Chapter 12 Chemical reactions, oxidation, and reduction: bringing molecules to life

Chapter 13 Reaction mechanisms: the chemical changes that drive the chemistry of life

Get some extra practice...

...drawing reaction mechanisms

- 1. Draw a structure for the product formed by the reaction of methyl bromide with sodium azide (NaN₃).
- 2. Draw a mechanism for the hydrolysis of 2-bromo-2-methylpropane in water.
- State whether the following species are nucleophiles or electrophiles.
 H₂O, HO⁻, CH₃+, NH₃, HCl, CH₃OH, H⁺, BH₃
- 4. Use curly arrows to show the product of the following reaction.

. € NaBr -

- 5. Draw a mechanism for the hydrolysis of ethyl ethanoate by sodium hydroxide.
- 6. Draw a scheme for the reaction of propanoic acid with methanol in the presence of an acid catalyst.

Scroll to the following pages to check your answers.

Chapter 12 Chemical reactions, oxidation, and reduction: bringing molecules to life

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Answers

 Draw the structure of the products formed from the reaction of methyl bromide with sodium azide (NaN₃).

 CH_3 — Br + NaN_3 — CH_3 — N_3 + NaBr

2. Draw a mechanism for the hydrolysis of 2-bromo-2-methylpropane in water.

First, we need to draw the structure of 2-bromo-2-methylpropane. Propane is a three-carbon alkane; the '2-bromo-2-methyl' prefix tells us that Br and a methyl group are attached to carbon 2:

The term 'hydrolysis' tells us that water is involved. In fact, we are considering a nucleophilic substitution reaction involving two molecules of water. First, we see homolytic cleavage of the C–Br bond:

$$\begin{array}{c} \begin{pmatrix} B^{r} \\ | \\ H_{3}C - C - CH_{3} \end{pmatrix} \xrightarrow{\oplus} H_{3}C - C - CH_{3} + Br^{-} \\ | \\ CH_{3} \end{pmatrix} \xrightarrow{\oplus} H_{3}C - C - CH_{3} + Br^{-} \\ H_{3}C - CH_{3} + Br^{-} \\ H_{3}$$

We then see water mounting a nucleophilic attack on the central carbon atom (a carbocation):



Finally, a second water molecule extracts a hydrogen to form a hydronium ion and the product of the reaction, 2-methyl-propan-2-ol:

Chapter 12 Chemical reactions, oxidation, and reduction: bringing molecules to life

Chapter 13 Reaction mechanisms: the chemical changes that drive the chemistry of life



Overall:



Notice how the net result of the reaction is the substitution of a Br with an –OH group.

State whether the following species are nucleophiles or electrophiles.
 H₂O, HO⁻, CH₃+, NH₃, HCl, CH₃OH, H⁺, BH₃

A nucleophile is a molecule or ion that can donate a pair of electrons to form a new covalent bond. An electrophile is a species that can *accept* a pair of electrons to form a new covalent bond.

So: H₂O, HO⁻, NH₃, and CH₃OH all have electron pairs to form new bonds and so are nucleophiles. The rest are electrophiles.

4. Use curly arrows to show the product of the following reaction:

$$\begin{array}{c} H \\ | \\ 0 \\ / \\ H_2 C - C H_2 \end{array} + NaBr \longrightarrow ?$$

Chapter 12 Chemical reactions, oxidation, and reduction: bringing molecules to life

Chapter 13 Reaction mechanisms: the chemical changes that drive the chemistry of life



Your initial instinct might be that the Br⁻ would attack the O^+ – but this would result in a highly unlikely O–Br bond. Instead, notice how the O^+ withdraws electrons from the C–O bond; this makes the C relatively positive – and hence susceptible to attack from the nucleophilic Br⁻ species.

5. Draw a mechanism for the hydrolysis of ethyl ethanoate by sodium hydroxide.

In this reaction, we're considering nucleophilic attack on the ester, ethyl ethanoate:

The nucleophile is the hydroxide group, OH⁻. The electronegative O of the carbonyl group withdraws electrons, making the carbonyl carbon relatively positive – and, hence, a target for the nucleophile:

The hydroxide nucleophile will attack the carbon of the carbonyl group, breaking the π bond and forming a tetrahedral carbon atom:

Chemical reactions, oxidation, and reduction: bringing molecules to life Chapter 12

Chapter 13 Reaction mechanisms: the chemical changes that drive the chemistry of life



This unstable intermediate gives rise to an alkoxide ion and a carboxylic acid:



Rapid equilibration occurs between the strong base (the alkoxide ion) and the weak acid (the carboxylic acid) to give ethanol and ethanoic acid:



Overall:



6. Draw a scheme for the reaction of propanoic acid with methanol in the presence of an acid catalyst.

Firstly, propanoic acid is activated by the acid catalyst (we're using HA here to represent a generic acid):



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Chapter 12 Chemical reactions, oxidation, and reduction: bringing molecules to life

Chapter 13 Reaction mechanisms: the chemical changes that drive the chemistry of life

This protonation has the effect of making the carbonyl carbon more susceptible to nucleophilic attack. This nucleophilic attack is mounted by the hydroxyl group of the methanol:



A hydrogen ion is then transferred within the structure:



And a water molecule is then lost:



Finally, a hydrogen ion is lost to reform the initial catalyst, yielding the final product, an ester:

