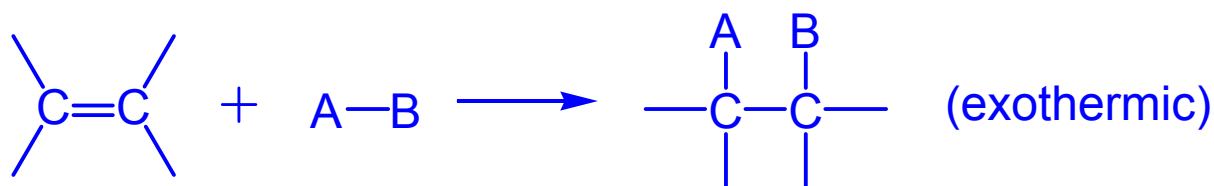


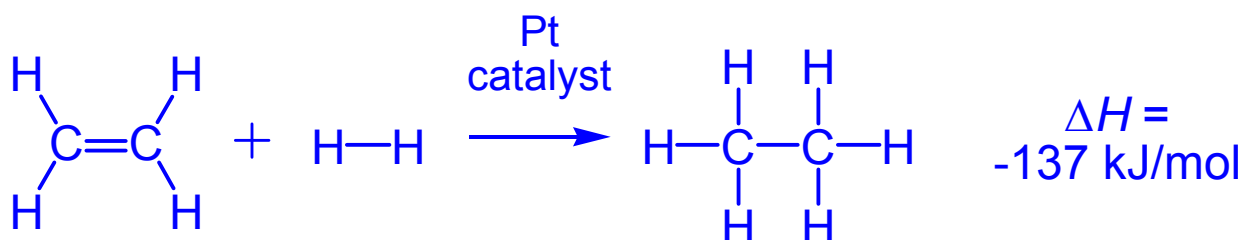
5. Reactions of Alkenes (text 5.1 – 5.5)

A. Addition Reactions

- In Chapter 4, we saw that π bonds have electron density on two sides of the π bond. The π bond is reactive and will attract electron-seeking reagents (**electrophiles**).
- The main reaction of alkenes is that some AB species reacts to break the π bond and forms two new σ bonds.



- Additions are usually exothermic and occur spontaneously at room temp as soon as the two reagents are mixed.



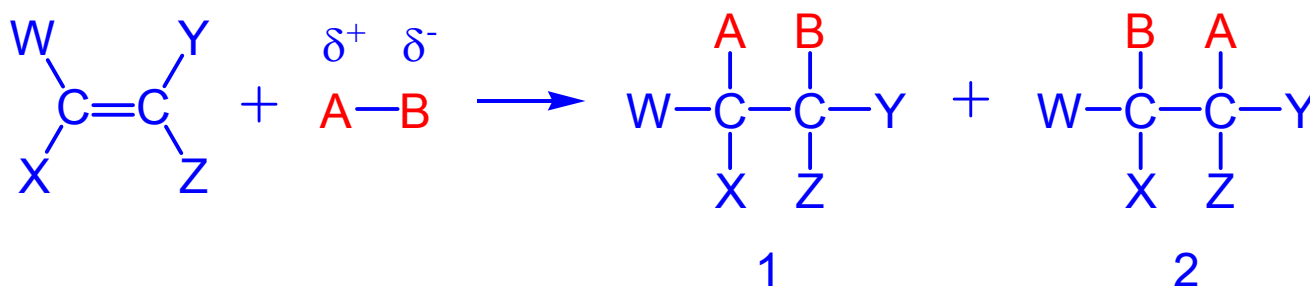
bonds broken =

bonds formed =

- Textbook page 120 lists the addition reactions we will study. They simply differ in AB (e.g. Br_2 , HCl , H_2O , H_2 , etc.).
- To fully understand the structure and stereochemistry of the products formed, we need to look at the **sequence of steps** which occur as the reaction proceeds, i.e. the **mechanism**.

B. Electrophilic Addition Reactions

- The addition of AB to a π bond proceeds well when the AB species contains a polar bond, *i.e.* $A^{\delta-}-B^{\delta+}$, or when the species behaves as though it were A^+ and B^- .
- Two constitutional isomers can be formed:

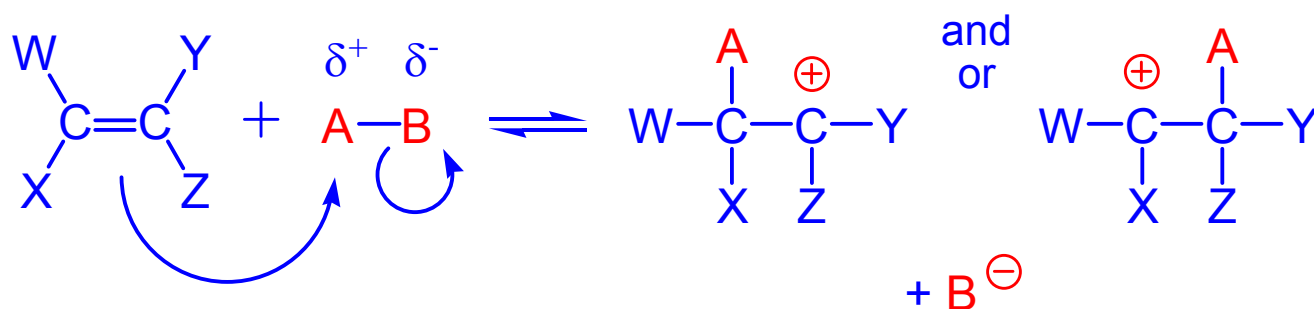


- The structural isomers (1 and 2), which are formed by reactions, are known as **regioisomers**. The addition of AB can take place on different regions of the alkene
- If, as is often the case, one regioisomer (1 or 2) is formed in greater amount, the reaction is said to be **regioselective**.
- All additions of polar AB to π bond proceed by a common sequence of steps (reaction mechanism) known as an **electrophilic addition reaction**.
- Electrophilic (electron loving) reactions are usually highly regioselective, *i.e.* they favour one regioisomer.

