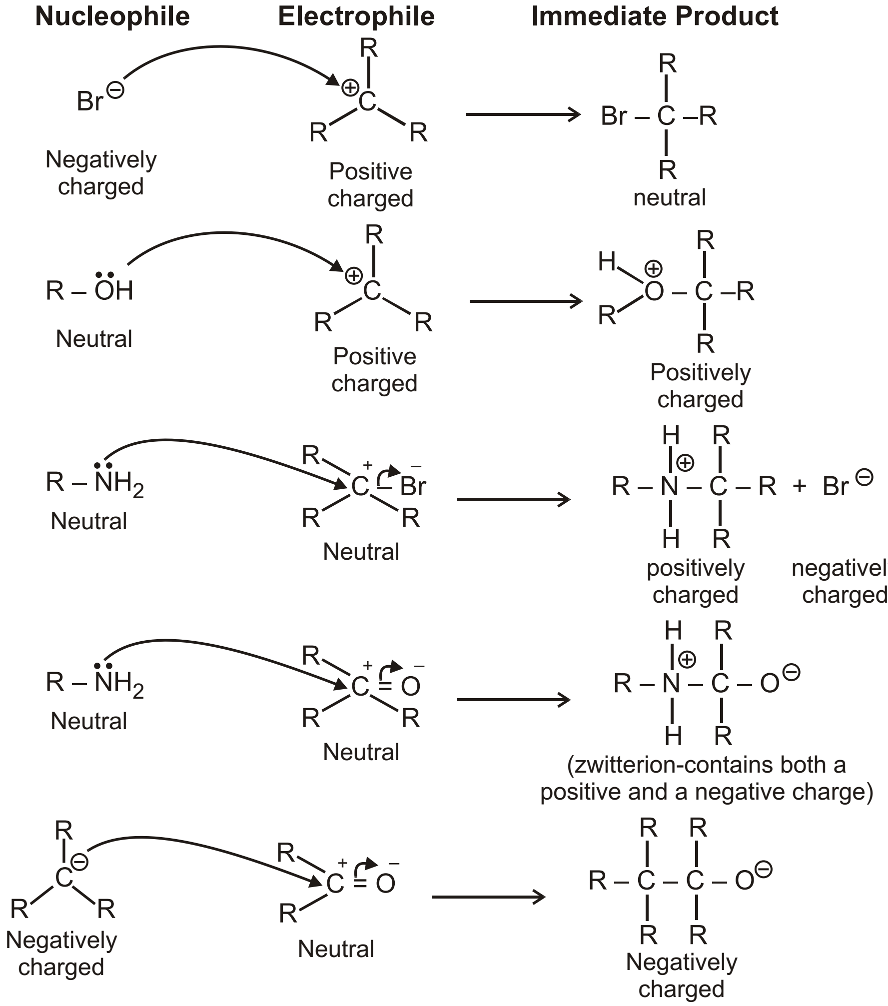


For maximum orbital overlap attack at 90º
is required. However, attack at – 107º is
observed because of the greater electron
density on the carbonyl oxygen atom,
which repels the lone pair on HO_2

Solved Example

- For each transformation below, complete the mechanism by drawing the proper arrows.





EXERCISE

SINGLE CHOICE QUESTIONS

1. Which of the following is not an electrophile?

(A) H (B) BF_3 (C) NO_2 (D) Fe ^{3}

(E) CH_2CH_2

2. Which of the following is not a nucleophile?

(A) $FeBr_3$ (B) Br (C) NH_3 (D)

(E) CH_3OCH_3

3. Which is the MOST basic nucleophile in the following series?

(A) F (B) CH_3CH_2OH (C) H_2O (D) CH_3CH_2O

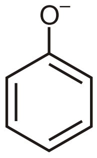
4. Which is an electrophile :

(A) BCl_3 (B) CH_3OH (C) NH_3 (D) None

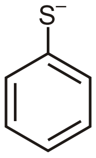
5. Which of the following is an electrophile :

(A) H_2O (B) SO_3 (C) NH_3 (D) ROR

6. Consider the following two anionic molecules. Which of the following statements is TRUE ?



I



II

(A) I is more basic and more nucleophilic than II.

(B) I is less basic and less nucleophilic than II.

(C) I is more basic but less nucleophilic than II.

(D) I is less basic but more nucleophilic than II.

7. How are basicity and leaving group ability related?

(A) They are not related to each other

(B) Good leaving groups are strong bases

(C) Good leaving groups are weak bases

(D) Leaving group   Basic strength

8. Ethers can act as :

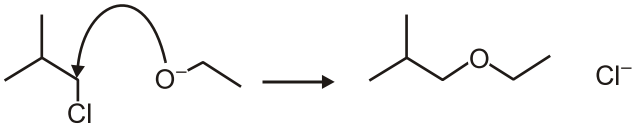
(A) Bronsted acids (B) Bronsted bases

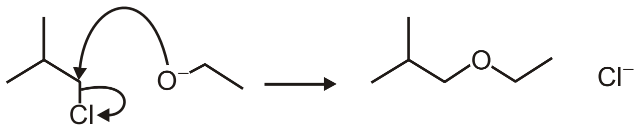
(C) Lewis acids (D) Lewis bases

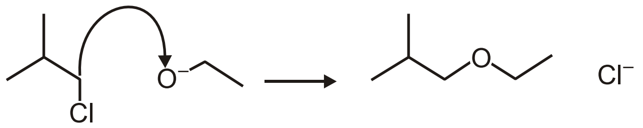
(E) An amphoteric species

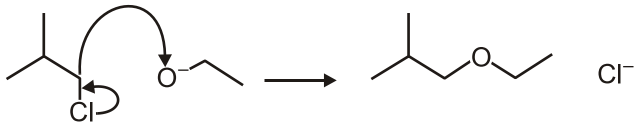
9. Which of the following reactions shows the correct use of "curly arrows"?

