

Objective 8: intro to Reactivity 2: identify polar bonds ($\delta +$ and $\delta -$), nucleophiles (Lewis base, electron pair donor), electrophiles (Lewis acid, electron pair acceptor). Use curved arrows to predict product. Identify common bond breaking and making processes.

Quiz Practice problems

Key ideas:

A chemical reaction occurs when bonds break and form.

Organic chemical reactions occur by three main reaction types:

1. polar reactions – involves electron pair donors (nucleophiles) and electron pair acceptors (electrophiles). WE WILL FOCUS ON POLAR REACTIONS.
2. radical reactions – involves substances that have an unpaired electron (radical).
3. pericyclic reactions – involves several pairs of electrons breaking and forming bonds in concert.

Polar reaction types: acid-base (see Objective 4), substitution, elimination, addition.

We used curved arrows to show how one resonance structure is converted to another.

We used curved arrows to show how an acid reacts with a base.

We will use curved arrows for polar reaction types to predict the product(s) of a reaction.

Curved arrows are used to show bonds breaking and forming. Start arrow tail at nucleophile (base) and point arrow head at electrophile (acid) to show bond forming. Keep in mind bonding rules. E.g., if 5 bonds to C, that means a bond to C must break.

Electrophiles are electron pair acceptors. See Reactivity Principles and Trends table.

Acids are electrophiles. See pK_a table. The H in acids are electron pair acceptors.

E.g., strong acids: HCl, HBr, HI, H_2SO_4 . Weak acids: CH_3COOH , H_2O , ROH.

H bonded to beta C (elimination reaction)

C in a C-X bond (substitution reaction).

C in a C-O bond (substitution reaction).

C in a C=O bond (addition reaction in Chem 12B).

Nucleophiles are electron pair donors. See Reactivity Principles and Trends table.

Bases are nucleophiles. See pK_a table. A lone pair on O or N or C are the electron pair donors.

E.g., Oxygen nucleophiles have one or two bonds to O; the lone pair on O is the nucleophile. E.g., H_2O , OH^- , ROH, RO^- , $C=O$, $RCOO^-$.

Nitrogen nucleophiles have two or three bonds to N; the lone pair on N is the nucleophile. E.g., NH_3 .

Carbon nucleophiles have three bonds and a lone pair on the C. The lone pair on the C is the nucleophile.

Carbon-carbon pi bonds are nucleophiles. The pi bond is the nucleophile.

Skills:

Identify nucleophilic atom or bond in a compound.

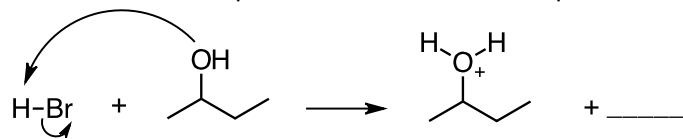
Identify electrophilic atom in a compound.

Given reactants, use curved arrows to show how nucleophile reacts with electrophile and predict the product of an acid-base, nucleophilic substitution, elimination, and electrophilic addition reaction.

Later: we will apply these skills to determine reaction conditions, describe mechanisms, and design synthesis of organic compounds.

USE Alchemie Mechanisms app or MOLECULAR MODELS.

1. Circle the nucleophilic atom. Box the electrophilic atom. What is the reaction type? What is the second product?

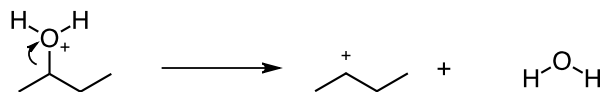


Answers:

Reaction type = acid-base (proton transfer)

2nd product = Br^-

2. The sigma bond (O-C bond) breaks and forms a _____. The H_2O is called the leaving group in the reactant. The carbon bonded to the leaving group (H_2O in this reaction) is called the alpha carbon. Circle the alpha C in the reactant. How many H's are bonded to the alpha C in the carbocation?



Answers:

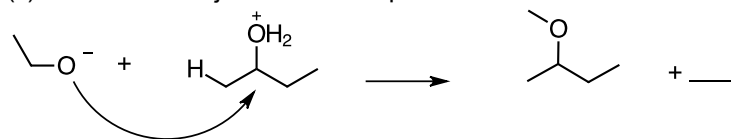
Carbocation

There is 1 H bonded to the alpha C in the carbocation.

3. a. H_2O is the leaving group.

(i) The carbon bonded to the leaving group is called the alpha carbon. Circle the alpha C.

(ii) The carbon adjacent to the alpha carbon is called the beta carbon. Box the beta C.



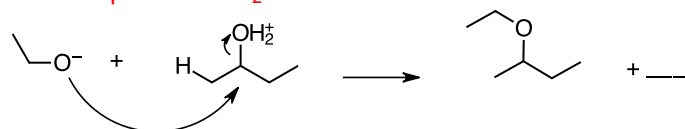
b. A curved arrow is missing. Draw in the curved arrow and identify the other product.

c. A carbon is missing from the product. Draw in the carbon.

