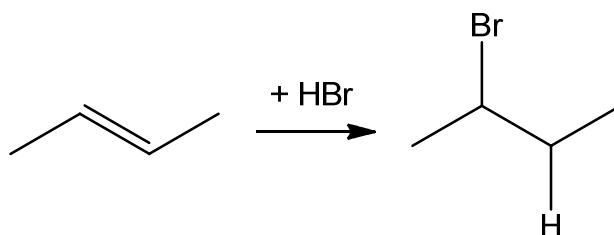


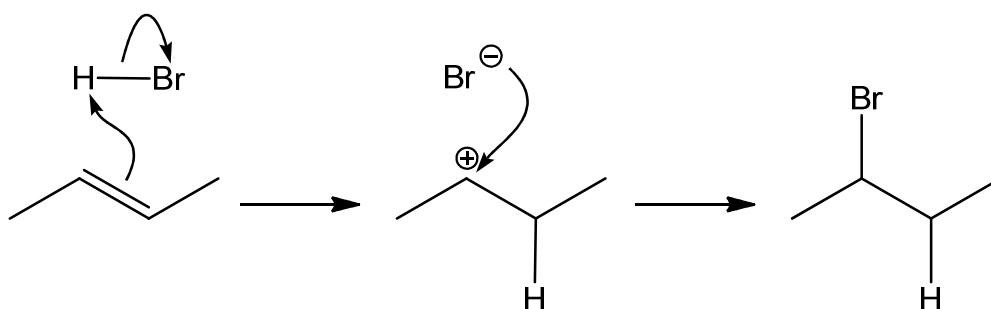
## CHEM1102 Worksheet 3: Addition and Substitution Reactions

### Model 1: Addition to Symmetrical Alkenes and Alkynes

In Worksheet 2, we saw that the double bond of an alkene is made up of one strong  $\sigma$ -bond and one weak  $\pi$ -bond. The process in which this  $\pi$ -bond is broken and two new  $\sigma$ -bonds are formed in its place is called an *addition* reaction.

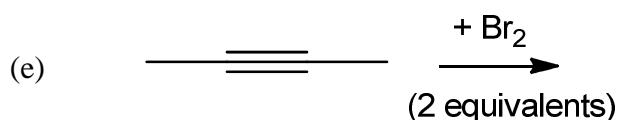
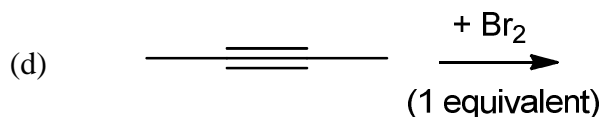
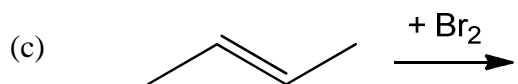
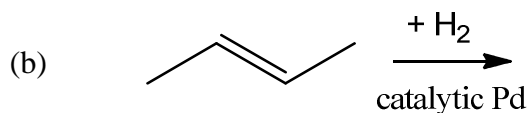
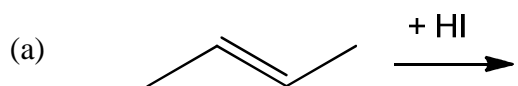


The addition reaction usually takes place in two steps. In the first step, an intermediate is formed called a *carbocation*.



### Critical thinking questions

1. In this reaction is the alkene acting as an electrophile or a nucleophile?
2. Highlight the bonds that are breaking in one colour, and the newly formed bonds in another.
3. Using the scheme above as a model, determine the outcome of the following reactions:

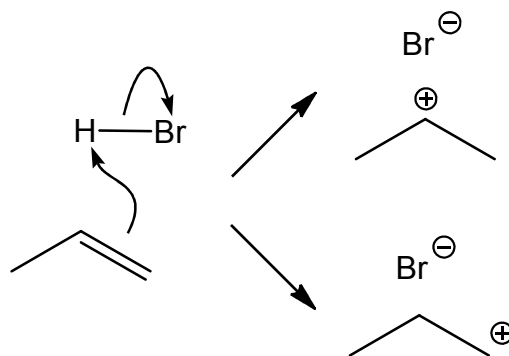


## Model 2: Addition to Unsymmetrical Alkenes and Alkynes

The alkene used in Model 1 was *symmetrical*: it had the same groups at the two ends of multiple bond.

For *unsymmetrical* alkenes, with different groups at the two ends of the multiple bond, two carbocations may be formed in the first step of the reaction, as illustrated in the scheme opposite.

Because of this, there are *two* possible products. However, experimentally, one is formed in much greater amount than the other.

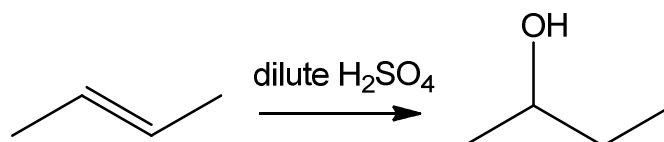


### Critical thinking questions

1. Draw and name the products arising from each of these carbocations.
2. Given that the alkyl groups ( $\text{CH}_n$  groups) stabilize carbocations, which carbocation do you expect to be the most stable in the scheme above?
3. Given your answers to Q2, which of the two products you drew in Q1 will be the major product?

***This is Markovnikov's rule. It states that in an addition to an unsymmetrical alkene, the hydrogen will go predominately to the end that already has the most hydrogen atoms.***

Another reaction you would have seen is the hydration of alkenes which is carried out using aqueous sulfuric acid. This is also an addition reaction but  $\text{H}_2\text{SO}_4$  is *not* added across the double bond.

