Chem Factsheet

www.curriculum-press.co.uk Number 267

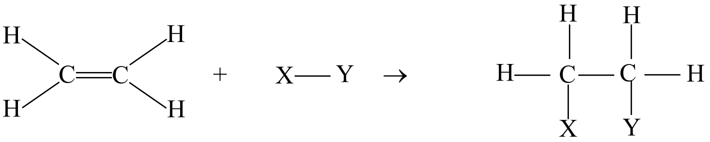
Addition Reactions in Asymmetric Alkenes

Addition Reactions

Simple alkenes of the general formula C_nH_{2n} undergo addition reactions with small electrophilic species such as hydrogen halides, halogen molecules, hydrogen gas and, under the right conditions, water.

A typical addition reaction can be summarised using the following equation: $C_nH_{2n} + X—Y \rightarrow C_nH_{2n}XY$

The reaction results in the formation of a single product with a 100% atom economy. However, the above reaction equation does not give any indication about the structural change that occurs. During an addition reaction, the π-component of the C=C breaks and the alkene loses its unsaturation to become a saturated (alkane-like) molecule. The two atoms in the electrophile (X and Y) bond, separately, to the two different carbons involved in the carbon-carbon double bond, C=C.

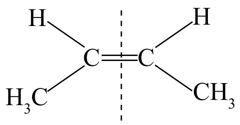


One Product or Two?

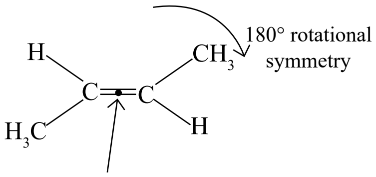
Although the above reaction scheme looks straightforward and appears to result in the formation of a single product, this is not always the case. In many reactions between alkenes and electrophiles, it is possible to generate two organic products, with one often favoured over the other. The simple reason for this is that the atoms within the electrophile have a 'choice' as to which of the two carbon atoms in the C=C they bond with. Two factors that complicate the addition process are: (i) the identity of the electrophile, and (ii) the symmetry of the alkene.

Where an alkene is symmetrical, that is to say, there is either reflectional symmetry (in the manner shown below; splitting the C=C between the carbon atoms), or rotational symmetry about the double bond, it is only possible to generate a single product irrespective of the electrophile.

For example, but-2-ene (in either *E* or *Z* configuration) exhibits symmetry about the centre of the double bond.



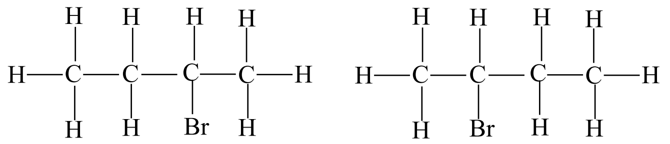
Plane of Symmetry



Centre of rotation

Consider two types of electrophile, homoatomic (e.g., Br_2), and heteroatomic (e.g., HBr) adding to either isomer of but-2-ene. In the first case, only bromine atoms can be added and these must be added to C2 and C3 (those involved in the C=C). The product will be 2,3-dibromobutane no matter which way around the bromine atoms add to the C=C and this is, of course, because the two atoms are identical.

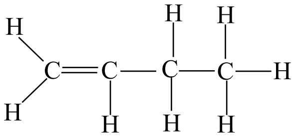
What happens when the atoms are different? When HBr adds to but-2-ene, there are two possible outcomes: either the H atom adds to C2 with the Br atom adding to C3 or *vice versa*. The structures of the products are, therefore:



However, we can quickly recognise that these two structures are, in fact, identical; both are called 2-bromobutane. In either case, using Br_2 or HBr, only one product is formed due to the inherent symmetry within the alkene molecule.

Asymmetric Alkenes

Let us now consider an alkene that does not exhibit the same sort of symmetry as either isomers of but-2-ene. Such a molecule is but-1-ene:

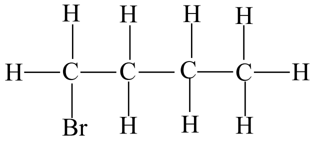


but-1-ene

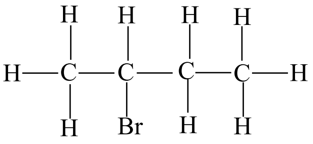
Although but-1-ene does contain planes of symmetry, these involve splitting atoms into halves (whereas this is not necessary for but-2-ene) and so, for the purposes of distinction, alkenes such as this will be termed asymmetric.

