

ORGANIC CHEMISTRY 1 LECTURE GUIDE 2019

BY RHETT C. SMITH

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Organic Chemistry 1 Lecture Guide 2019

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

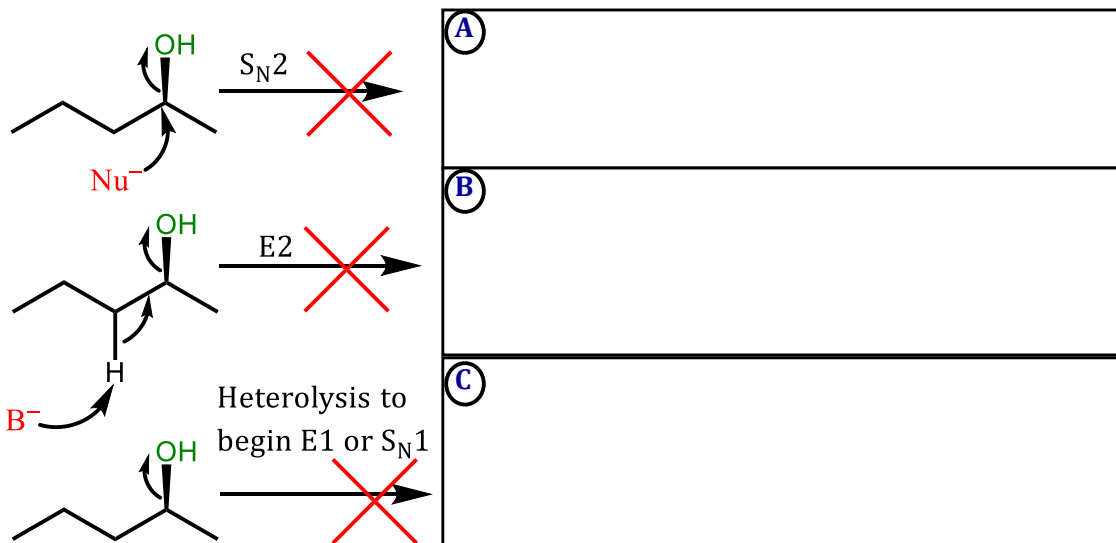
Organic Chemistry 1 Primer 2019,

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

Lecture Topic II.11: Substitution and Elimination Reactions of Alcohols

Hydroxide is a Bad Leaving Group

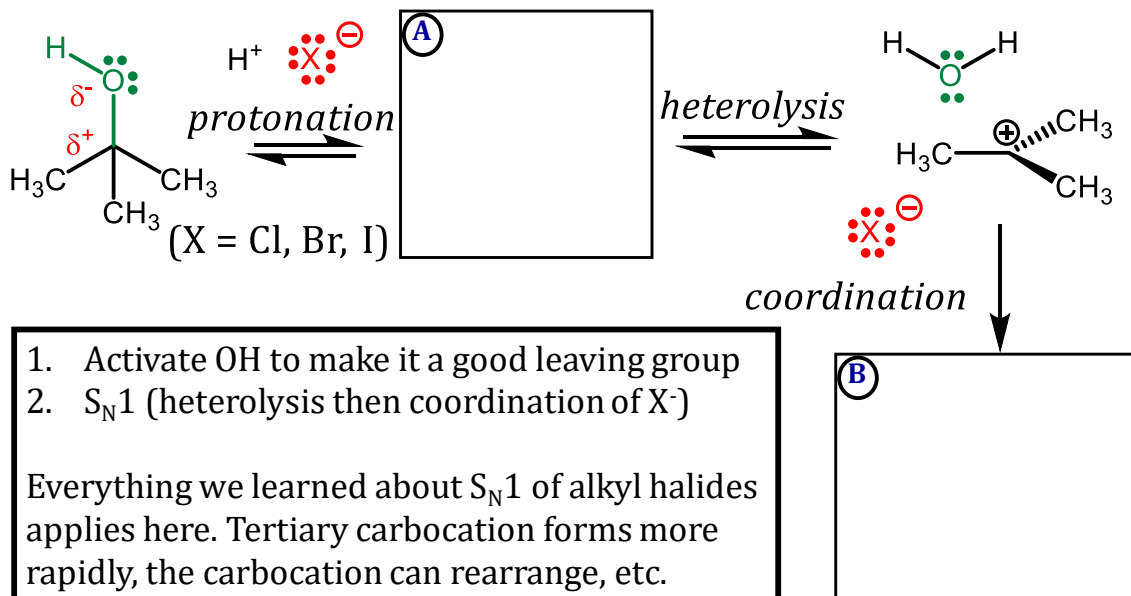
So far we have only explored alkyl halides as substrates for S_N1 , S_N2 , E1 or E2 reactions because alkyl halides with Cl, Br or I substituents have the good leaving groups required. If we propose using an alcohol in these reactions:



