An Oxidation Puzzle

It is often the case that a compound may have multiple functional groups. It may not always be obvious which of these functional groups may react under a given set of conditions. In the case of 2-ethyl-1,3-hexanediol, both primary and secondary alcohol functional groups are present. Both, in theory, are susceptible to oxidation to form carbonyl compounds. In this case the oxidizing system is bleach (NaOCl) and acetic acid. The goal of this experiment is to successfully execute the oxidation reaction and determine which of the possible products is formed using the technique infrared spectroscopy.



##### **Experimental**

*Week 1*

Using the special “prebroken” pipet, transfer 0.50 g of the viscous 2-ethyl-1,3-hexanediol to a 25 mL round bottom flask. Add a stir bar and 4.5 mL of acetic acid. Place the reaction vessel in a glass bowl which is filled with water and a small amount of ice (2 or 3 small pieces) and begin stirring. In small portions over a period of about ten minutes add 3.5 mL of household bleach solution while monitoring the temperature.**1** Do not allow the temperature of the solution to rise above 30o C. After the addition is complete, remove the water bath and stir the mixture for 1 hour.**2**

 Pour the reaction mixture into a beaker containing 10-15 mL of saturated sodium chloride and ice. Extract the resultant mixture with three 10 mL portions of diethyl ether. Wash the combined organic extracts with four 3 mL portions of 10 % (w/v) aqueous sodium carbonate solution. Finally, wash the organic layer with two 3 mL portions of 5 % (w/v) sodium hydroxide solution. Pour the organic layer into an Erlenmeyer flask, cover the bottom with sodium sulfate, cork, and parafilm.

*Week 2*

Gravity filter the dried organic mixture into a pre-weighed, appropriately sized round bottom flask. Be sure to rinse the Erlenmeyer flask and the filter paper to ensure quantitative transfer. Remove the solvent on the rotary evaporator using a low heat setting. Rotovap for 5 minutes past the point which it appears that the volume in the round bottom flask remains constant. Weigh the flask to determine the mass of the product.

To determine the functionality present in the product, take an infrared spectrum.

##### Procedural notes

1. Carefully insert a thermometer in the reaction mixture to monitor the temperature. Remove the thermometer after making a temperature reading (to minimize the possibility of breaking the thermometer).

2. Check the reaction mixture after 30 minutes to ensure that a slight yellow green color persists (an indication of excess oxidant). If it does not, consult with the instructor.

 Starch-iodide paper also can be used to check for the presences of excess oxidant.

##### Write-up notes

Follow the sample write-up. Be sure to include the structure of the product in your balanced equation for the reaction – this is where we will look to see if you solved the structure correctly!! For the balanced equation and the reagent table, assume that the diol, bleach, and acetic acid react in a 1:1:1 ratio. Don’t worry about trying to determine the actual moles of the bleach (NaOCl) which is present in excess (you should include theoretical moles, though). Interpret the IR. Label relevant functional group absorptions (bond AND functional group) on the IR spectrum and attach it to your lab write-up. Do not worry about naming the product or finding its density or boiling point. The mechanism is N/A. Answer the following questions in the write-up.

Questions

1. Describe how you determined the product of the reaction. The five possible products are listed on the first page of this chapter. What information from the IR spectrum led you to the structure of the product? What information from the IR spectrum helped you rule-out the other four structures?

 You should provide a thorough and detailed explanation. Cite relevant signals (by wavenumber) from your IR spectrum. If the absence of a particular signal (such as an OH stretch or C=O stretch) helped you identify your product, be sure to indicate *where* in the IR spectrum that signal would be observed.

2. Clearly the degree of substitution affects the relative reactivity of alcohols. Provide another chemical example from your knowledge of organic chemistry where degree of substitution affects reactivity (multiple possibilities).

3. The compound we started with, 2-ethyl-1,3-hexanediol is sold as a mixture of stereoisomers. How many stereoisomers exist for this compound? Draw them.

4. Pick another of the potential products. Draw its structure (so we know which compound you chose). How would the IR spectrum of this compound differ from the IR spectrum of the actual product? Your answer should be fairly specific and it should compare and contrast the IR spectra of the two compounds (the compound you actually made and the compound you chose from the other potential products).

 When describing an absorbance, list the atom and functional group involved (such as “ O-H stretch of an alcohol) and give approximate location of the absorbance in the IR spectrum.

**Adapted from:**

Pelter, M. W.; Macudzinski, R. M.; Passarelli, M. E. *J. Chem. Educ.* **2000,** *77,* 1481.