C. Mechanism of Electrophilic Addition

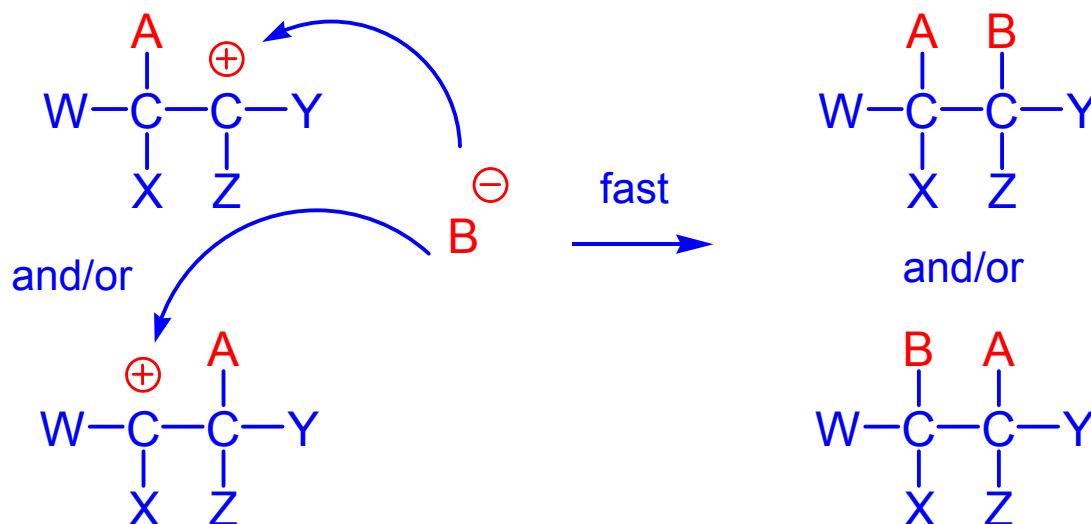
- The reaction proceeds in two sequential steps.

Step 1 (an electrophilic step)

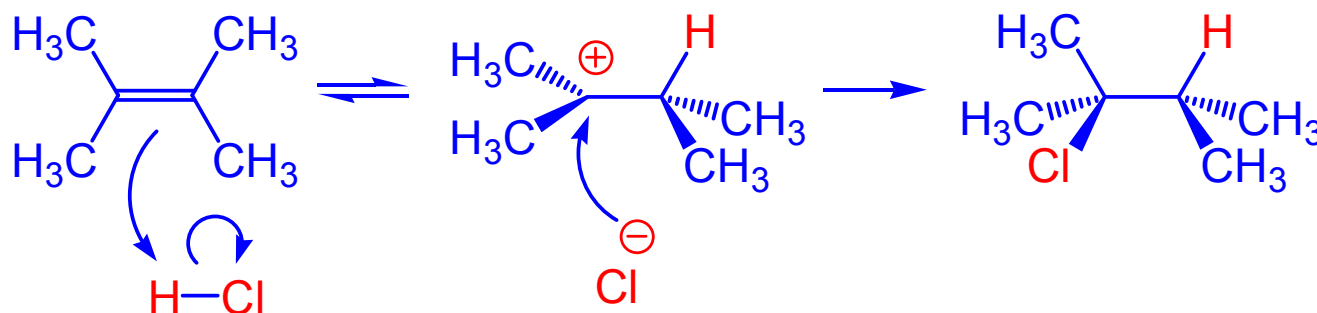


- The first step involves an electrophilic *attack* of the positive A species (termed an electrophile) on the π electron pair of the alkene C=C.
- This results in:
 - The breaking of the original A–B bond, where the σ bond of AB moves entirely onto the B group
 - The breaking of the C=C π bond
 - And the formation of a C–A σ bond
- This step results in the formation of a positively charged intermediate known as a *carbocation*.
- Since two bonds are broken ($\sigma + \pi$), but only one is formed (σ), this step is endothermic and is the slower, rate-determining step of the reaction.

Step 2 (a nucleophilic step)



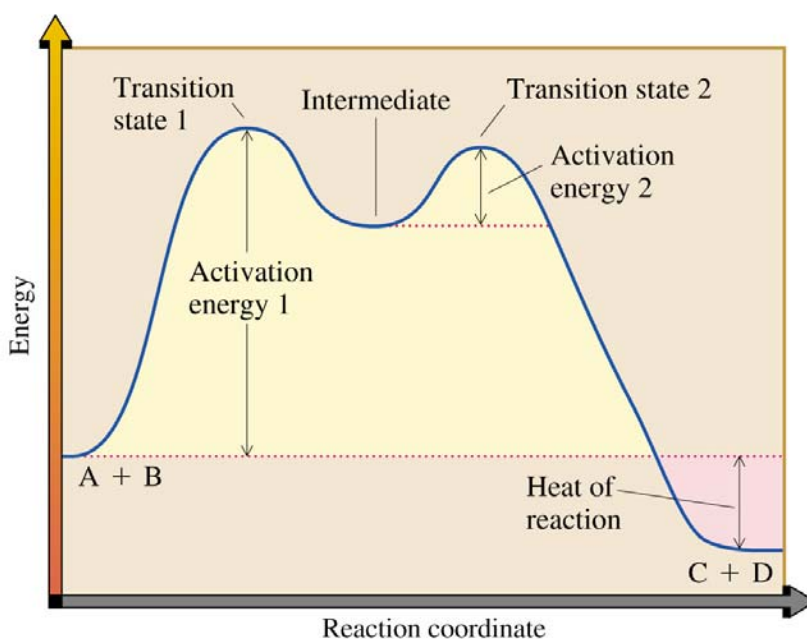
- The second step involves nucleophilic (nucleus/positive loving) attack of the carbocation by B^- (the nucleophile). This forms a new C–B σ bond, and is fast and exothermic.
- The general mechanistic scheme can be used as a model to draw the mechanism for the addition of specific reagents to specific alkenes, e.g., addition of HCl.



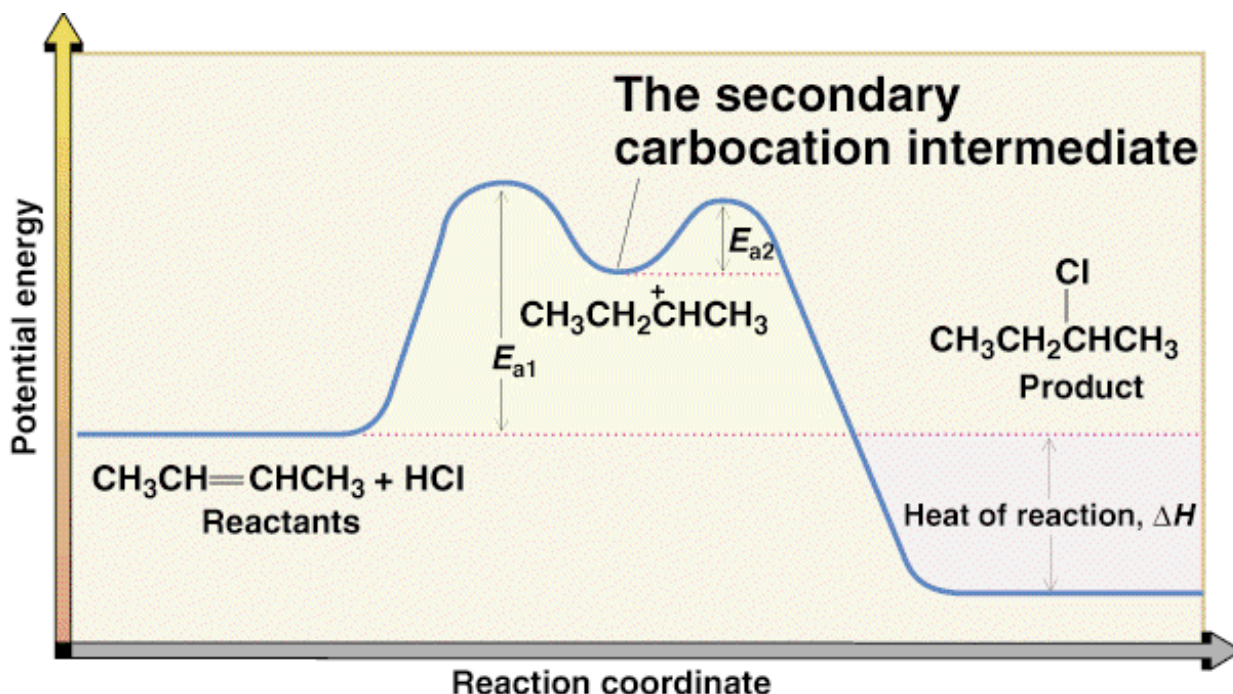
- In the above case, the addition of H and Cl to different atoms gives the same product (symmetric starting material).

