9.3: ALKENE ASYMMETRY AND MARKOVNIKOV'S RULE

Learning Objective

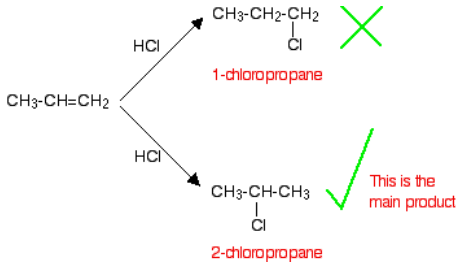
- predict the products/specify the reagents for EAR of hydrohalic acids (HX) with asymmetrical alkenes using Markovnikov's Rule for Regioselectivity
- apply the principles of regioselectivity and stereoselectivity to the addition reactions of alkenes

ADDITION TO UNSYMMETRICAL ALKENES

In terms of reaction conditions and the factors affecting the rates of the reaction, there is no difference whatsoever between these alkenes and the symmetrical ones described above. The problem comes with the orientation of the addition of the hydrogen and the halogen across the double bond.

MARKOVNIKOV'S RULE

If HCl adds to an unsymmetrical alkene like propene, there are two possible ways it could add. However, in practice, there is only one major product according to Markovnikov's Rule.



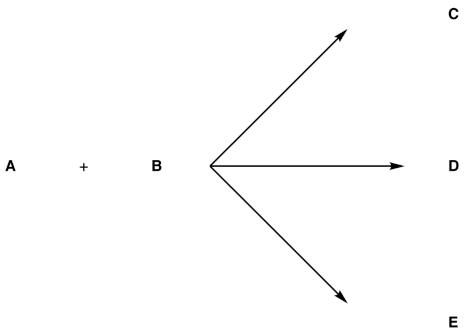
Markovnikov's Rule: When HX is added to an unsymmetrical alkene, the hydrogen becomes attached to the carbon with the most hydrogens attached to it already.

Applying Markovnikov's Rule to the reaction above, the hydrogen bonds with the CH_2 group, because the CH_2 group has more hydrogens than the CH group. Notice that only the hydrogens directly attached to the carbon atoms at either end of the double bond count.

REGIOSELECTIVITY - A CLOSER LOOK

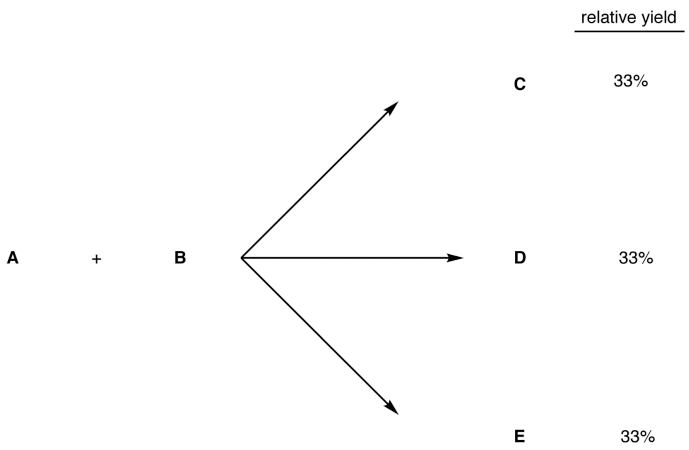
If more than one reaction could occur between a set of reactants under the same conditions giving products that are constitutional isomers and if one product forms in greater amounts than the others, the overall reaction is said to be regioselective.

Say three reactions could occur between the hypothetical reactants **A** and **B** under the same conditions giving the constitutionally isomeric products **C**, **D**, and **E**.



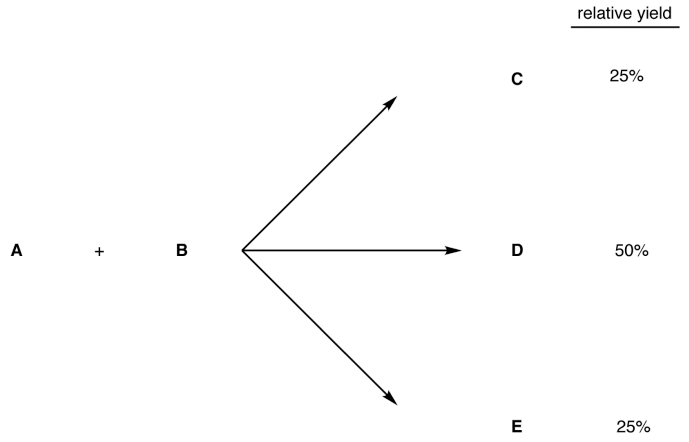
There are two possibilities:

1. The three products form in equal amounts, i.e., of the total product 33% is **C**, another 33% **D**, the remaining 33% **E**. (These percentages are called relative yields of the products.)



