

17.3: PREPARATION OF ALCOHOLS- A REVIEW

OBJECTIVES

After completing this section, you should be able to describe in detail the methods of preparing alcohols and diols, which you encountered in previous chapters.

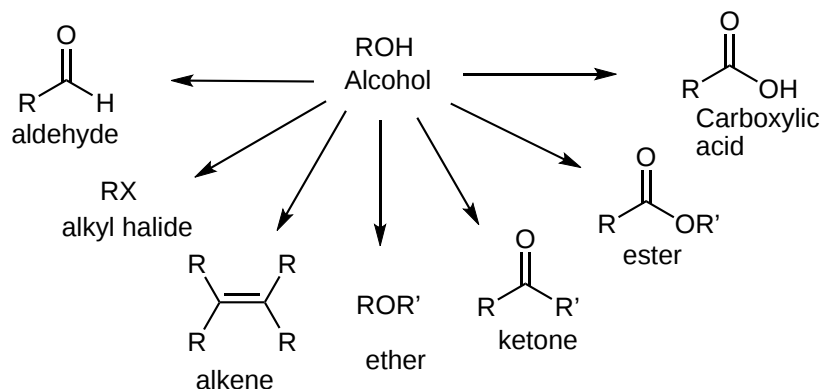
STUDY NOTES

If necessary, you should review Sections 8.4 and 8.5 describing direct hydration of alkenes, and Section 8.7 describing preparation of cis and trans diols from alkenes. Section 8.7 also gives more details on the formation of the respective osmate and epoxide intermediates of these reactions.

INTRODUCTION

Alcohols are considered one of the more important functional groups in organic chemistry. They can be prepared from compounds containing a wide assortment of functional groups. Also, they can be used to create compounds with a wide variety of functional groups such as: alkenes, ketones, carboxylic acids, and others. Many functional group conversions can be accomplished through the preparation of an alcohol giving them an important central position in organic synthesis. ex. Alkene \rightarrow Alcohol \rightarrow Ketone.

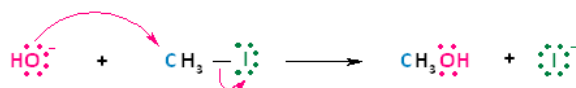
Many methods for the preparation of alcohols have been discussed in previous chapter of this textbook and will be reviewed in this section.



ALCOHOLS FROM SUBSTITUTION REACTIONS

Methyl and primary alkyl halides can be converted to alcohols by using an S_N2 reaction with OH^- as a nucleophile (Section 11.5). Also, secondary and tertiary alkyl halides can be converted to alcohols by an S_N1 reaction using water as the nucleophile (and it can even be the solvent). Recall that S_N1 reactions are promoted in polar, protic solvents (Section 11.7).

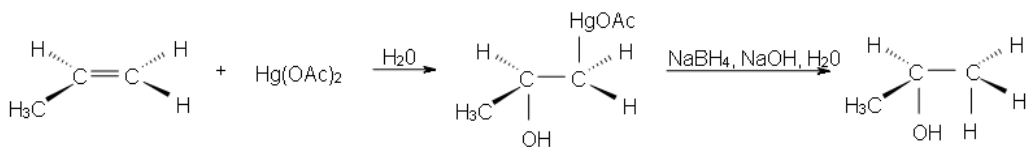
Example #1



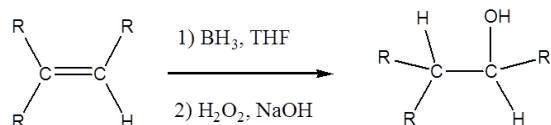
The Synthesis of Methanol Using an S_N2 Reaction

ALCOHOLS FROM ALKENES

Oxymercuration - demercuration is a special electrophilic addition (Section 8.5). It is anti-stereospecific and regioselective. This reaction involves mercury undergoing electrophilic addition to the alkene double bond forming a *Mercurinium Ion Bridge*. A water molecule then attacks the most substituted carbon to open the mercurinium ion bridge, followed by proton transfer to form a hydroxyl group ($-\text{OH}$). The organomercury intermediate is then reduced by sodium borohydride. Notice that overall, the oxymercuration - demercuration mechanism follows Markovnikov's Regioselectivity with the OH group attached to the most substituted carbon and the H is attached to the least substituted carbon. Also, the H and OH species will be anti to each other in the product.