D. Energy Diagram for Electrophilic Addition

- If AB adds to asymmetrical alkenes, one of the two possible regioisomers is usually formed in a greater amount. To predict the predominant product, we need to know how the course of the reaction depends on the energy of the carbocation intermediate.
- The progress of a reaction can be plotted against the energy of the species involved.
 - Difference between reactants and products is approximated by ΔH (enthalpy of reaction)
 - An energy barrier (activation energy) between the reactants and products.
 - The high points are transition states. Intermediates are short-lived species formed in one step of a reaction mechanism and used in the next.



- The plot below shows the addition of HCl to 2-butene.



- Features of the plot
 - The E_a for the first step (E_{a1}) is the highest point on the curve, so the first step is the slow, rate-determining step.
 - The intermediate carbocation, with a + charge on a 2° carbon, is more stable than the transition states that will lead it to the product or back to the reactant.
 - The E_a for the second step (E_{a2}) is much smaller than E_{a1} , so the second step is fast once the carbocation is formed.
 - The products are more stable than the reactants (negative ΔH is exothermic).
- The shape of the plot is typical for the addition of most polar compounds to alkenes.

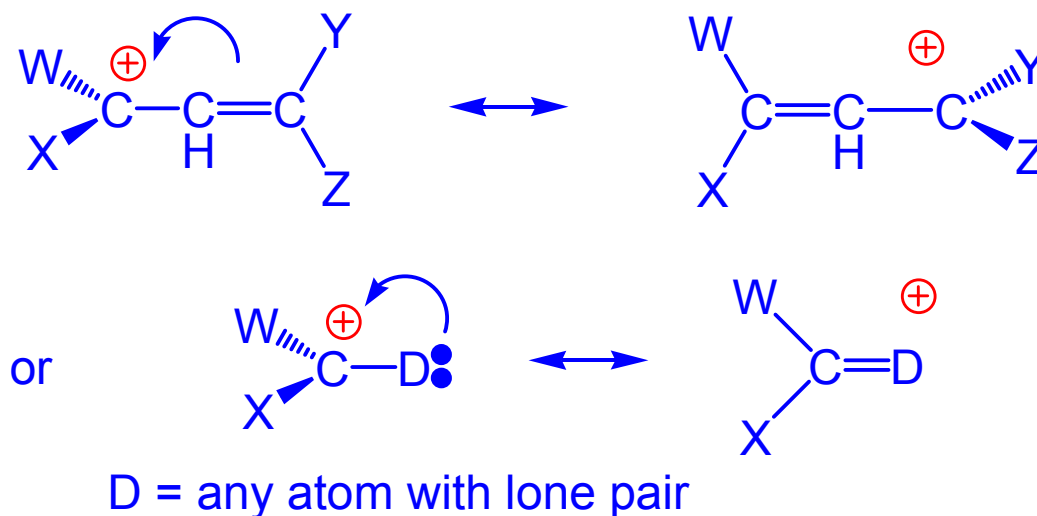
- **Note:** Since formation of the carbocation is the slow step of the reaction, it follows that:
 - The rate of the addition increases as the stability of the carbocation intermediate increases.
 - Of the two possible carbocations that can form, the one that is more stable will be formed in the greater amount.
 - This means that the regioisomer formed in the greater amount will be the one with the nucleophile (B species in AB) bonded to the carbon atom which is the more stable carbocation.
 - This statement is a better and more modern restatement of a 19th-century generalization known as Markovnikov's Rule
- Therefore, to be able to predict the predominant regioisomer, we need to predict carbocation stability. Recall that stability refers to *thermodynamic* stability.
- The more stable carbocation will be formed in a greater amount, which leads to the predominant regioisomer.

E. Assessing Carbocation Stability

- We use the same criteria that we used for electrons (acids and bases), but we only need to look at the C atoms. Thus, the two most important criteria are **resonance and induction**.

Resonance Stabilization

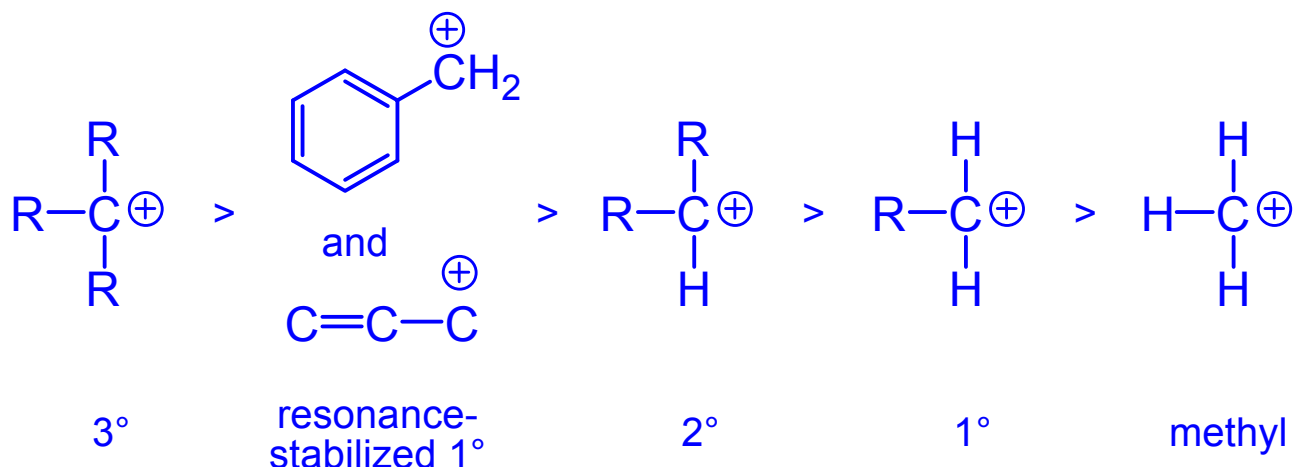
- A carbocation is sp^2 -hybridized, with three σ bonds and an empty p orbital. Resonance stabilization of the positive charge by neighbouring groups (π bonds or electron-pair donors) is possible.