Answers:

a (i) and (ii)

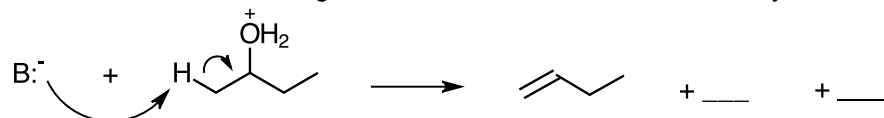
b. Other product is H_2O



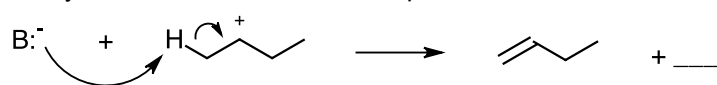
c. There should be two C's bonded to the O in the ether group.

4. a. Circle the alpha C. Box the beta C. Triangle the leaving group.

b. A curved arrow is missing. Draw in the curved arrow and identify the two other products.

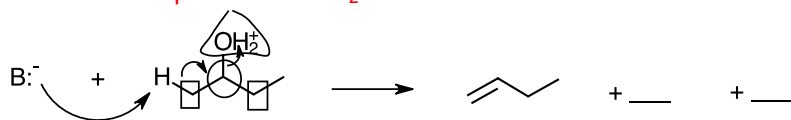


c. Why is the carbocation like an alpha C? Box the beta C. Identify the other product.



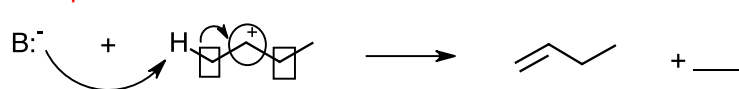
Answers:

a and b. Other products are H_2O and H-B.

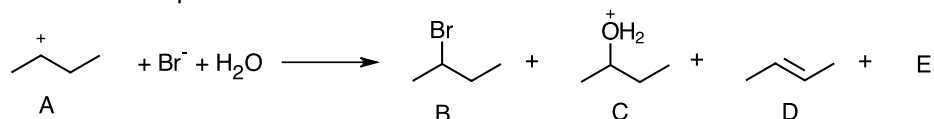


c. The carbocation forms when the leaving group leaves the alpha carbon.

Other product is H-B.



5. Circle the alpha C in Structure A. Box the 2 beta carbons in Structure A.



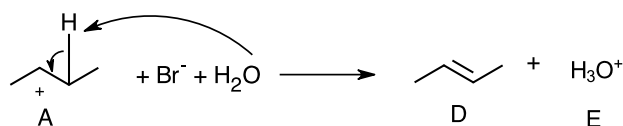
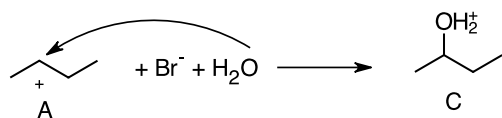
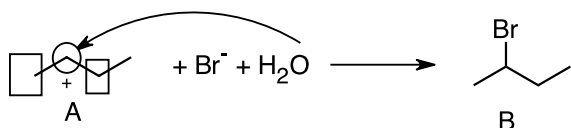
Use curved arrows to show how Structure B is formed.

Use curved arrows to show how Structure C is formed.

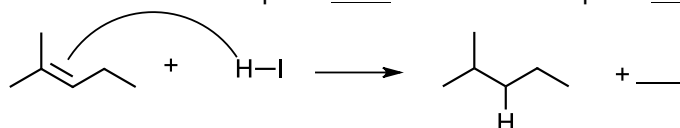
Use curved arrows to show how Structure D is formed.

Use curved arrows to show how Structure E is formed. Draw the structure of E.

Answers:



6. a. Circle the nucleophilic bond. Box the electrophilic atom.



b. The arrow head on the curved arrow is missing. Draw in the arrow head.

c. A second curved arrow is missing. Draw in the curved arrow.

d. A charge is missing in the product. Draw in the charge and confirm the charge with a formal charge calculation.

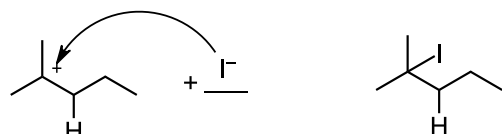
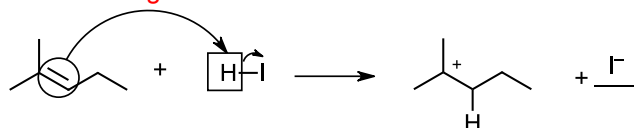
e. Identify the second product.

f. The two products react to form another compound. Use curved arrows to show how this compound forms.