Let's go back to the same reactions as we had previously looked at for but-2-ene. When but-1-ene reacts with a homoatomic species such as Br_2, only one product can be formed as, irrespective of the order with which the bromine atoms add, the same atom (Br) is added to each carbon atom in the double bond. The product will always be 1,2-dibromobutane.

However, with HBr, depending on which way around the H and Br atoms add to C1 and C2, the result is two different products: 1-bromobutane and 2-bromobutane.



1-bromobutane forms when H adds to C2 and Br adds to C1



2-bromobutane forms when H adds to C1 and Br adds to C2

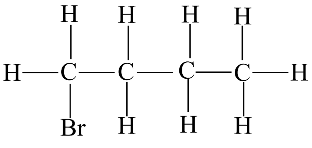
When a heteroatomic species, such as a hydrogen halide or water adds to an asymmetric alkene such as but-1-ene, the result is two different organic products. It might be reasonable to believe that the resulting mixture would contain equal quantities of each of the two products. However, this is very rarely the case—the formation of one product is favoured over the other.

Predicting the Major Product

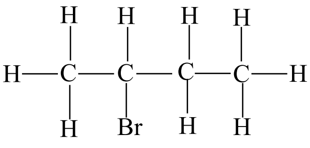
The two organic products produced in the reactions of asymmetric alkenes are termed major (greater abundance) and minor (lower abundance) products. Is it possible to determine which of the products is which? The answer is 'yes', with the use of a simple memory aid,

Markovnikov's rule

The essence of Markovnikov's rule is that when a molecule HX (where X is typically a halogen) adds to an asymmetric alkene, the hydrogen atom will bond to the carbon atom in the double bond that is already bonded to the greater number of hydrogen atoms. You can think of this as 'safety in numbers' or as 'those that have, shall have more' if it helps. In but-1-ene, C1 is bonded to two hydrogen atoms, whereas C2 is only bonded to a single hydrogen atom. Applying Markovnikov's rule to but-1-ene, we would predict the hydrogen atom in HBr to bond, preferentially, to C1 which has the greater number of hydrogens attached. This would leave the bromine atom to attach to C2. The outcome is that 2-bromobutane should be produced in greater abundance, and this is exactly what is observed experimentally.



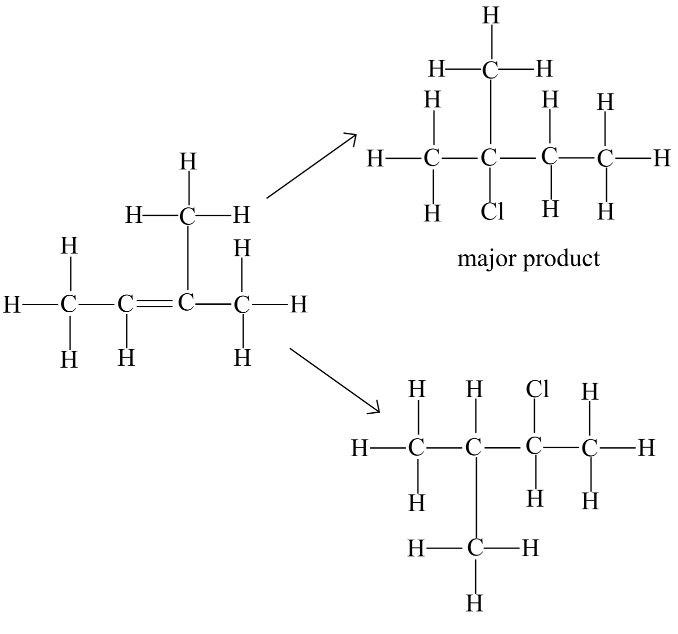
minor product



major product

As a further example of applying Markovnikov's rule, let us consider the addition of HCl to 2-methylbut-2-ene:

In 2-methylbut-2-ene, C2 has no hydrogen atoms attached whereas C3 has a single hydrogen atom attached. Markovnikov's rule suggests that when this alkene reacts with HCl, the hydrogen atom should bond to C3, leaving the chlorine atom to bond to C2 and give 2-chloro-2-methylbutane as the major product with a small quantity of 2-chloro-3-methylbutane also produced.



