

Synthesis and Cleavage of Ethers

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DESCRIPTION

Chemical substitution processes that result in the cleavage of ethers are referred to as ether cleavage. The breaking of the C-O bond is uncommon in the absence of specialist reagents or under extreme conditions due to the strong chemical stability of ethers. Cleavage of the C-O link by strong acids is the most common reaction of ethers. For 3-O-alkyl groups, SN₁ or E₁ mechanisms may be used, while for 1-O-alkyl groups, an SN₂ mechanism may be used.

The first two reactions are carried out in a series of SN₂ steps, in which the iodide or bromide anion first displaces an alcohol, then transforms the conjugate acid of that alcohol to an alkyl halide in the second. The methyl group in Example #1 is cleaved first because SN₂ reactions prefer least hindered locations. 2-O-alkyl group is most likely split by an SN₂ mechanism, but the possibility of an SN₁ process cannot be ruled out. Because SN₂, SN₁, and E₁ reactions do not occur on aromatic rings, the phenol produced in this reaction does not react further. The last example shows a strong acid cleaving a 3-O-alkyl group. Acids with poorly nucleophilic conjugate bases are frequently used for this purpose, favouring E₁ products.

Ether cleavage is an acid-catalyzed nucleophilic substitution process in organic chemistry. Cleavage can occur via either SN₁ or SN₂ pathways, depending on the ether. In order to distinguish between the two mechanisms, inductive and mesomeric effects that could stabilise or destabilise a possible carbocation in the SN₁ route must be considered. Hydrohalic acids are used because they may protonate the ether oxygen atom while simultaneously providing a sufficient nucleophile in the form of a halide anion. However, because ethers have similar basicity to alcohols, protonation equilibrium favours the unprotonated ether, and cleavage is possible usually very slow at room temperature.

Strongly basic agents, such as organolithium compounds, can cleave ethers. Cleavage is more common in cyclic ethers, but it can also happen in acyclic ethers.

Cleavage of SN₁ ether

A carbocation is used in the unimolecular SN₁ mechanism (provided that the carbocation can be adequately stabilized). The oxygen atom in methyl tert-butyl ether is reversibly protonated in this example. The oxonium ion that results decomposes into methanol and a rather stable tert-butyl cation. A nucleophile halide (here bromide) attacks the latter, resulting in tert-butyl bromide.

Cleavage of SN₂ ether

Ether cleavage follows a bimolecular, concerted SN₂ mechanism if the putative carbocation cannot be stabilised. The ether oxygen is reversibly protonated in this scenario. The halide ion (in this case bromide) then attacks the sterically less hindered carbon atom, resulting in methyl bromide and 1-propanol.

Organometallic agents cleave ethers

Mechanism

Deprotonation in position causes basic ether cleavage. After that, the ether breaks down into an alkene and an alkoxide. Cyclic ethers provide a particularly rapid concerted cleavage.

Impact

Often, organometallic compounds are handled with etheric solvents, which bind to the metallic centres and increase the reactivity of the organic rests. The ether cleavage is problematic in this case because it not only decomposes the solvent but also consumes the organometallic substance.

As a result, reactions involving organometallic compounds are usually carried out at very low temperatures (-78°C). Deprotonation is kinetically hindered and slow at these temperatures, relative to several other reactions that are supposed to happen.

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