Chapter 16

Ethers, Epoxides, and Sulfides

Chapter 16 suggested problems: 21, 25, 26, 31, 32, 33

Class Notes

I. Nomenclature of ethers, epoxides, and sulfides

   A. General

      1. Ethers: C-O-C

      2. Epoxides: cyclic ethers, 3-membered rings

      3. Sulfides: R-S-R (ether analogues)

   B. Ethers

      1. Symmetrical and unsymmetrical (mixed) ethers

      2. Can be named as alkoxy derivatives of alkanes (substitutive nomenclature), esp. if the alkyl groups do not have simple or common names

      3. If the alkyl groups do have simple or common names (functional class nomenclature), ethers can be named by listing the alkyl groups in alphabetical order as separate words, followed by "ether"

         a. Diethyl ether (ethoxyethane)

         b. Ethyl methyl ether (methoxyethane)

         c. Anisole (methoxybenzene)

         d. Methyl tert-butyl ether (MTBE; 1-methoxy-1,1-dimethylethane)

         e. Isopropyl phenyl ether (1-phenoxy-1-methylethane)

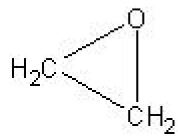
         f. Diphenyl ether (phenoxybenzene)

         g. p-ethoxybenzoic acid

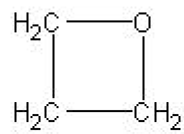
h. 3-methoxyhexane

4. Cyclic ethers - heterocyclic compounds

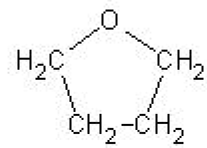
a.



oxirane

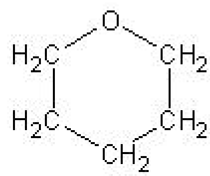


oxetane



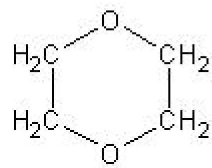
oxolane

tetrahydrofuran



oxane

tetrahydropyran



1,4-dioxane

5. Di, tri, and polyethers: compounds can have more than one ether linkage

   a. 1,2-dimethoxyethane

C. Epoxides

1. As substituted oxiranes: 2-(chloromethyl)oxirane (also known as epichlorohydrin)

2. 1,2-epoxypropane and 3,4-epoxy-1-butene

D. Sulfides: the sulfur analogues of alkoxy groups are called *alkylthio* groups

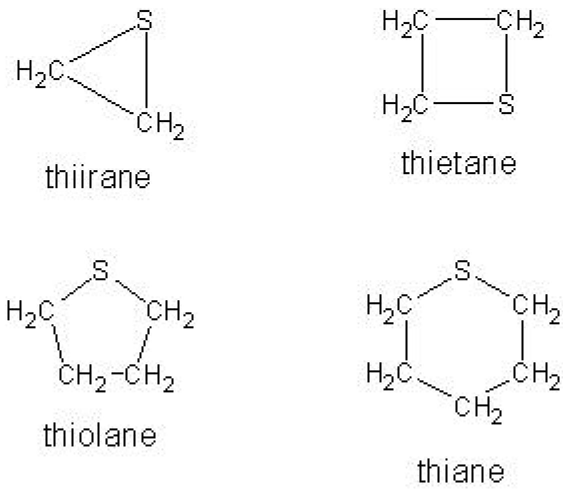
1. For either substitutive or functional class nomenclature, rules are exactly the same as for ethers with simple accommodations for the sulfur atom

   a. Ethylthioethane and diethyl sulfide

   b. (Methylthio)cyclopentane and cyclopentyl methyl sulfide

2. Cyclic sulfides

a.



II. Physical properties of ethers

A. Structure and bonding in ethers and epoxides

1. The oxygen atom is sp^3 hybridized and has two lone pairs, resulting in bent geometry

2. The more substituted the oxygen atom, the greater the steric hindrance between the groups and the more distorted the R-O-R bond angle

a. H_2O - 105°

b. Methanol - 108.5°

c. Dimethyl ether - 112°

d. Di-tert-butyl ether - 132°

3. The bond angle in epoxides is seriously distorted at about 60°

4. Ethers are polar

5. Ethers have BPs similar to those of alkanes, since they lack the ability to form intermolecular hydrogen bonds

6. Ethers have aqueous solubilities similar to those of alcohols, since they can form dipole-dipole interactions with water (H-bond recipients)