The hydroxide anion is a strong base (unstable anion) and is a bad leaving group. It must be **activated** prior to reaction by these routes.

Notes

One way to convert OH into a good leaving group is to protonate it with a strong acid. This leads to a water leaving group. This allows a **tertiary or secondary alcohol to undergo an S_N1 reaction**:

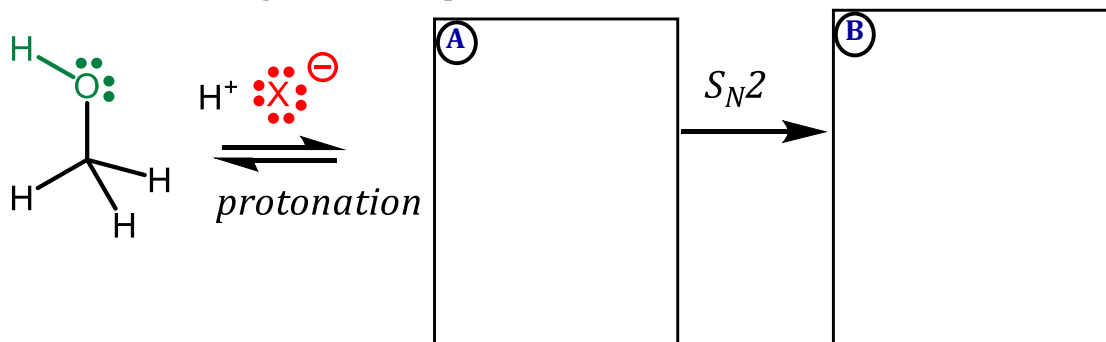


1. Activate OH to make it a good leaving group
2. S_N1 (heterolysis then coordination of X^-)

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

Notes

An activated **methyl or 1° alcohol** will undergo **S_N2 reaction** with the halide, which is a good nucleophile:



1. Activate OH to make it a good leaving group
2. S_N2 (concerted)

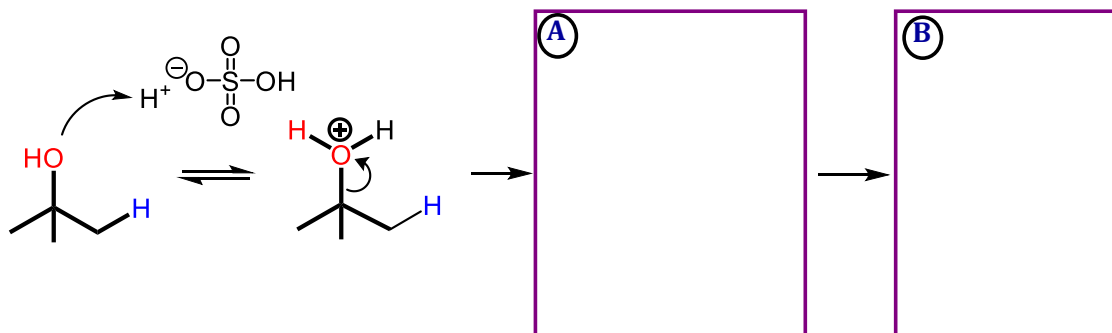
Everything we learned about S_N2 of alkyl halides applies here. Walden inversion occurs, less sterically-encumbered substrates react faster, etc.

Notes

Lecture Topic II.11: Substitution and Elimination Reactions of Alcohols

E1 of 2° and 3° ROH: Dehydration

If a 2° or 3° alcohol is activated with an acid having a non-nucleophilic counteranion (i.e., H_2SO_4 or H_3PO_4), an E1 Reaction will occur. Net reaction is loss of water from the alcohol, this particular type of E1 reaction is also called **dehydration**.