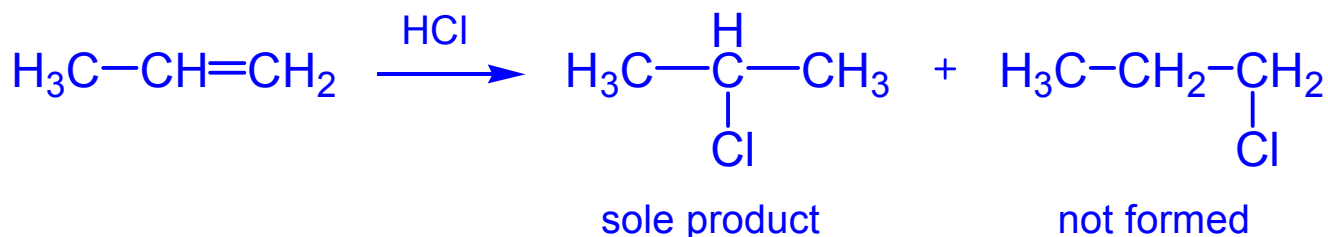
Inductive Stabilization

- Alkyl groups allow their σ electrons to shift slightly towards the carbocation, thus stabilizing by induction.
- So, the more alkyl groups attached to the C^+ , the more stable it is.

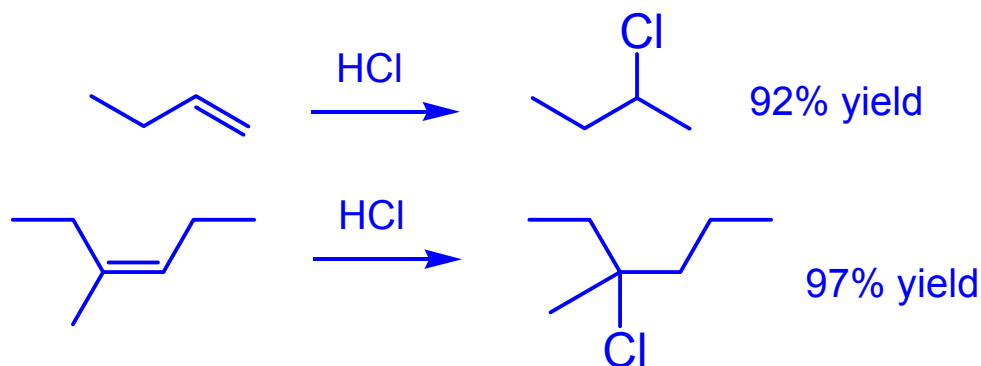
- Combining resonance effects, we have this order for carbocation stability. Note that on exams, we will only give you scenarios that you can compare and deduce.



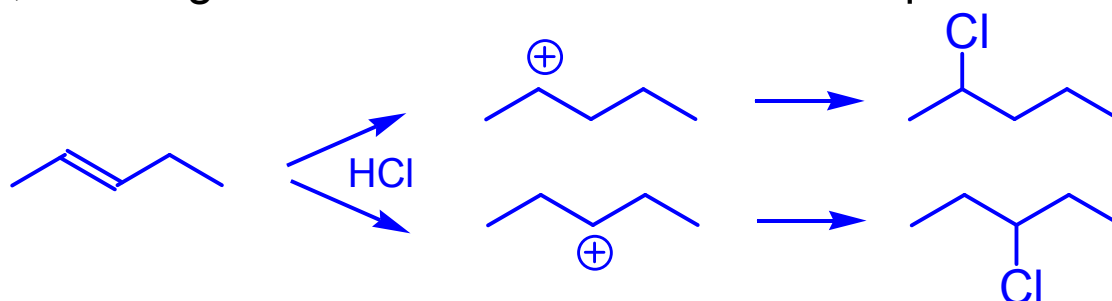
- So, we can understand why some reactions are region-selective. In the example below, only one product is made.



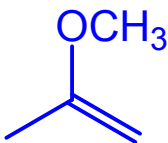
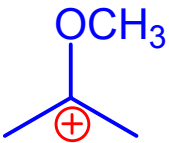
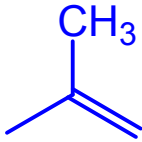
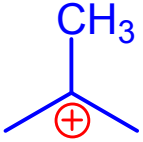
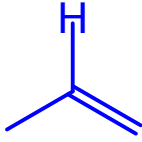
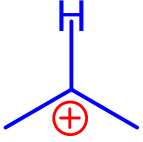
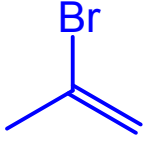
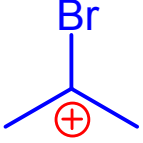
- Some real examples from the lab (you have to be able to predict the major product, but not the yield):



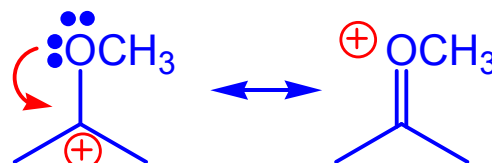
- In some alkenes, both carbocations are of similar stability. So, both regioisomers are formed in about equal amounts.



- It is also possible to predict the relative rates of addition reactions by examining the relative stabilities of the intermediate carbocations (the slow step). e.g. measured relative rates for the addition of water to these alkenes:

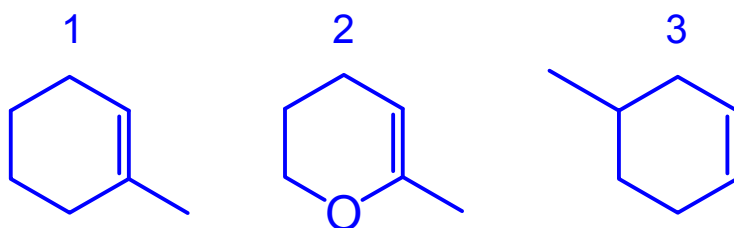
Alkene	Carbocation	Rel. Rate for water addition	Stability rank
		17000	1
		7500	2
		1	3
		0.22	4

- The 1st is a resonance-stabilized 2° cation, while the 2nd is a 3° cation, and the 3rd is 2° cation.