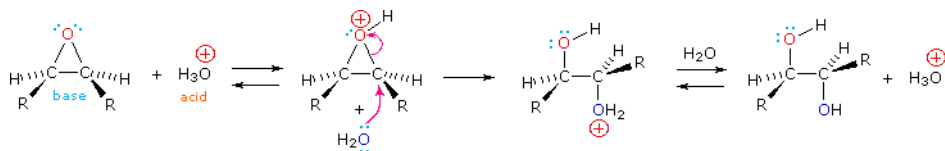


Hydroboration-Oxidation is a two step pathway used to produce alcohols (Section 8.6). It is syn-stereospecific and regioselective. The reaction proceeds in an Anti-Markovnikov manner, where the hydrogen (from BH_3 or BHR_2) attaches to the more substituted carbon and the boron attaches to the least substituted carbon in the alkene double bond. The organoborane intermediate is then converted to an alcohol by reaction with hydrogen peroxide (H_2O_2) and sodium hydroxide (NaOH). The hydroboration mechanism has the elements of both hydrogenation and electrophilic addition and it is a stereospecific (*syn addition*), meaning that the addition of the H and OH species takes place on the same face of the double bond leading to their *cis* configuration in the product. Because the BH_3 can attack either face of the alkene, this reaction can product a racemic mixture of enantiomers in the product.

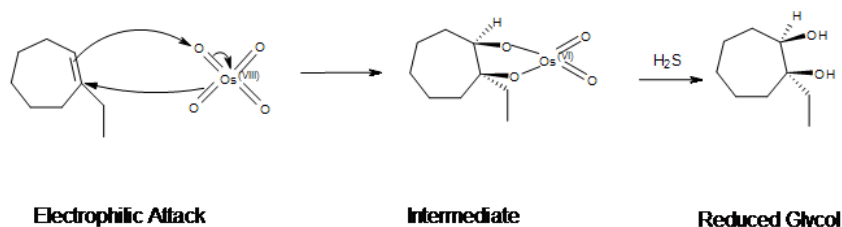


DIOLS FROM ALKENES

Epoxides may be cleaved by aqueous acid to give anti-1,2-diols which are also called glycols. Proton transfer from the acid catalyst generates the conjugate acid of the epoxide, which is attacked by a water nucleophile. Because the nucleophilic attack utilizes an $\text{S}_{\text{N}}2$ mechanism the result is an anti-stereospecific configuration of the diol product. The water nucleophile prefers to attack the more substituted carbon on the epoxide which allows for regioselectivity in the reaction.



Osmium tetroxide oxidizes alkenes to give 1,2-diols through syn addition. The reaction with OsO_4 is a concerted process that creates a cyclic intermediate with no rearrangements. The intermediate osmium compound is reduced to the diol product by reduction with H_2S or NaHSO_4 with H_2O .

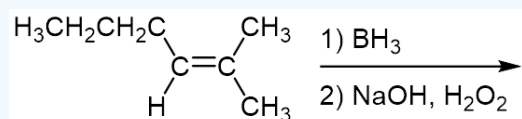


This *syn*-dihydroxylation complements the epoxide-hydrolysis sequence which creates an *anti*-dihydroxylation product. This reaction lack regioselectivity so an alkene reacts with osmium tetroxide there is a possibility of a reaction producing a racemic mixture as the product. In general for this reaction, *cis* alkenes produce a meso product while *trans* alkenes produce a racemic mixture as the product.

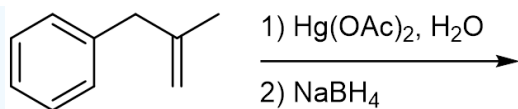
? EXERCISE 17.3.1

1) Predict the products of the following reactions:

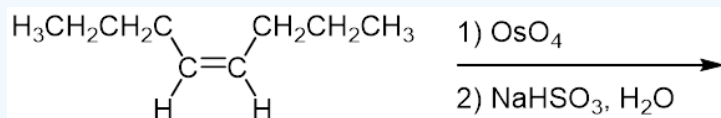
a)



b)



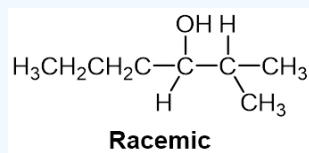
c)



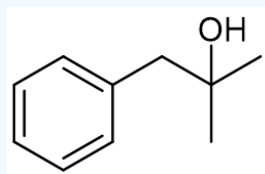
Answer

1)

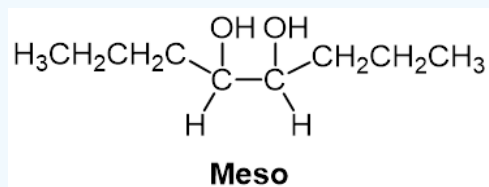
a)



b)



c)



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