Answers:

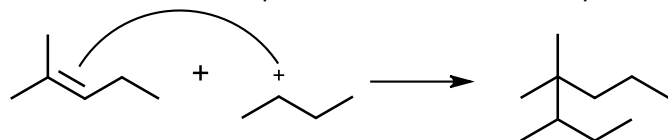
a-e.

Formal charge on carbocation = $4 - 3 - 0 = 1$



This is an addition reaction.

7. a. Circle the nucleophilic bond. Box the electrophilic atom.



b. The arrow head on the curved arrow is missing. Draw in the arrow head.

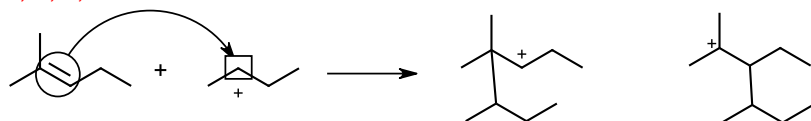
c. A charge is missing in the product. Draw in the charge and confirm the charge with a formal charge calculation.

d. Another carbocation is formed. Draw the structure of this carbocation.

e. Which carbocation, the structure shown above or the one you drew in (d) is the more likely product? Why?

Answers:

a, b, c, and d.

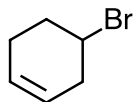


e. The carbocation on the left is a 2° carbocation. The carbocation on the right is a 3° carbocation. The likely product is the 3° carbocation because it is more stable than the 2° carbocation.

8. The compound shown below has 1 nucleophilic bond and at least 3 electrophilic atoms.

a. Circle the nucleophilic bond and atom. Which nucleophile is the strongest? See Reactivity Principles and Trends Table 1.

b. Box the electrophilic atoms. Which electrophile is the strongest? See Reactivity Principles and Trends Table 1.



c. This compound reacts with HBr. At which atom does HBr react? Use curved arrows to show bonds breaking and forming. Draw the structure of the product.

d. This compound reacts with CH_3O^- . At which atom does CH_3O^- react? Use curved arrows to show bonds breaking and forming. Draw the structure of the product.

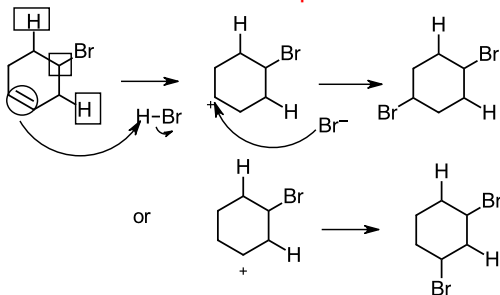
e. This compound reacts with CH_3MgBr . At which atom does CH_3MgBr react? Use curved arrows to show bonds breaking and forming. Draw the structure of the product.

Answers:

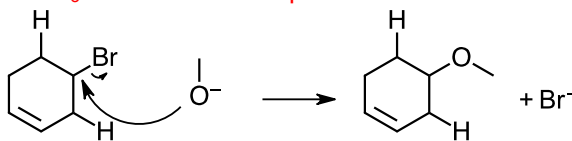
a. nucleophile: C=C pi bond.

b. electrophile: C bonded to Br (this is an alpha carbon), H on two beta carbons.

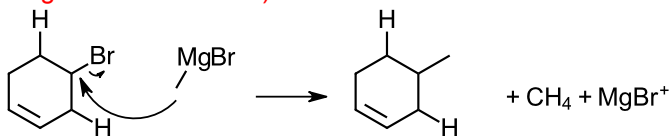
c. HBr reacts at the C=C pi bond. This is an addition reaction.



d. CH_3O^- reacts at the alpha carbon. This is a substitution reaction.



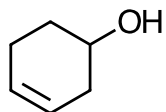
e. The C in CH_3MgBr is the nucleophile because the C-Mg bond is polar and C is more electronegative than Mg. CH_3MgBr reacts at the alpha carbon. This is a substitution reaction. CH_3MgBr is a Grignard reagent. (You'll see this reagent in Chem 12B.)



9. The compound shown below has 2 nucleophilic bonds or atoms and at least 4 electrophilic atoms.

a. Circle the nucleophilic bond and atom. Which nucleophile is the strongest? See Reactivity Principles and Trends Table 1.

b. Box the electrophilic atoms. Which electrophile is the strongest? See Reactivity Principles and Trends Table 1.



c. This compound reacts with HBr. At which atom does HBr react? Use curved arrows to show bonds breaking and forming. Draw the structure of the product.

d. This compound reacts with CH_3O^- . At which atom does CH_3O^- react? Use curved arrows to show bonds breaking and forming. Draw the structure of the product.

e. This compound reacts with CH_3MgBr . At which atom does CH_3MgBr react? Use curved arrows to show bonds breaking and forming. Draw the structure of the product.

