Ethers and epoxides pdf

If you're seeing this message, it means we're having trouble loading external resources on our website. If you're behind a web filter, please make sure that the domains *.kastatic.org and *.kasandbox.org are unblocked. 18.0 Introduction Ethers are molecules containing oxygen which is bonded to two carbon groups. Thiols are sulfur analogues of alcohols with an SH group instead of OH. Sulfides are sulfur analogues of ethers with sulfur bonded to two carbon groups instead of oxygen. 18.1 Names and Properties of Ethers Ether groups are named as alkoxy groups. Ethers do not have intramolecular hydrogen bonding (unlike alcohols), therefore ethers have significantly reduced intermolecular forces causing boiling points that are much lower than similar sized alcohols. 18.2 Preparing Ethers Alkoxymercuration can be used to prepare an ether from an alkene. 18.3 Reactions of Ethers: Acidic Cleavage The carbon-oxygen bonds of ethers can be cleaved with strong acids through either nucleophilic substitution or elimination reactions. 18.4 Reactions of Ethers: Claisen Rearrangement The Claisen rearrangement is a [3, 3] sigmatropic rearrangement reaction that converts aryl or enol ethers into carbonyl compounds (though the aromatic version rearranges into a phenol to re-establish aromaticity. 18.5 Cyclic Ethers: Epoxides Epoxides, also called oxiranes, have a three-membered ring structure with one oxygen and two carbon atoms. Epoxides can be formed from alkenes by reaction with peroxy acids (MCPBA for example). Epoxides can be formed from halohydrin molecules by reaction with a base, which causes an intramolecular Williamson ether synthesis. 18.6 Reactions of Epoxides: Ring Opening When epoxides are ring opened under basic conditions, they follow SN2 mechanism leading to the nucleophile adding to the less substituted side of the epoxide. When epoxides are ring opened under acidic conditions, they follow SN1 mechanism leading to the nucleophile adding to the more substituted side of the epoxide. When epoxides are ring opened in aqueous reactions, the result is an anti-diol. Halo acids can be added to epoxides to form anti-halohydrins. 18.7 Crown Ethers Crown ethers are cyclic ethers containing several oxygen atoms. Crown ethers are named by the number of total atoms in the ring, followed by the word crown and finally the number of oxygen atoms (18-crown-6 for example). 18.8 Thiols and Sulfides Thiols can be prepared from alkyl halides through reaction with hydrosulfide ion (SH-) or through a more complicated series of reactions including thiourea. Thiols can be oxidized with mild oxidizing agents to form disulfides. Disulfide bridges link cysteine residues in protein structures. Sulfides are sulfur analogues of ether, though are much better nucleophiles with sulfur in place of oxygen. 18.9 Spectroscopy of Ethers Ethers show standard C-H stretches and bends in IR along with a strong C-O stretch around 1000 cm-1. In 1H NMR, hydrogens on carbons adjacent to the oxygen typically appear between 3.4-4.5 ppm. Hydrogens on carbons of an epoxide ring typically appear between 2.5-3.5 ppm in 1H NMR. 18.10 Interchapter: A Preview of Carbonyl Chemistry Carbonyl groups are one of the most important features in organic chemistry and consist of a sp2 carbon double-bonded to oxygen. Carbonyl groups are present in ~10 different functional groups. Carbonyl groups are polarized with a partial positive charge on carbon and partial negative charge on oxygen. This makes the carbon atom an electrophile, while the oxygen can act as a nucleophile. Carbonyl groups can react through several mechanisms including nucleophilic addition and nucleophilic acyl substitution, alpha substitution and condensation. Skills to Master Skill 18.1 Name ethers using common naming and IUPAC. Skill 18.2 Write reaction equations for preparation of ethers. Skill 18.3 Write mechanisms for reactions of ethers with strong halogen acids. Skill 18.4 Draw mechanisms for Cope and Claisen rearrangements. Skill 18.5 Draw mechanisms for ring-opening epoxides under acidic and basic conditions. Skill 18.6 Draw and name crown ethers. Skill 18.7 Explain how disulfide bridges contribute to protein structure. Skill 18.8 Give an example of S-adenosyl methionine activity in biological systems. Skill 18.9 Use IR and NMR spectra to identify ethers. Ether and Epoxide Preparation Ether Reactions Epoxide Reactions Sulfur Compound Reactions Key Terms Sulfide Ether Alkoxy group Vicinal (Vicinal) halohydrin Epoxidation Objectives Recognize the structure of ethers and epoxides Determine the IUPAC names for simple ethers and epoxides Identify several reactions, including synthesis reactions, for ethers and epoxides Through condensation reactions, we can form ethers from alcohols. The basic condensation reaction is shown below when performed in the presence of sulfuric acid. Also note that thiols are compounds that are structurally identical to alcohols except that they replace the oxygen atom in the hydroxyl group with a sulfur atom. Likewise, sulfides are structurally identical to ethers, but they replace the oxygen atom with a sulfur atom, as shown below. We will not discuss sulfides in detail, but you should be aware of this type of molecule. Note that its chemical properties differ from those of ethers. A chemical compound that is very similar to an ether is an epoxide. Epoxides involve an oxygen and two carbon atoms in a three-atom ring structure, as illustrated below. Whereas ethers are relatively stable molecules, epoxides are highly reactive. Nomenclature The fundamental functional group for naming ethers is the alkoxy group, several examples of which are shown below with their corresponding names. Note that the names closely resemble the names of the similar alkyl groups. To