

ORGANIC CHEMISTRY 1 LECTURE GUIDE 2019

BY RHETT C. SMITH

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By Rhett C. Smith, Ph.D.

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Companion Books from the Proton Guru:

Organic Chemistry 1 Reactions and Practice Problems 2019

by Rhett C. Smith

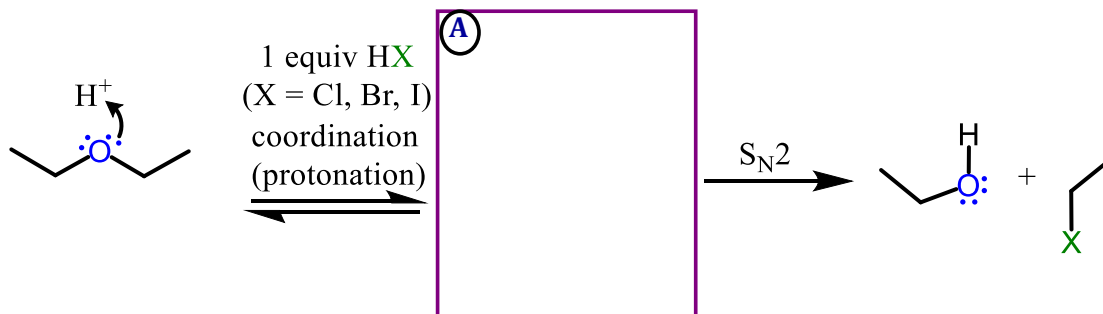
Organic Chemistry 1 Primer 2019,

by Rhett C. Smith, Andrew G. Tennyson, and Tania Houjeiry

Lecture Topic II.14: Acid Cleavage of Ethers

S_N2 Reactions occur at Methyl and Primary Carbons

Like alcohols, ethers do not have a good leaving group for substitution reactions. However, the O atom of an ether can be protonated by HX (X = Cl, Br, I) to create a good leaving group. An S_N1 or S_N2 reaction follows:



In this example, the ether is symmetric, so it does not matter which side we choose to attack with the nucleophile.

If the carbon to be attacked is methyl or primary:

B

Because:

Notes

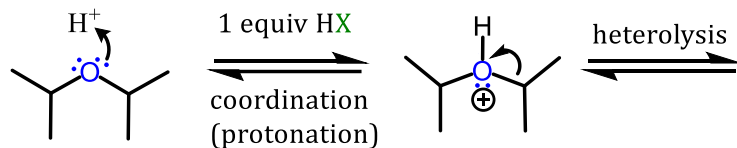
Lecture Topic II.14: Acid Cleavage of Ethers

S_N1 Reactions occur at Secondary and Tertiary Carbons

If the carbon to be attacked by the nucleophile is 2° or 3° :

(A)

This is the case even though a good nucleophile (Cl^- , Br^- or I^-) is present, so this is a **difference from alkyl halides**.



(B)

coordination

(C)

1. Activate OR to make it a good leaving group
2. S_N1 (heterolysis then coordination of X^-)

Everything we learned about S_N1 of alkyl halides applies here. Tertiary carbocation forms more rapidly, the carbocation can rearrange, etc.

Notes

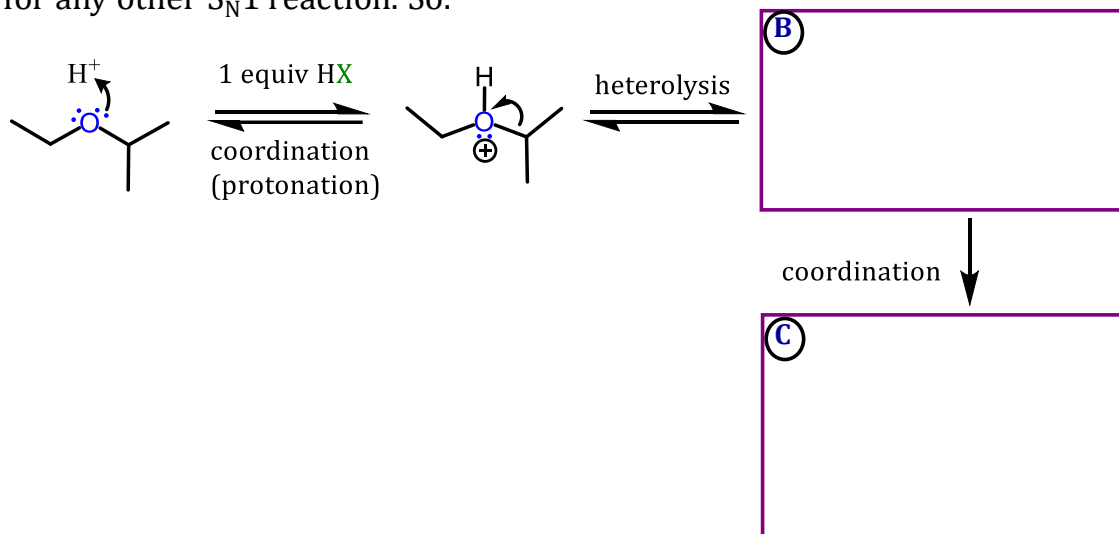
Lecture Topic II.14: Acid Cleavage of Ethers

S_N1 is Preferred over S_N2 where Possible

The ether may not be symmetrical. In these cases:

(A)

If both sides of the ether are capable of S_N1 , 3° reacts faster than 2° , as for any other S_N1 reaction. So:



Notes