

EXP. 35 A

OXIDATION OF BORNEOL TO CAMPHOR

LEARNING OBJECTIVES: To illustrate the concepts of oxidation and reduction in organic chemistry and the stereochemical effects of these reactions in certain systems.

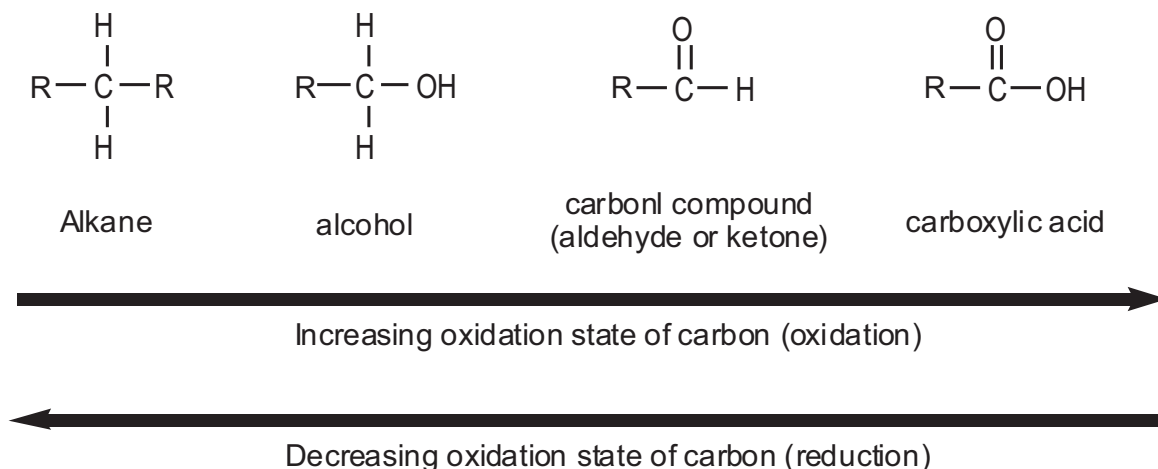
OXIDATION AND REDUCTION IN ORGANIC CHEMISTRY

The concepts of oxidation and reduction in chemistry are fundamentally related to the loss and gain of electrons, respectively. For a specific atom, oxidation brings about an increase in the oxidation number, whereas reduction does the opposite. This is of course true in organic reactions as well, but it is frequently less clear where the gain or loss of electrons is taking place. For this reason, the concepts of oxidation and reduction are addressed from a different perspective in organic chemistry.

Since carbon is the most important element in organic chemistry, we can define **oxidation as a process whereby carbon gains bonds to more electronegative atoms**. These can be any atoms more electronegative than carbon, such as chlorine or sulphur, but the most commonly seen in organic oxidations is **oxygen**. The more bonds to oxygen, the higher the oxidation state of the carbon involved. Examples of oxidation reactions are those that convert alkanes into alcohols, or alcohols into carbonyl compounds. The functional groups that contain the most highly oxidized form of carbon in organic compounds are the carboxylic acids and their derivatives.

Reduction is the opposite of oxidation. We can define **reduction as a process whereby carbon adds bonds to less electronegative atoms**. Again, the most common of these atoms is **hydrogen**. Therefore, any reactions that cause carbon to add more bonds to hydrogen can be referred to as reductions. Examples are the conversion of carbonyl compounds into alcohols, or even alkanes. Obviously, alkanes represent the most reduced (least oxidized) type of organic compounds possible.

The following scheme shows the most common functional groups involved in organic oxidations and reductions. Any chemical conversions that proceed to the right can be classified as oxidations, and any reactions that proceed to the left can be classified as reductions.



THE REACTIONS OF EXPERIMENT 35

Refer to pages 289 - 290 of your textbook.

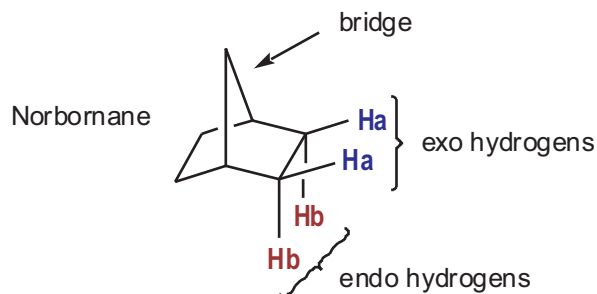
It is clear now how the oxidation-reduction scheme of p. 289 is being used here to illustrate the concept experimentally. An alcohol (borneol) is being oxidized into a ketone (camphor). A subsequent reduction takes us back to another alcohol (isoborneol), which is an isomeric form of the original.