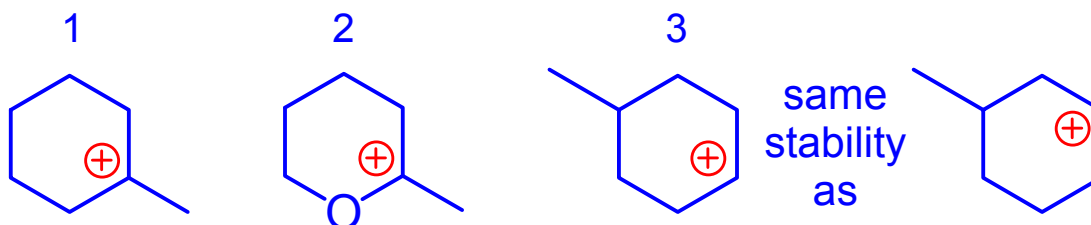


- Although oxygen is electronegative, resonance donation of the lone pair makes O an excellent carbocation stabilizer. Electron donation by resonance greatly outweighs withdrawal by induction.
- The 4th is destabilized by an inductively withdrawing Br. (Halogens stabilize negative charges, not positive). Br cannot donate by resonance because of poor orbital overlap (it is not on the same row as oxygen).
- Recognize the factors that stabilize carbocations. Do not simply memorize that 3° is more stable than 2°, etc.
- Summary: the mechanism of electrophilic addition allows...
 - The prediction of the major regioisomer formed
 - The prediction of the relative rates of addition of different alkenes.

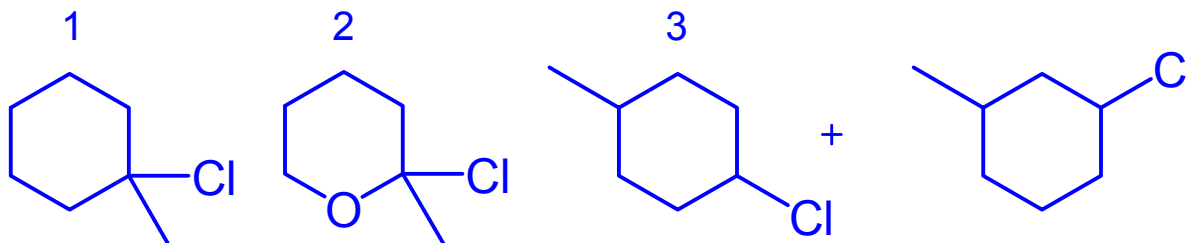
- For each of the three following alkenes, draw the structure of the most stable carbocation, the structure of the major addition product upon reaction with HCl, and indicate their relative rates of reaction.



most stable carbocations are:



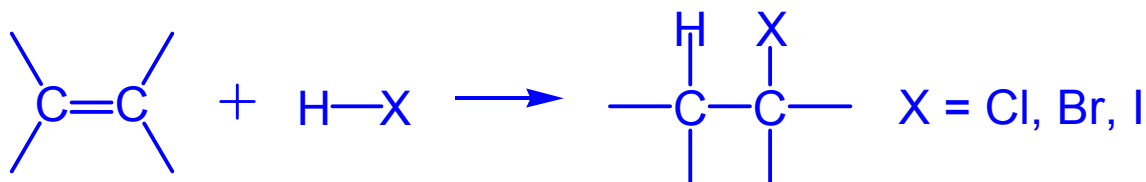
major products after reaction with HCl:



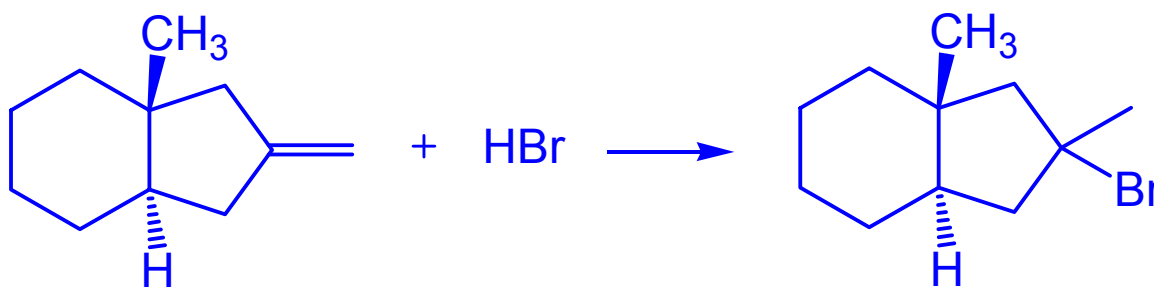
- The relative carbocation stabilities are compounds $2 > 1 > 3$, so the relative rates of reaction are $2 > 1 > 3$.

F. Alkene Addition Reactions

1. Addition of Hydrogen Halides (HCl, HBr, HI)

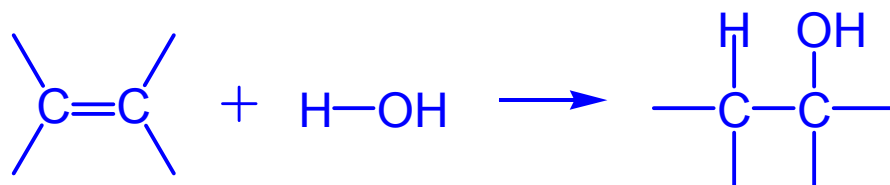


- Specific example:

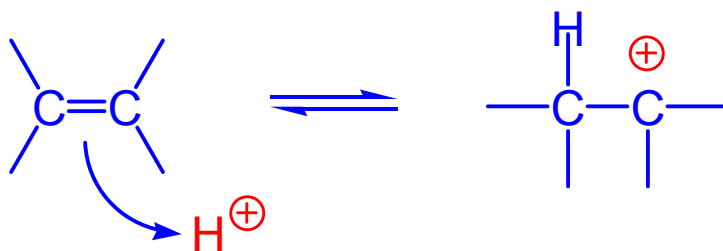


- Note: When applying generic reactions to specific molecules, you only need to focus on the functional group undergoing the reaction. The non-reactive part of the molecule remains unchanged.

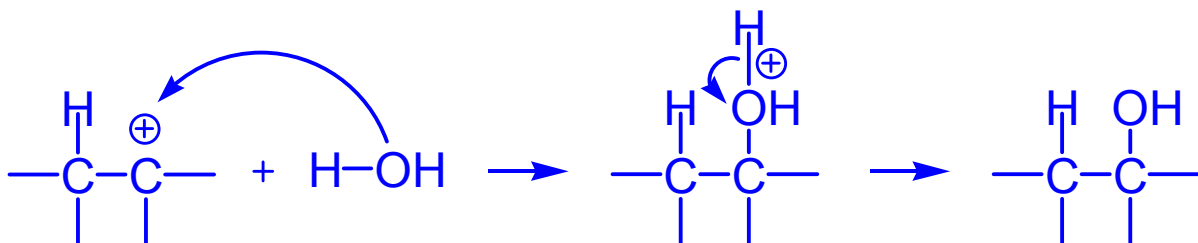
2. Addition of Water



- Although the H-OH bond is polar, usually the reaction requires the addition of a small amount of acid (usually a drop of a strong inorganic acid, *e.g.* H₂SO₄) to initiate the electrophilic step of the addition. Thus, the 1st step is:

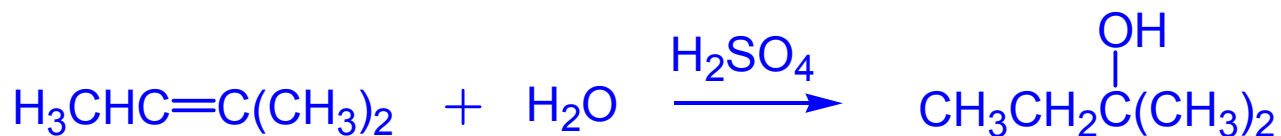


- H⁺ is present as H₃O⁺, but we can write H⁺ for simplicity.
- In the acid-catalyzed addition of water, there is no OH⁻, so the second step must use H₂O as the nucleophile. H₂O can function as such because it has a lone pair of electrons.