B. Crown ethers: cyclic ethers named by (# atoms in ring - "crown" - # oxygen atoms) e.g. 12-crown-4, 18-crown-6

III. Preparation of ethers

A. Preparation of ethers via acid-catalyzed condensation of alcohols (Ch. 15.7)

1. Mostly limited to synthesis of symmetric ethers using primary alcohols as starting materials

B. The Williamson ether synthesis: $RO^- + R'X \rightarrow ROR' + X^-$

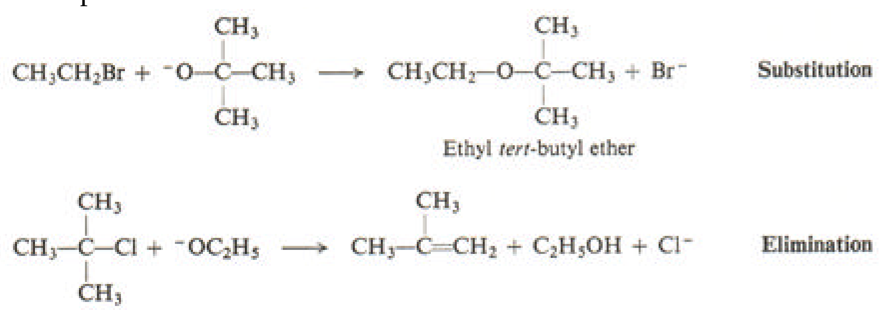
1. Can be used to prepare symmetric and unsymmetric alkyl and aryl ethers

2. Involves nucleophilic substitution of an alkoxy group for a halide ion and is comparable to preparation of alcohols by the reaction of alkyl halides with hydroxide ion

3. Order of reactivity for alkyl halides: methyl > 1° > 2° > 3°

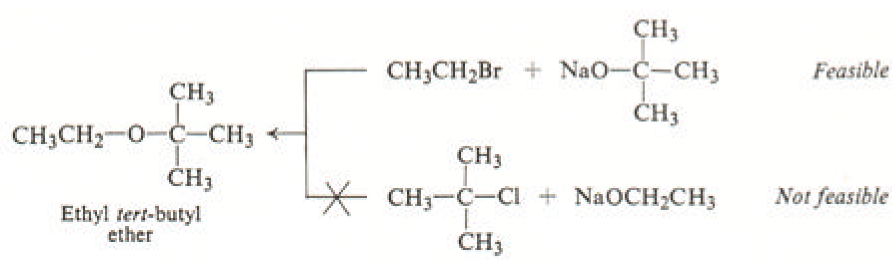
   a. Tendency of alkyl halides to undergo dehydrohalogenation: 3° > 2° > 1°

   b. Aryl halides cannot be used because of their low reactivity in nucleophilic substitutions

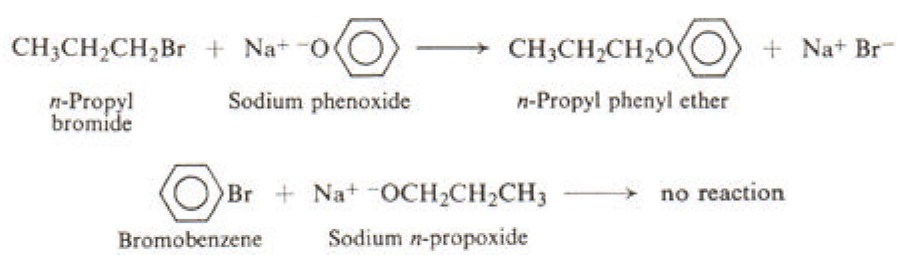


4. Examples and considerations

   a.



   b.