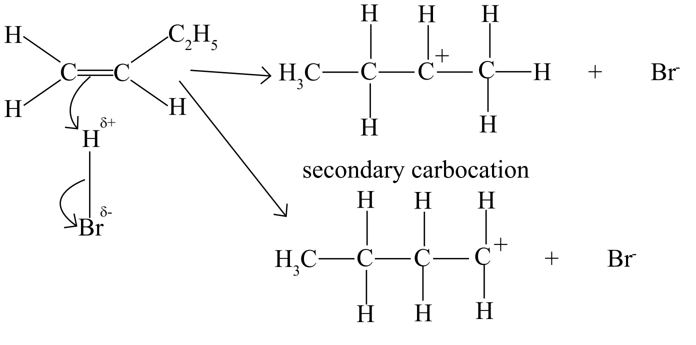
major product

minor product

Why Are There Two Products?

Although Markovnikov's rule is useful for predicting which of the possible products of an addition reaction is likely to be produced in the higher quantity, it does nothing to explain why there is such a clear preference for one product over the other. The production of major and minor products can be accounted for by considering the electrophilic addition mechanism via which these reactions proceed. Here, we will use the reaction of but-1-ene and HBr to illustrate the key points.

In the first step of the mechanism, a pair of electrons from the π-component of the C=C attacks the δ^+ hydrogen atom in the HBr molecule with concurrent heterolytic fission of the H—Br bond. The result is the formation of an intermediate carbocation and a bromide ion. In the case of but-1-ene, there are two possible carbocation intermediates depending on which carbon atom of the double bond the hydrogen atom attaches to.



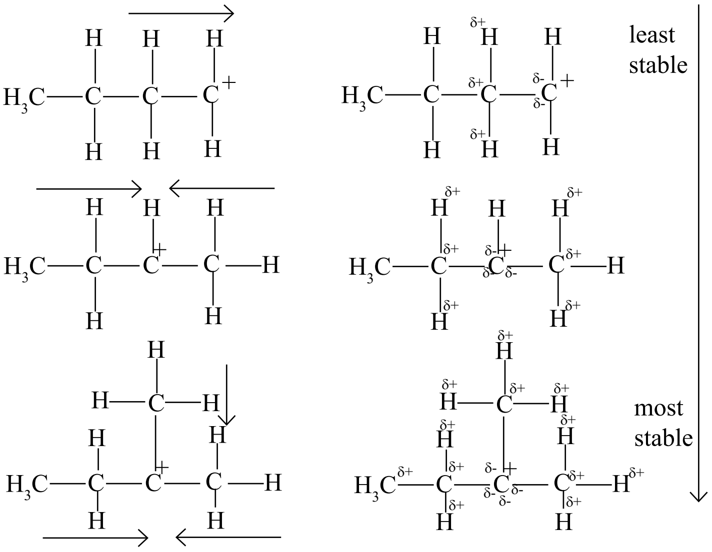
secondary carbocation

primary carbocation

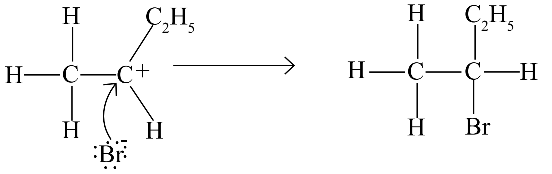
It is during this first step, involving the formation of the carbocation, that the preferential production of the major product is determined. Carbocations have different stabilities depending on whether they are primary, secondary or tertiary. The general rule for the stability of carbocations is:

PRIMARY < SECONDARY < TERTIARY
least stable most stable

Carbocation stability depends on the availability of **electron-releasing** alkyl groups to stabilise the positive charge through a **positive inductive effect**. Typically, the more alkyl groups that surround the positive charge, the greater the degree of stabilisation as the charge can be spread more effectively. In tertiary carbocations, the positive charge is surrounded by three alkyl groups whereas in primary carbocations there is only a single alkyl group adjacent to the positive charge.