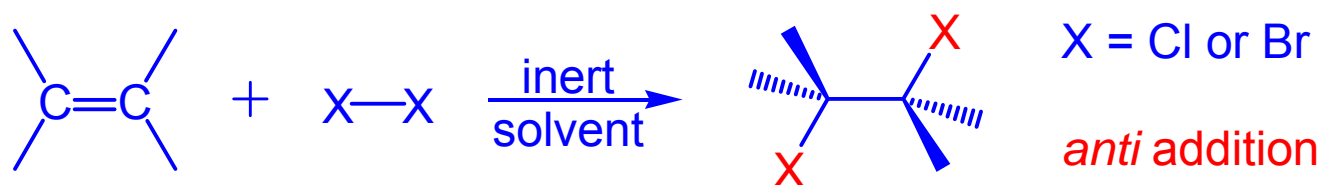
- After H₂O forms a new σ bond, the O atom acquires a formal charge of +1 and is therefore called the **oxonium ion**. This ion releases an H⁺ to give the uncharged product.

- Note that in the overall mechanism, H^+ is consumed in the first step but regenerated in the second step. There is no overall change in H^+ concentration, *i.e.* it is a catalyst.
- Specific example:

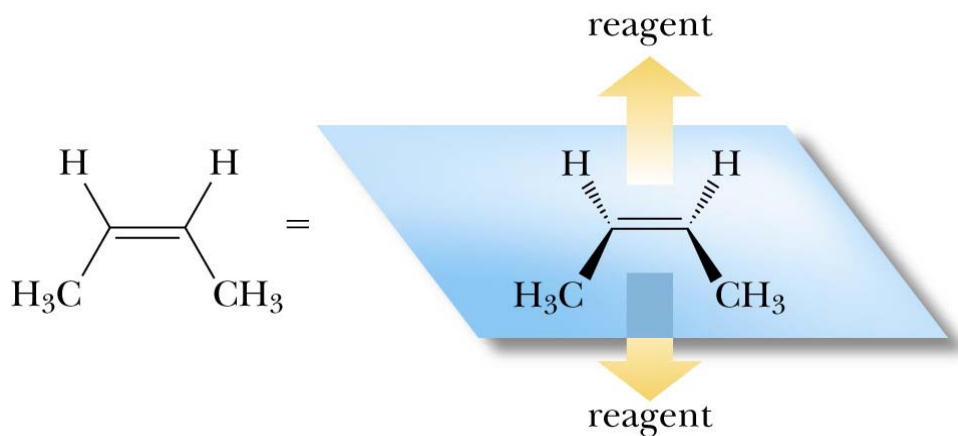


- Compounds written over or under the reaction arrow are usually catalysts or solvents; *i.e.* they don't act as reagents.

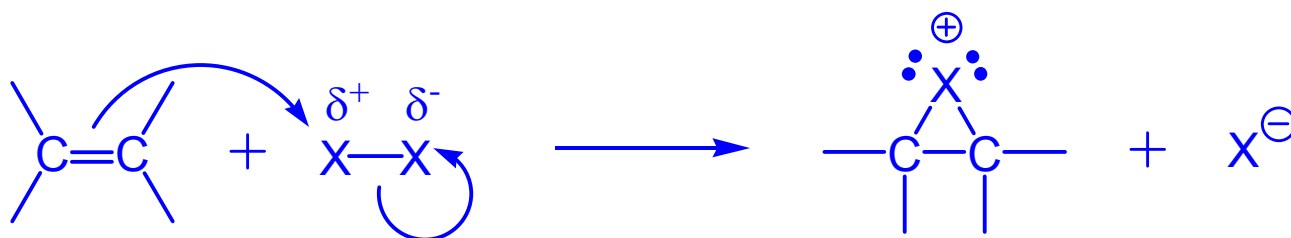
3. Addition of Halogens (Cl_2 and Br_2)



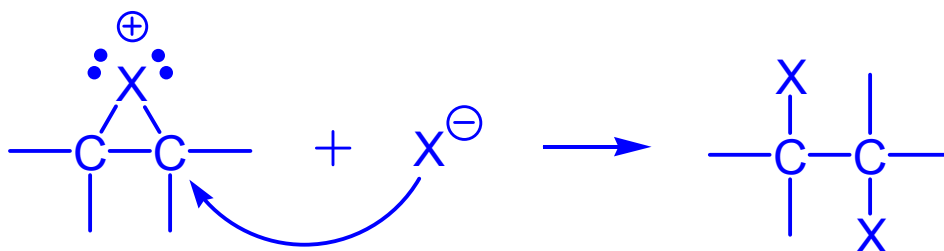
- Inert solvent is usually CCl_4 or CH_2Cl_2 . *Anti* addition means that the two X atoms add to the opposite sides of the double bond (recall planar nature of $\text{C}=\text{C}$ bond).



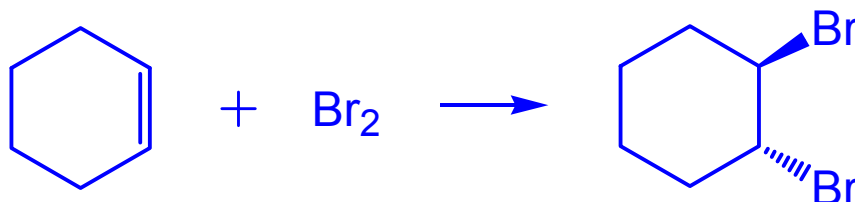
- *Anti* addition is achieved by the formation of a cyclic, or bridged, **halonium ion** in the first step of the reaction.



- The normally non-polar X_2 is polarized into δ^+ and δ^- when the halogen molecule approaches the electron-rich π bond.
- The positively charged X forms bonds to each of the alkene C, forming a 3-membered ring and a +1 formal charge.
- When $X = \text{Cl}$, the cyclic ion is called a *chloronium ion*. If $X = \text{Br}$, then it is called a *bromonium ion*.
- In the second step of the reaction, the intermediate halonium ion blocks attack by X^- from one side of the C-C bond. The X^- forms a new bond only from the opposite side; this is called **anti addition**.



