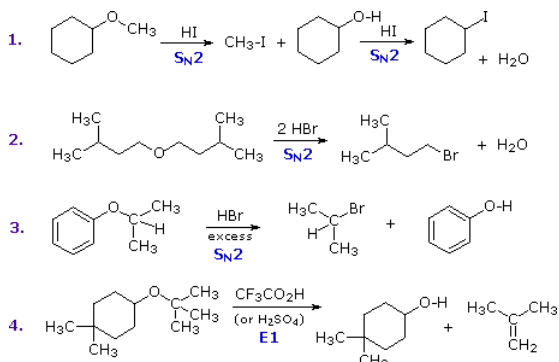


9.5: Reaction of Ethers with Strong Acid

The most common reaction of ethers is cleavage of the C–O bond by strong acids. This may occur by S_N1 or $E1$ mechanisms for 3° -alkyl groups or by an S_N2 mechanism for 1° -alkyl groups. Some examples are shown in the following diagram. The conjugate acid of the ether is an intermediate in all these reactions, just as conjugate acids were intermediates in certain alcohol reactions.



The first two reactions proceed by a sequence of S_N2 steps in which the iodide or bromide anion displaces an alcohol in the first step, and then converts the conjugate acid of that alcohol to an alkyl halide in the second. Since S_N2 reactions are favored at least hindered sites, the methyl group in example #1 is cleaved first. The 2° -alkyl group in example #3 is probably cleaved by an S_N2 mechanism, but the S_N1 alternative cannot be ruled out. The phenol formed in this reaction does not react further, since S_N2 , S_N1 and $E1$ reactions do not take place on aromatic rings. The last example shows the cleavage of a 3° -alkyl group by a strong acid. Acids having poorly nucleophilic conjugate bases are often chosen for this purpose so that $E1$ products are favored. The reaction shown here (#4) is the reverse of the tert-butyl ether preparation described earlier.

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