In our reaction, the mechanism can proceed via a primary carbocation or a secondary one. Given the greater stability of the secondary carbocation, the mechanism proceeds via this intermediate far more often than it does via the primary alternative. This means that in the final step of the mechanism, when the bromide ion attacks the positively-charged carbon atom, this is more likely to be occurring at C2 than C1, resulting in more 2-bromobutane be formed.

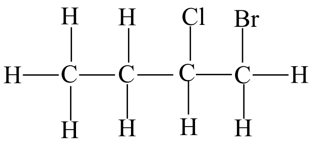


Interhalogen Compounds

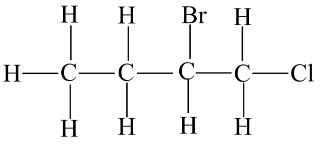
In the majority of questions, the electrophile will be a hydrogen halide and so a quick application of Markovnikov's rule should get you to the correct major product. Note that Markovnikov's rule cannot be used as an explanation of the formation of the major product, and any such effort should go into the details of carbocation stability. Remember that there is a choice of two different carbocations (one will be more stable that the other) and so your explanation should be written as a comparison. In trickier questions, the hydrogen halide may be switched for an interhalogen compound, a diatomic molecule comprising two different halogen atoms, e.g. I—Br or Br—Cl. Most descriptions of Markovnikov's rule refer only to where to place the hydrogen atom in a molecule of HX, and here we have no hydrogen.

Again, thinking about the mechanism becomes useful. In the very first stage of the reaction, the π-electrons attack the hydrogen atom; why? This is because the hydrogen atom is the δ^+ end of the polar HX molecule and so there is an attraction between the π-electrons and the small positive charge on the hydrogen atom. We can apply this to the interhalogen compounds. In each case, one halogen atom will be less electronegative than the other and will form the δ^+ end of the molecule. For halogens, the lower down the group the element, the less electronegative the atom. Therefore, in I—Br, the iodine atom will be δ^+ but in Br—Cl the bromine atom will be δ^+. The δ^+ atom can now be treated in the same way as the hydrogen atom in HX and Markovnikov's rule applied. The δ^+ atom will bond to the carbon atom in the C=C with more hydrogen atoms attached.

For example, in the reaction of but-1-ene with Br—Cl, the bromine atom will join to C1 and the chlorine atom will join to C2 giving 1-bromo-2-chlorobutane as the major product.



major product



minor product

Questions

1. Predict the major product in each of the following reactions:
   (a) Hydrogen iodide with propene
   (b) Hydrogen bromide with 2-methylpent-2-ene
   (c) I—Cl with pent-1-ene

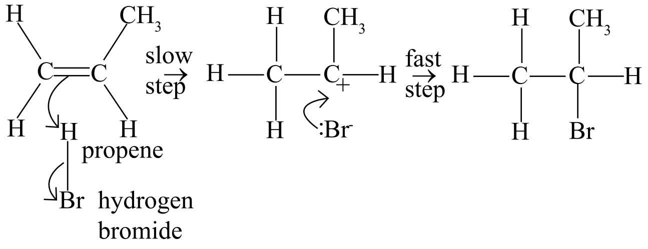
2. Explain the formation of the major product in the reaction of hydrogen chloride with methylpropene.

3. Give the mechanism for the reaction of propene with HBr resulting in the formation of the major product.

Answers

1. (a) 2-iodopropane
   (b) 2-bromo-2-methylpentane
   (c) 2-chloro-1-iodopentane

2. Major product is 2-chloropropane.
   Reaction can proceed via primary or secondary carbocation intermediates.
   Secondary carbocation is more stable than the primary.
   Secondary carbocation has two electron-releasing alkyl groups whereas primary only has one.
   Stronger positive inductive effect in secondary carbocation.



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