(A)



(B) 

(C) 

(D) 

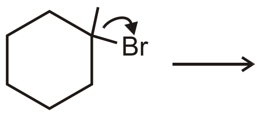
10. There are a number of definitions for acids and bases. Match the following definitions to the correct theory.

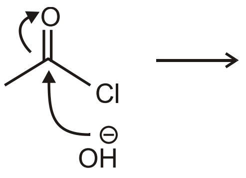
	Theory		**Definition**
A.	Arrhenius	I.	Donates or accepts protons
B.	Bronsted-Lowry	II.	Donates or accepts a lone pair of electrons
C.	Lewis	III.	Donates a proton or a hydroxide

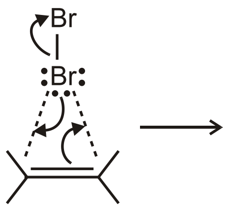
(A) A(I), B(II), C(III)
(B) A(I), B(III), C(II)
(C) A(II), B(III), C(II)
(D) A(II), B(I), C(III)
(E) A(III), B(I), C(II)
(F) A(III), B(II), C(I)

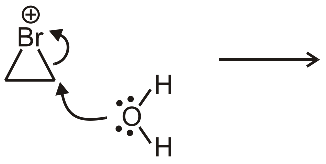
UNSOLVED EXAMPLE

1. For each problem below, draw the intermediate that you get after pushing the arrows.

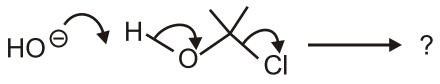
(a) 

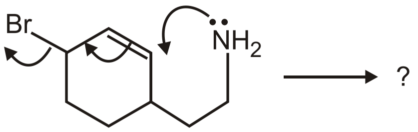
(b) 

(c) 

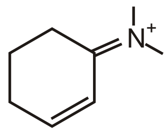
(d) 

2. Complete these mechanisms by drawing the structure of the products in each case.

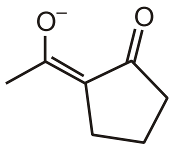
(a) 

(b) 

3. Circle all the electrophilic carbon atoms in the following structure.
Explain your answer with resonance contributors.



4. Draw in all lone pairs. Circle all the nucleophilic atoms in the following structure. Explain your answer with resonance contributors.



SUBJECTIVE TYPE QUESTIONS

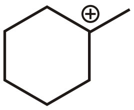
1. What are isohyptic and non-isohyptic reactions? Explain with reactions.

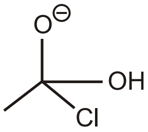
Answers

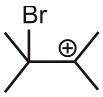
Single Choice Questions

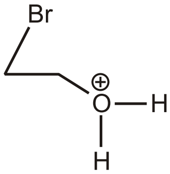
1. (E) **2.** (A) **3.** (D) **4.** (A) **5.** (B) **6.** (C) **7.** (C) **8.** (D)
9. (B) **10.** (E)

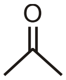
Unsolved Examples

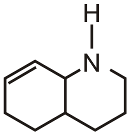
1. (a)  Br^-

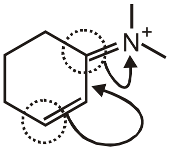
(b) 

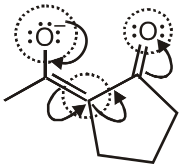
(c)  + Br⊖

(d) 

2. (a)  + H–O–H + Cl^-

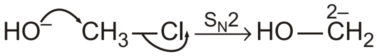
(b)  + HBr

3. 

4. 

Subjective Type Questions

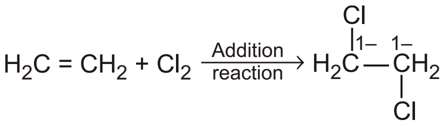
1. Isohyptic reactions are those reactions in which there is no change in the oxidation states of the carbon atoms participating in the reactions. Substitution reactions are found to be isohyptic reactions.



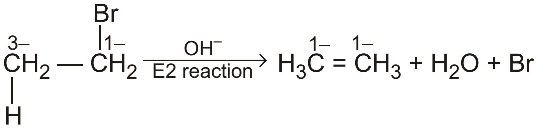
$$HO^- \; CH_3 - Cl \xrightarrow{S_N2} HO - \overset{2-}{C}H_2$$

In this reaction, the oxidation state of the carbon atom has not changed after the reaction. Therefore, it can be identified as an 'isohyptic reaction'.

In the case of addition and elimination reactions, there are changes in the oxidation state of the carbon atoms involved in the reaction.



$$H_2C = CH_2 + Cl_2 \xrightarrow[\text{reaction}]{\text{Addition}} H_2\overset{\overset{Cl}{|}\,1-}{C} - \underset{\underset{Cl}{|}}{\overset{1-}{C}}H_2$$



$$\underset{\underset{H}{|}}{\overset{3-}{C}}H_2 - \overset{\overset{Br}{|}\,1-}{C}H_2 \xrightarrow[\text{E2 reaction}]{OH^-} H_3\overset{1-}{C} = \overset{1-}{C}H_3 + H_2O + Br$$

The above mentioned two reactions, namely addition and elimination, may be considered as isohyptic reactions because they involve a change in the oxidation levels of the carbon atoms involved in the reactions.

❑❑❑