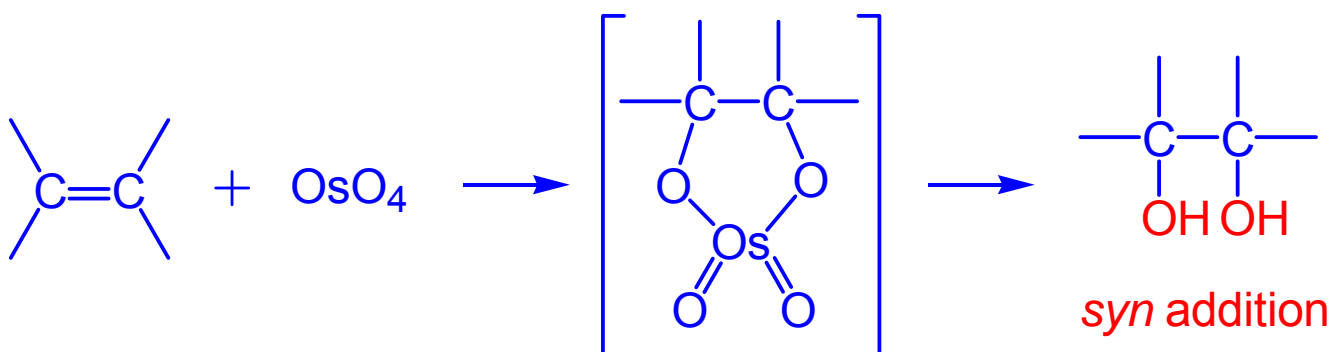
- *Anti* addition is most noticeable for cyclic compounds, where the *trans* isomer is always formed.
- Because one stereoisomer is preferentially formed in halogen addition reactions, the reaction is also *stereoselective*.



- The treatment of a compound with Br_2 provides a good, simple test for the presence of a π bond in a molecule. Br_2 is red-coloured and the addition product is colourless.
- If the red colour disappears quickly upon reaction with that compound, it is likely the compound contains a π bond (but rings themselves don't react).
- Thus, treatment with Br_2 is an easy way to decide if a unit of unsaturation is caused by a ring or a π bond.
- Example: One mole of C_8H_{12} decolourizes exactly 2 moles of Br_2 solution. How many rings does the compound contain?

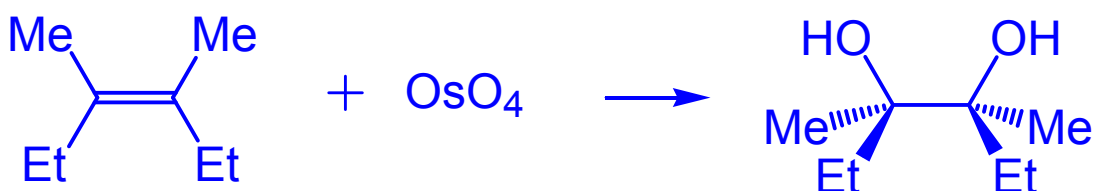
G. Oxidation of Alkenes

- In intro chem, we learned that C has oxidation states ranging from -4 (CH_4) to $+4$ (CO_2).
- Reactions that increase the oxidation number of C are called oxidation reactions, while those that reduce the oxidation number are called reduction reactions. (See review sheet on the assignment of oxidation numbers).
- Oxidation of an alkene by osmium tetroxide (OsO_4):



- Produces a 1,2-dihydroxy compound known as a glycol
- The intermediate forms both C–O bonds on the same side of the double bond. Both OH groups end up on the same side, and this is called *syn addition*.
- In the reaction, both C atoms of the π bond are oxidized, so the original alkene as a whole is said to have been oxidized.

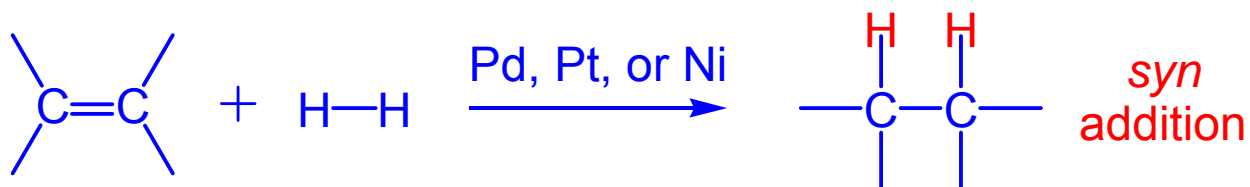
- The reduction products of OsO_4 are usually not included in the reaction equation. Organic reactions are usually not shown in their fully balanced form! Only changes in organic molecules are shown... organic chemists only care about the molecule they're after.
- Specific example of alkene oxidation:



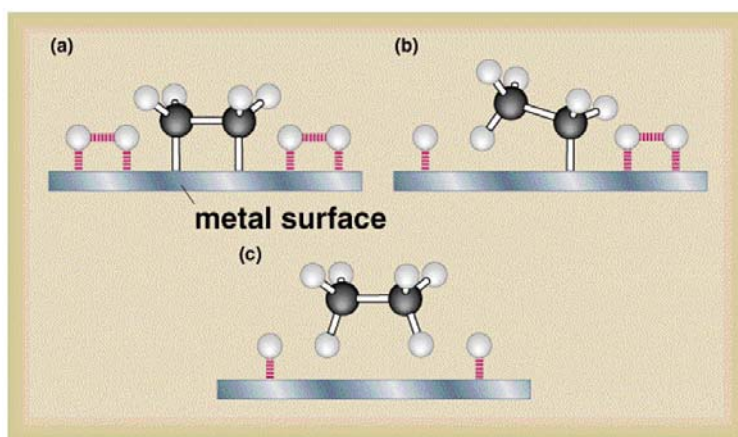
- The same product can be made using potassium permanganate (KMnO_4). In Expt 3, its purple colour disappears as the reaction proceeds in the presence of an alkene.
- Be sure you know how to determine oxidation numbers.

H. Reduction of Alkenes by Hydrogenation

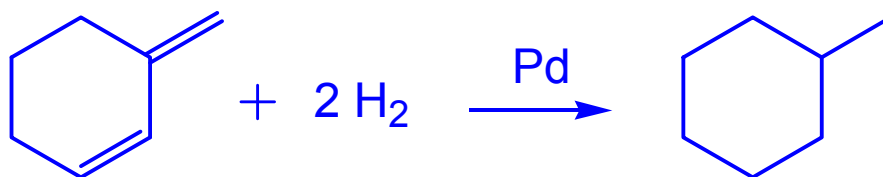
- In reductive hydrogenation by H_2 , a metal catalyst is usually required for the reaction to proceed.



- Hydrogenation occurs on the metal surface; both H add to the same side of the double bond (*syn*). Both C of the π bond are reduced, so the alkene as a whole is reduced.