1. Activate OH to make it a good leaving group
2. E1 (heterolysis then electrophilic elimination)

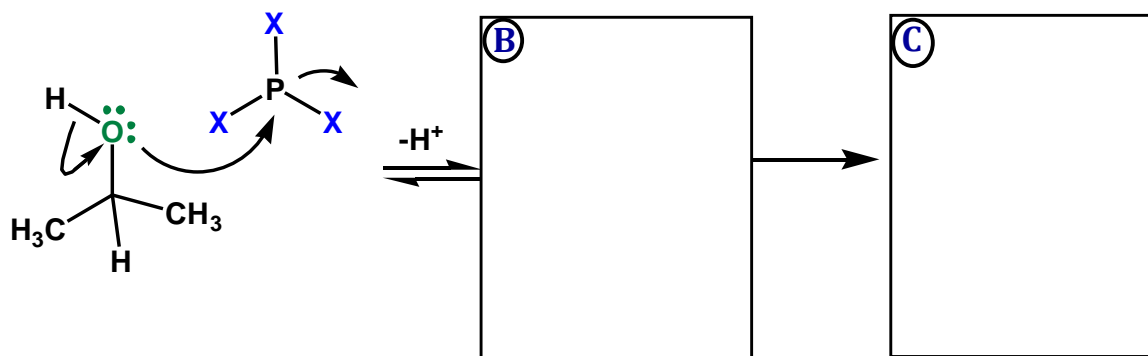
Everything we learned about E1 of alkyl halides applies here. Tertiary carbocation forms more rapidly, the carbocation can rearrange, etc.

Note: cannot do E2 (needs strong **base**) of an alcohol with strong acid!

Notes

Lecture Topic II.11: Substitution and Elimination Reactions of Alcohols
Activation with Phosphorus Trihalide

Another way to activate an OH group is by reaction with PX_3 ($X = Cl$ or Br):

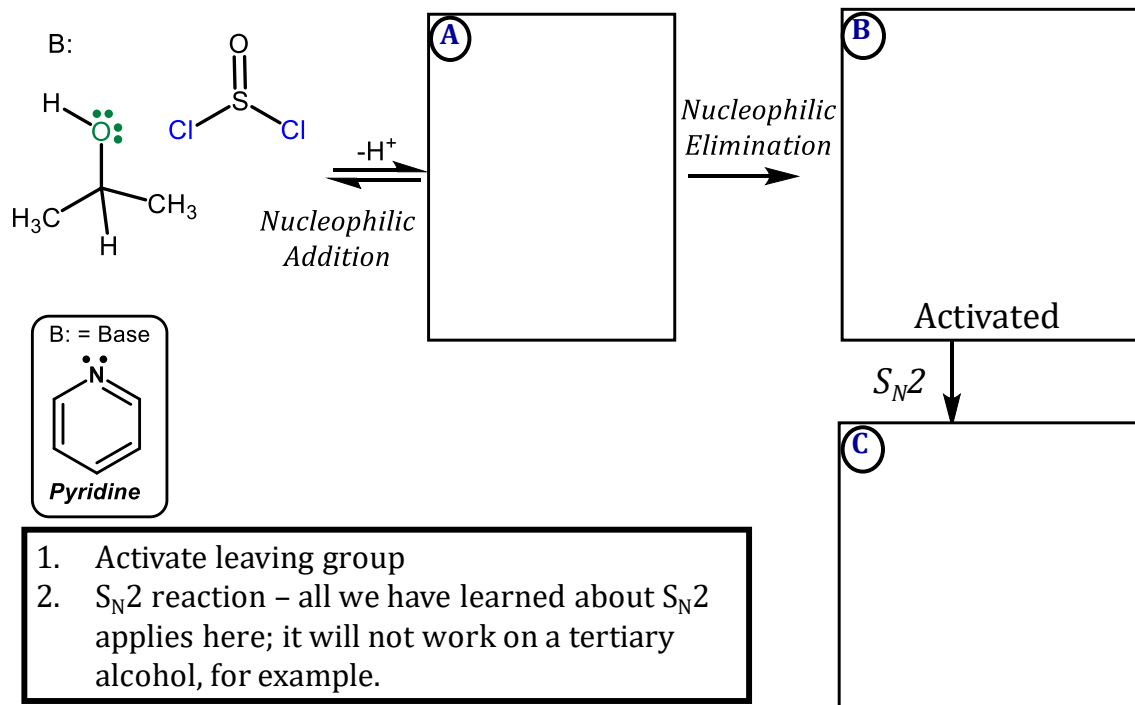


1. Activate leaving group
2. S_N2 reaction – all we have learned about S_N2 applies here; it will not work on a tertiary alcohol, for example.