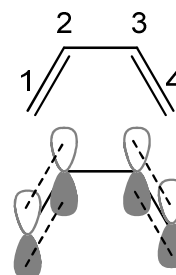


4. What is being added across the double bond? (Remember that atoms are added to *both* ends.)
5. What is the role of the  $\text{H}_2\text{SO}_4$ ?

## Model 3: Resonance and Electrophilic Aromatic Substitution

The  $\pi$ -bond in an alkene arises from the overlap of  $p$  orbitals on adjacent C atoms. The structure of 1,3-butadiene is normally drawn with  $\pi$ -bonds between C1 and C2 and between C3 and C4 due to overlap of their  $p$ -orbitals.

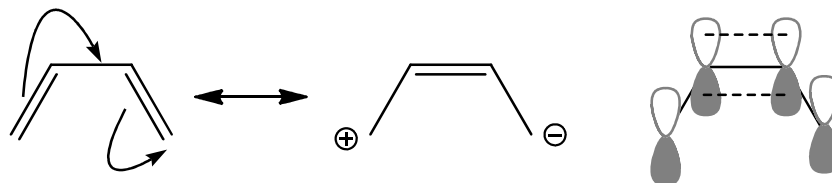
This structure suggests that there is no overlap, and so no  $\pi$  bonding, between the  $p$  orbitals of C2 and C3.



### Critical thinking questions

1. Is this a realistic picture of the bonding in 1,3-butadiene?

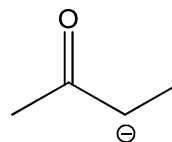
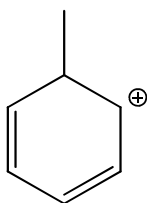
Indeed, we could also draw the structure like below. The double headed arrow is used to show that the two Lewis structures are both possible.



2. Do you think this resonance form is stable? Why?

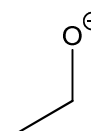
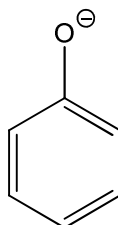
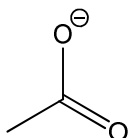
The reality, of course, is somewhere in between – each C-C bond is more than a single bond, but slightly less than a double bond. It is hard to picture “one-and-a-bit” bonds, so chemists like to draw the different **resonance structures** instead. Resonance structures differ only in the location of electrons, *not* in the position of nuclei.

3. Draw resonance structures for the following:



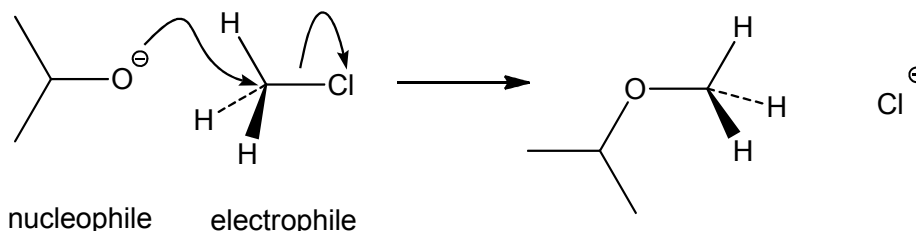
4. Do you think the molecules above are more or less stable than typical carbocations and carbanions?

5. Acetic acid is a stronger acid than phenol and phenol is a stronger acid than ethanol. Draw resonance structures for the following anions and use them to explain the relative acidities of the conjugate acids.



### Model 4: Nucleophilic Substitution

In Worksheet 2, you practiced drawing curly arrows in the reaction below in which substitution occurs.



### Critical thinking questions

1. Here it has been drawn as a one step (concerted) process. Can you draw an alternative two-step mechanism? (*Hint*: make sure you never draw *more* than 4 bonds to carbon so break a bond first.)

2. The first mechanism is called  $S_N2$ , the second  $S_N1$ . Can you suggest what each component of these names might refer to?

## Exercises

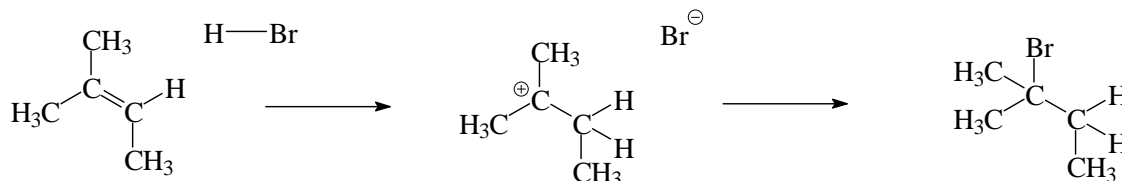
CHEM1102

2008-J-13

June 2008

- The incomplete proposed mechanism for the reaction of 2-methyl-2-butene with HBr is shown below. Complete the mechanism by adding curly arrows to illustrate the bonding changes that take place.

**Marks**  
**2**



Which one of the two reactants is the electrophile?

CHEM1102

2009-J-12

June 2009

- Give the mechanism of the reaction that occurs when 1-methylcyclohexene is converted to 1-bromo-1-methylcyclohexane by the addition of HBr. Give the structure of the intermediate carbocation that is formed and indicate (with curly arrows) all the bonding changes that occur.

**Marks**  
**3**



CHEM1102

2009-J-8

June 2009

- Complete the following table. Make sure you indicate any relevant stereochemistry.

**Marks**  
**2**

Starting Material	Reagents / Conditions	Major Organic Products
	$\text{H}_2/\text{Pd}/\text{C}$ (catalyst)	
	aqueous $\text{H}_2\text{SO}_4$	