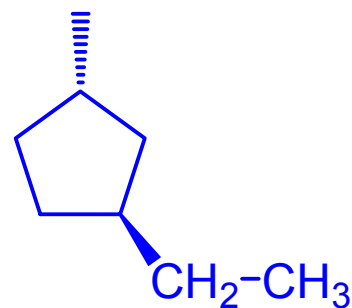
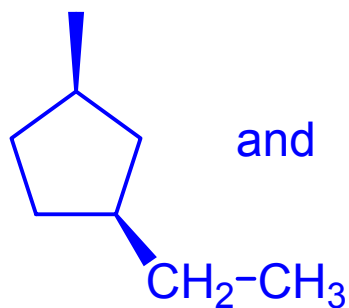
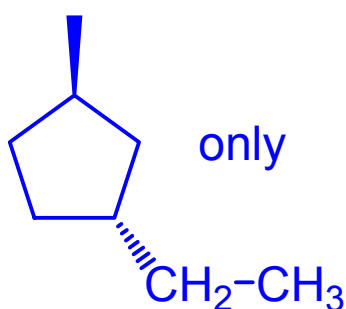
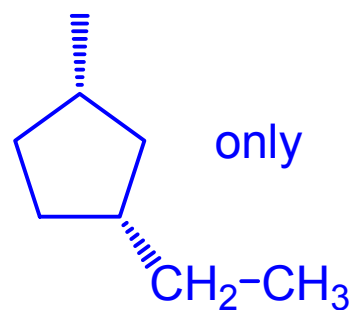
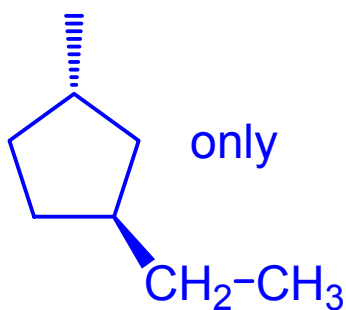
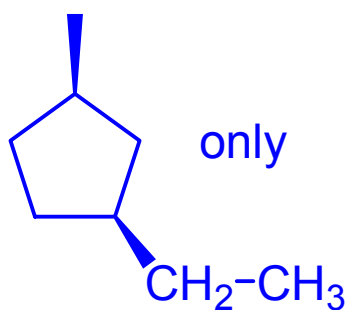
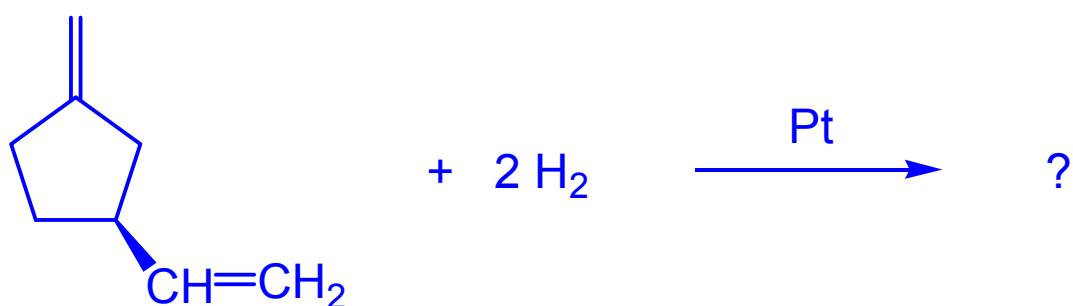


- Example shown below: Both π bonds are reduced because 2 mol of H_2 were used. Each π bond requires 1 mol for complete reduction. However, it is normally not possible to *selectively* reduce just one π bond with 1 mol of H_2 .

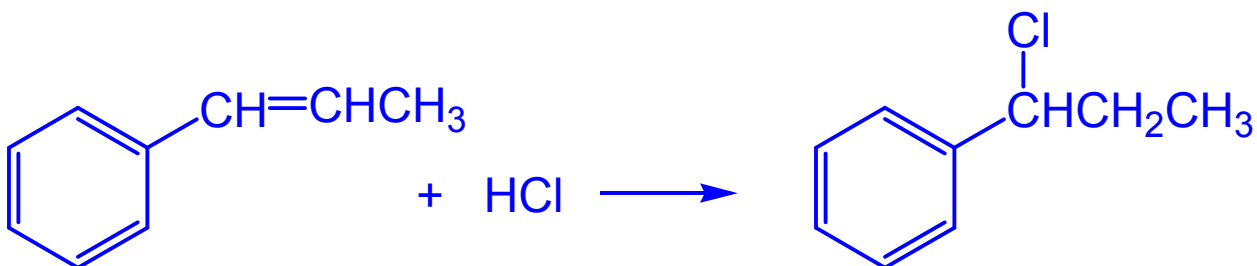


Summary

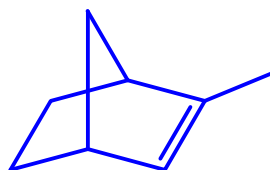
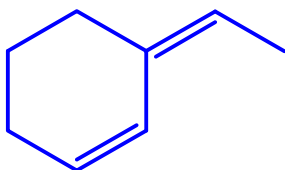
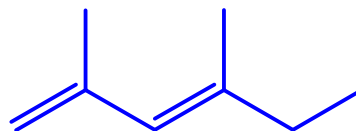
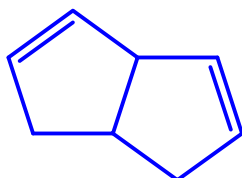
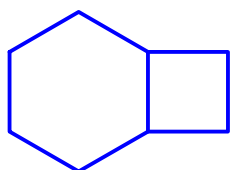
- Chapter 5, pages 119-136.
- Problems: 13-16, 21, 22, 25, 29, 32, 33, 39, 40.
- 2005: 19-22. 2006: 21-25. 2007: 19-21, 23, 24. 2008: 21-23
- Past test question: What product(s) is/are formed by the following hydrogenation reaction?



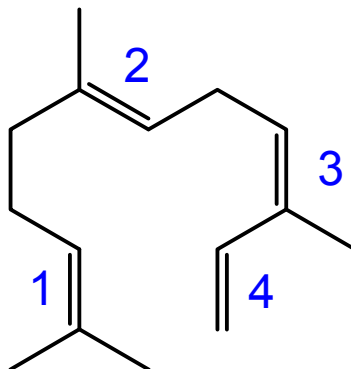
- Past test question: For the reaction shown below, which one of the following statements is NOT correct?



- The product is the one predicted by Markovnikov's Rule
 - The H^+ acts as the electrophile
 - Addition of Cl^- to the carbocation is the slow, rate-determining step of the reaction
 - Cl^- functions as a nucleophile
 - The intermediate carbocation is resonance-stabilized
- Past test question: 0.01 moles of a compound with the formula C_8H_{12} decolourizes exactly 0.02 moles of Br_2 . Which one of the following is a possible structure of the compound?



- MCAT question: A terpene that is contained in oil of citronella is α -farnesene. Refer to its structure to answer the following questions.



- How many moles of H_2 would be required to produce a saturated alkane from α -farnesene?
A. 1 B. 4 C. 8 D. 16
- In the reaction of α -farnesene with excess HBr , which double bond would be the slowest to react?
A. 1 B. 2 C. 3 D. 4
- How many isoprene units are in α -farnesene?
A. 1 B. 2 C. 3 D. 4