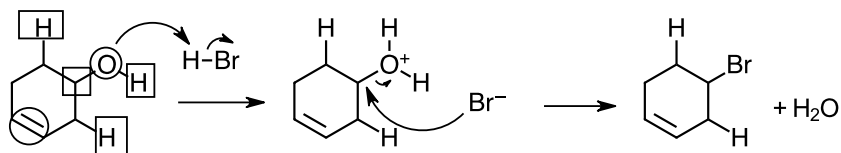
Answers:

a. nucleophiles - Lone pair on O and C=C pi bond. Lone pair is stronger nucleophile.

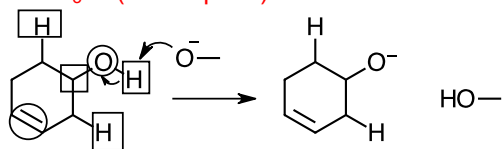
b. electrophile - H bonded to O (acidic H), C bonded to O (this is an alpha carbon), H on two beta carbons.

c. HBr (electrophile) reacts with lone pair on O.

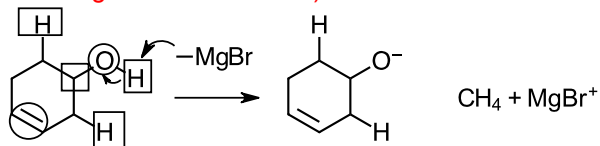
The 1st step is an acid-base reaction. The 2nd step is a nucleophilic attack on C bonded to a leaving group. The overall reaction is a substitution reaction.



d. CH_3O^- (nucleophile) reacts at H bonded to O (acidic H).

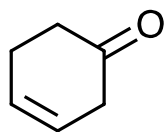


e. The C in CH_3MgBr is a nucleophile and reacts at H bonded to O (acidic H). CH_3MgBr is a Grignard reagent. (You'll see this reagent in Chem 12B.)



10. a. Circle the nucleophilic bond and atom. Which nucleophile is the strongest? See Reactivity Principles and Trends Table 1.

b. Box the electrophilic atoms. Which electrophile is the strongest? See Reactivity Principles and Trends Table 1.



c. This compound reacts with HBr. At which atom does HBr react? Use curved arrows to show bonds breaking and forming. Draw the structure of the product.

d. This compound reacts with CH_3O^- . At which atom does CH_3O^- react? Use curved arrows to show bonds breaking and forming. Draw the structure of the product.

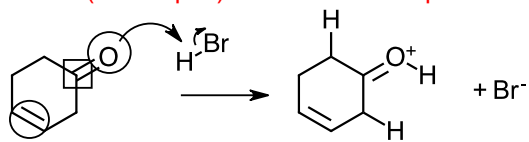
e. This compound reacts with CH_3MgBr . At which atom does CH_3MgBr react? Use curved arrows to show bonds breaking and forming. Draw the structure of the product.

Answers:

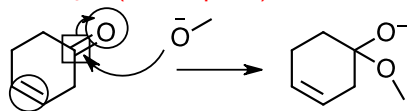
a. nucleophiles - Lone pair on O and C=C pi bond. Lone pair is stronger nucleophile.

b. electrophile - C bonded to O (this is called a carbonyl carbon).

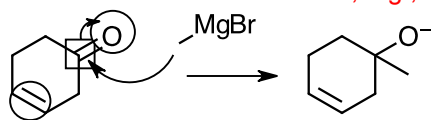
c. HBr (electrophile) reacts with lone pair on O.



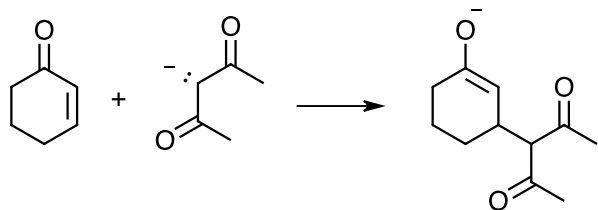
d. CH_3O^- (nucleophile) reacts at C bonded to O (carbonyl carbon).



e. The C in CH_3MgBr is a nucleophile and reacts at C bonded to O (carbonyl carbon). CH_3MgBr is a Grignard reagent. The anion reacts with an acid, e.g., H_3O^+ , to form an alcohol. We will look at this reaction in Chem 12B.



11. Identify the bond making/breaking process in each step. (See Reactivity Principles and Trends, Table 2.) Use curved arrows to show bonds breaking/forming.



Answers:

1st reactant – draw resonance structure that shows (-) charge on O and (+) charge on C-3.

Nucleophilic attack by lone pair nucleophile on 2nd reactant with electron deficient species on 1st reactant forms product.