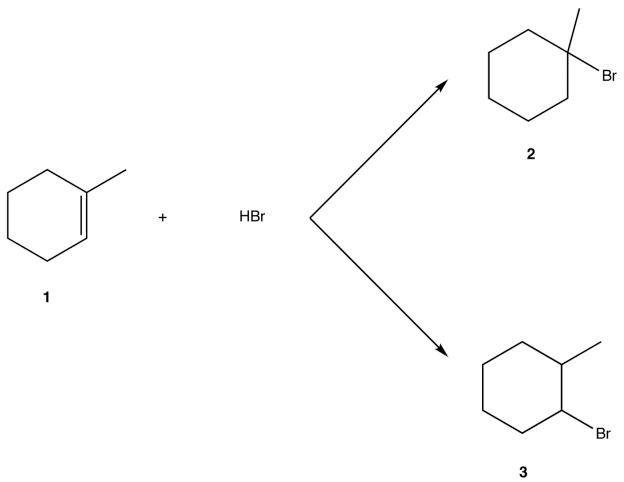
If this is what is observed, the overall reaction between **A** and **B** is not regioselective.

2. One product forms in greater amounts than the others. Say, for example, the relative yields of **C**, **D**, and **E** are 25%, 50%, and 25%, respectively.



If this is what is observed, the overall reaction between **A** and **B** is regioselective.

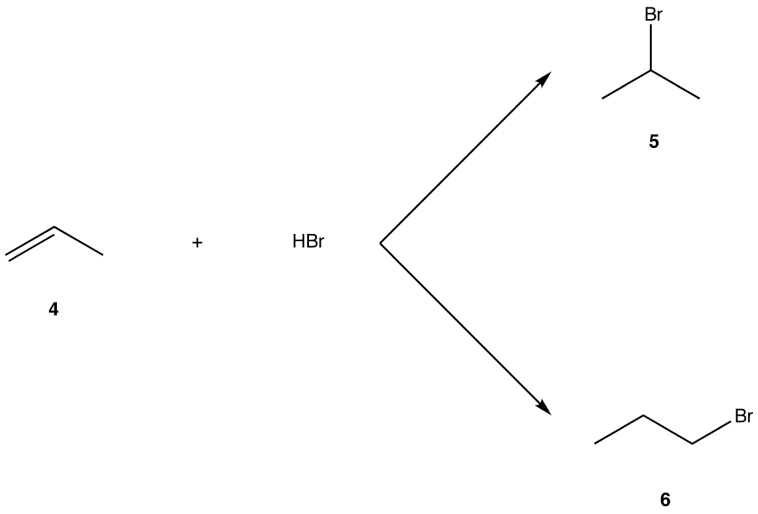
eg:



Experimentally, **2** is the major product; **3** is the minor product. Thus, the overall reaction between **1** and HBr is regioselective toward **2**.

If more than one reaction could occur between a set of reactants under the same conditions giving products that are constitutional isomers and if only one product is observed, the overall reaction is said to be 100% regioselective or regiospecific.

eg:

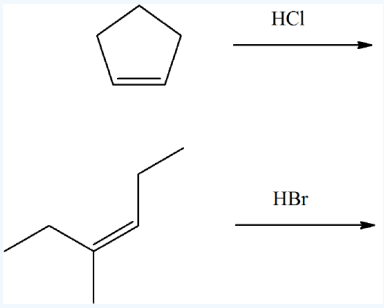


The only observed product is **5**. (Relative yields of **5** and **6** are 100% and 0%, respectively.) Thus the overall reaction between **4** and HBr is regiospecific toward **5**.

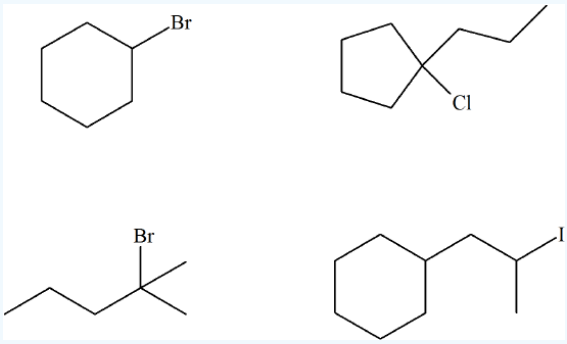
Regiospecificity is merely the limiting case of regioselectivity. All regiospecific reactions are regioselective, but not all regioselective reactions are regiospecific.

Exercises

1. Predict the product(s) for the following reactions:

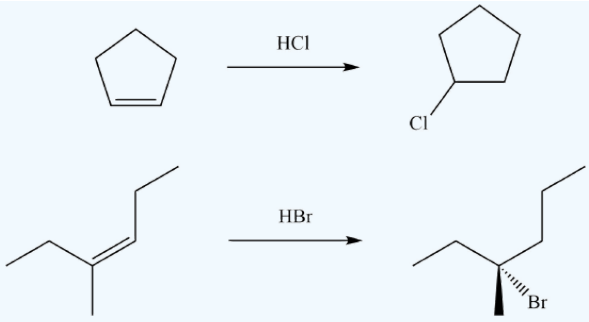


2. In each case, suggest an alkene that would give the product shown.

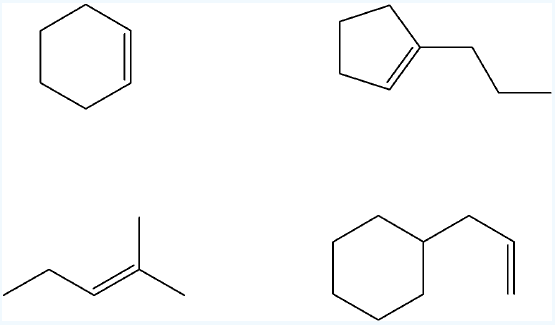


Answers

1.



2.



CONTRIBUTORS AND ATTRIBUTIONS

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