properly name an ether according to IUPAC rules, identify the shortest alkyl chain attached to the oxygen atom and consider that portion the alkoxy group. Then follow the usual rules for naming molecules, where the alkoxy group is a substituent of the alkane. Another acceptable naming procedure is to write the two alkyl group names followed by the word ether (similarly to how we named alcohols, such as ethyl alcohol). For example, consider the two molecules below and their acceptable IUPAC names. Cyclic ethers have non-systematic names, so we will not focus on this aspect of the nomenclature, but the IUPAC names for several cyclic ethers are given below. Oxolane also goes by the name tetrahydrofuran. For epoxides, the functional group name is epoxy when used in the same manner as, for example, ethyl or methyl (that is, following the rules of substitutive nomenclature). When used in the manner of, for instance, ethyl alcohol (functional class nomenclature), the term oxide is used. In the substitutive approach, the epoxy- prefix is preceded by the numbers of the two carbons to which the oxygen is bound. Thus, the following are acceptable IUPAC names for several epoxides. Also note that because of the structure of epoxies, these molecules can exhibit stereoisomerism. For instance, 3,4-epoxyhexane can actually be either cis-3,4-epoxyhexane or trans-3,4epoxyhexane, as shown below. In addition to cyclic structures (such as epoxides), ethers can involve multiple oxygen atoms in a carbon chain. For instance, so-called crown ethers are cyclic ethers with multiple oxygen atoms in the ring. An example is shown below, along with its simplified name (we will not discuss nomenclature for crown ethers). Practice Problem: Determine the IUPAC name for the molecule shown below. Solution: This molecule is an ether with two four-carbon chains (butyl groups) attached to the central oxygen atom. Thus, it can be legitimately called either dibutyl ether or butoxybutane. Practice Problem: Determine the IUPAC name for the molecule shown below. Solution: This compound is 2,3-epoxy-5-methylheptane. Note that the main carbon chain is numbered as shown below. Synthesizing Ethers and Epoxides As mentioned previously, we have already studied the acid-catalyzed synthesis of ethers from alcohols. Another method is the Williamson ether synthesis, which involves a reaction between a metal alkoxide and an alkyl halide. For instance, consider sodium ethoxide and bromopropane. The overall reaction is shown below. The mechanism for this reaction involves dissociation of the metal from the alkoxide and then nucleophilic attack (SN2) on the alkyl halide. The alkoxide ion acts as a Lewis base with respect to the alkyl halide. Again, note that this reaction is a nucleophilic substitution involving two molecules (SN2). For epoxides, one approach to synthesis essentially follows this mechanism but involves a single molecule in which a hydroxyl group and a halide attached to adjacent carbon atoms (these functional groups are said to be vicinal, and this particular type of molecule is called a vicinal halohydrin). In the presence of a base (such as hydroxide ions), the halohydrin donates the proton (an acid-base reaction) bound to the oxygen atom. Consider the case below of 3-iodobutanol. The remaining molecule can then dissociate an iodide ion as follows, creating the epoxide. The product in this case is 2,3-epoxybutane. The stereoisomer of the product depends on the configuration of the starting molecule. Another method of synthesizing an epoxy is through epoxidation of an alkene. The reaction involves a peroxy acid, a generic example of which is shown below. Consider the example of cyclohexene. In the presence of peroxyacetic acid, the following reaction yields 1,2-epoxycyclohexane and acetic acid. Reactions of Ethers and Epoxides Let's consider a couple reactions that involve ethers and epoxides: in particular, cleavage of ethers by hydrogen halides and acid-catalyzed ring opening of epoxides (two similar reactions). The first reaction, cleavage of ethers by hydrogen halides, is exemplified (overall) below for the case of ethoxypropane and hydrogen bromide. The reaction mechanism in this case proceeds in two steps to yield an alkyl halide and an alcohol. The next step is a cleavage that, in this non-symmetrical case, can yield two slightly different results. or Given the conditions of the reaction (which likely involve hear), however, the alcohol (in either case) undergoes an SN2 reaction with hydrogen bromide to form another alkyl halide and water. Thus, in this case, the final products of the reaction are ethyl bromide, propyl bromide, and water. Epoxides can undergo ring opening in the presence of hydrogen bromide in a reaction very similar to that shown above. The mechanism is illustrated below for 1,2-epoxybutane. In the first step, the dissociated bromide ion attacks the less substituted carbon bound to the oxygen atom. A proton (originating from dissociation of the hydrogen and bromine atoms in hydrogen bromide) then bonds with the oxygen to form 1-bromo-2-butanol. Practice Problem: Describe the relationship between cleavage of ethers in hydrogen bromide and acid-catalyzed ring opening of epoxides in hydrogen bromide. Solution: In each case, an oxygen-carbon bond is broken, and a halide ion replaces this broken bond. The oxygen atom also bonds to a hydrogen in both cases. These steps occur in a different order for epoxides compared with ethers. Also, in the case of the ether, the resulting alcohol product may be converted to another alkyl halide, meaning the ether is ultimately broken into two alkyl halide molecules. In the case of the epoxide, the result is a single vicinal halohydrin product.

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