Note: 1 mol PX_3 can produce 3 mol $RX + H_3PO_3$

Notes

A third way to activate an OH group is by reaction with thionyl chloride:

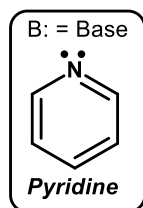
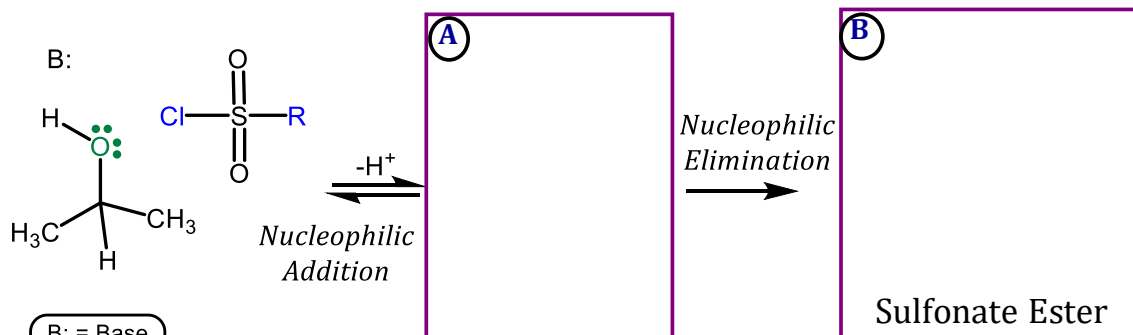


Notes

Lecture Topic II.11: Substitution and Elimination Reactions of Alcohols

Conversion of ROH to Sulfonate Ester

Alcohols can also be converted into sulfonate esters. This is not a substitution or elimination reaction, but it is a good way to change the OH into a good leaving group:



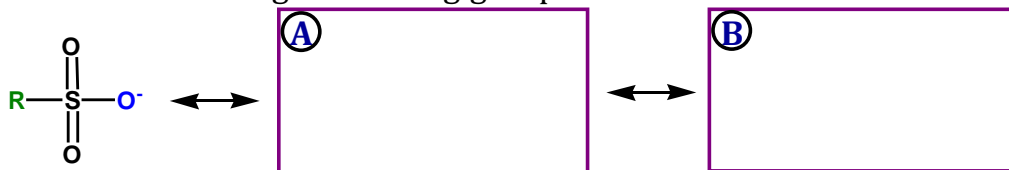
C Sulfonate Esters are useful because:

Notes

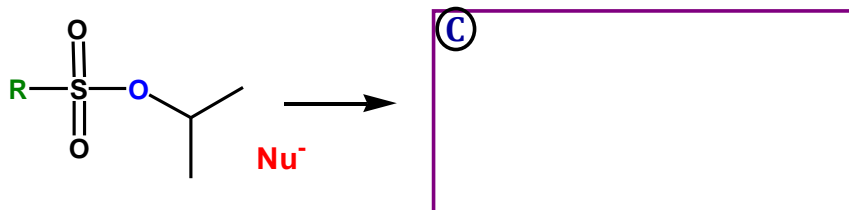
Lecture Topic II.11: Substitution and Elimination Reactions of Alcohols

Useful Sulfonate Esters

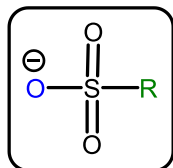
The sulfonate is a good leaving group because of resonance stabilization:



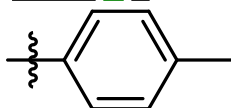
A sulfonate ester is ideal starting material for nucleophilic substitution:



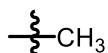
Three specific sulfonates are common:



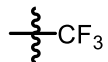
When $R \equiv$ *Anion Name*



Tosylate



Mesylate



Triflate

Notes