IV. Reactions of ethers: a review and a preview

A. Ethers are one of the least reactive functional groups studied

1. Ether linkage is stable toward bases, oxidizing agents, and reducing agents

2. This makes ethers preferred solvents in syntheses of reactive materials

3. Combustion of ethers

4. Reaction with O_2 to form peroxides

B. Acid-catalyzed cleavage of ethers: R-O-R' + HX -> R-X + R'-OH + HX -> R'-X

1. Cleavage requires high temperatures and concentrated acids

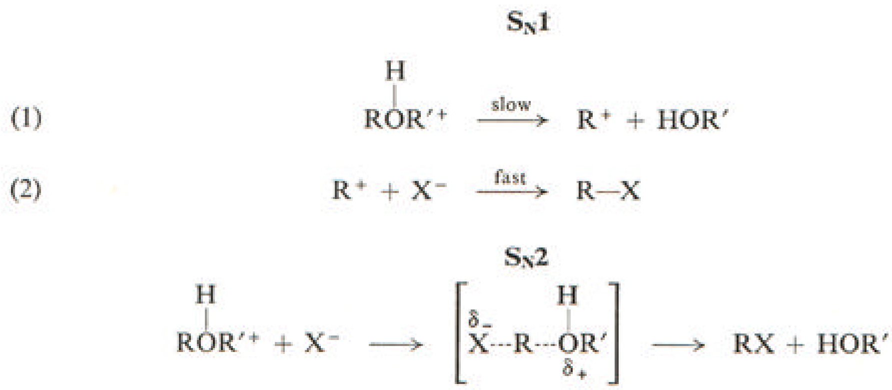
2. Order of acid reactivity: HI > HBr > HCl

3. Cleavage involves nucleophilic attack by the halide ion on the protonated ether, with the weak base (good leaving group) R'-OH being displaced

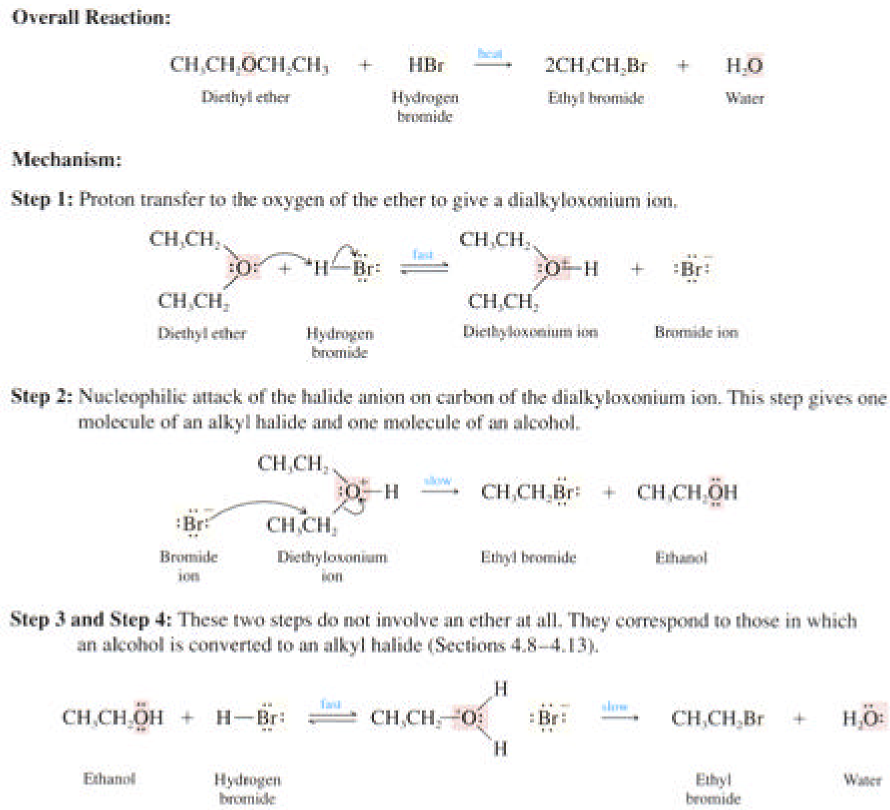
4. The reaction of the protonated ether with the halide ion can be either S_N1 or S_N2 and depends on the ether structure and reaction conditions

    a. Primary alkyl groups (R, not R') undergo S_N2 substitution

    b. Tertiary R groups undergo S_N1 substitution



5. Mechanism: the acid-catalyzed cleavage of diethyl ether (Carey: 629)



V. Preparation of epoxides: (skip)

VI. Reactions of epoxides: ring-opening reactions

A. Epoxides are highly reactive due to the strain associated with a three-membered ring

1. Bond angles of abt. 60° are far less than the tetrahedral bonds angles of tetrahredral carbons and also less than the approximate 110° bond angles of open-chain ethers

2. This prevents good orbital overlap and results in weaker bonds

B. Epoxides not only undergo acid-catalyzed cleavage as "normal" ethers, but also undergo base-catalyzed cleavage and will react with Grignard reagents

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Last Modified Sunday, July 28, 2002 17:42:06