The **oxidizing agent** in the first step is **sodium hypochlorite**, which is present in commercial bleach as an aqueous solution. In fact, the reaction can be performed using bleach, but it must be relatively fresh. Sodium hypochlorite decomposes in water slowly, and using old bleach could introduce a source of error in the experiment.

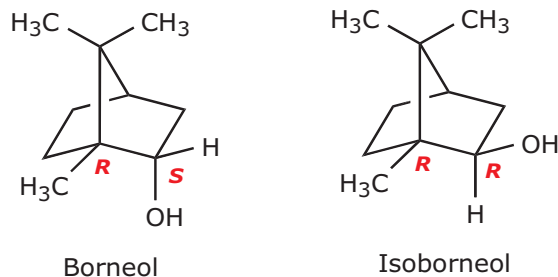
The reducing agent in the second step is sodium borohydride, which will be used in alcoholic solution. Again, sodium borohydride reacts with alcohols slowly. Therefore it is important that the solution be freshly prepared. If you monitor your reactions by IR you'll have a good indicator of the effectiveness of the conversions, and therefore of the quality of the reagents used. Ineffective reagents can result in incomplete conversions, which will show the presence of starting material in the IR spectrum of products.

STEREOCHEMISTRY OF THE REACTION

The diagram at the bottom of p. 290 shows the stereochemical detail of the mechanism of the reactions. It is important to understand the meaning of the **endo** and **exo** terminology. This terminology is used in reference to bicyclic systems such as the **norbornane** molecule shown below. The rigidity of these systems makes hydrogens (a) and (b) stereochemically nonequivalent. The exo hydrogen points outward from the ring, and the endo hydrogen points downward, opposite to the bridge, as shown.

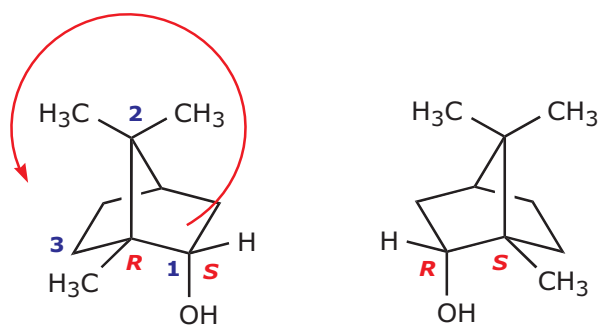


If we apply this terminology to the alcohols borneol and isoborneol, we can see that they are not interconvertible, and therefore they are isomers. What kind of isomers are they? The fact that the carbon bearing the hydroxyl group is chiral, and that there are other chiral centers in each of these molecules, makes these alcohols **diastereomers**. An instance showing some of these chiral centers (but not all, for clarity) is seen below.



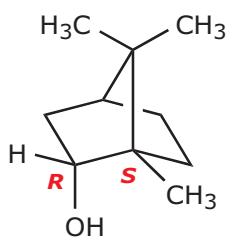
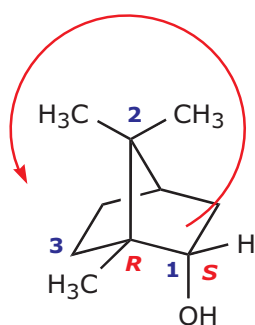
Diastereomers

The next question is, since the starting material (borneol) can exist as a racemic mixture (see below), is it being used as such in the lab, or is it a pure enantiomer? The answer is easy. Pure enantiomers are expensive and difficult to prepare. Therefore, **the reagent used in the lab is a racemic mixture**. As extra information, the configuration assignment for one of the carbons is also shown.

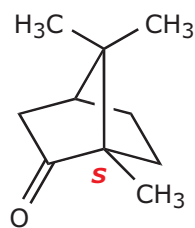
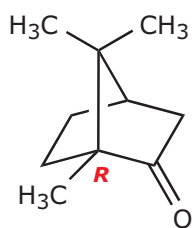
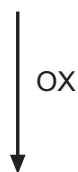


Racemic borneol (enantiomers)

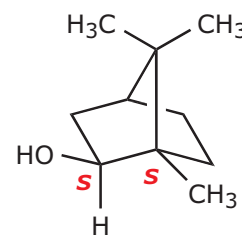
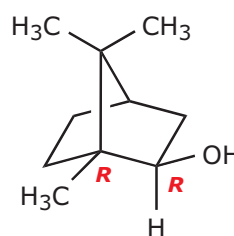
Now, how does the presence of enantiomers in the starting material affect the final outcome of these conversions? Each step of the reaction effects the same conversion on both enantiomers, therefore, **each product from each step is obtained as an enantiomeric mixture**, including the final product.



Racemic borneol (enantiomers)



Enantiomeric camphor



Racemic Isborneol (enantiomers)