ORGANIC CHEMISTRY 1 LECTURE GUIDE 2019

BY RHETT C. SMITH

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Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

ISBN 978-1074137434

Organic Chemistry 1
Lecture Guide 2019

By Rhett C. Smith, Ph.D.

Companion Books from the Proton Guru:

Organic Chemistry 1 Reactions and Practice Problems 2019

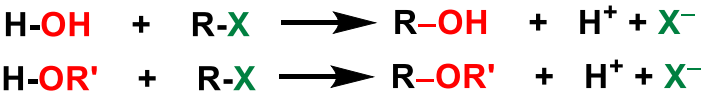
by Rhett C. Smith

Organic Chemistry 1 Primer 2019,

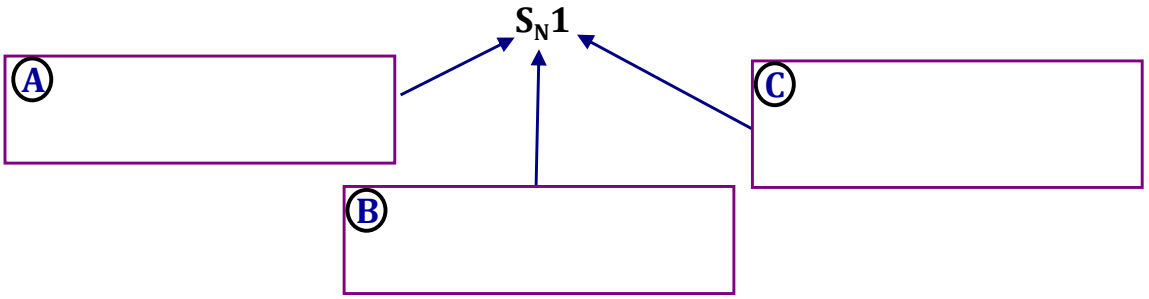
by Rhett C. Smith, Andrew G. Tennyson, and Tania Houjeiry

Lecture Topic II.3: The S_N1 Mechanism
Alkyl Halides can undergo the S_N1 Reaction

Alkyl Halides react with even poor nucleophiles, often solvents such as water or alcohols, to yield alcohols or ethers:

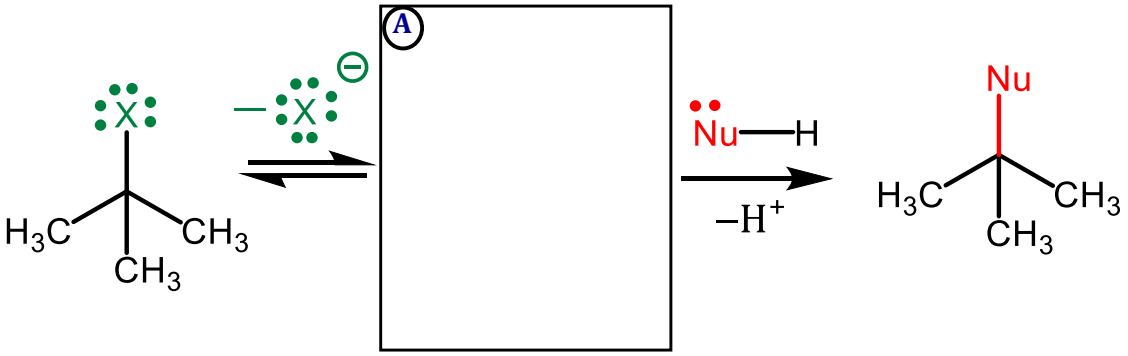


This is a **substitution reaction**, and it proceeds by a specific mechanism called the **S_N1** mechanism. This is an abbreviation meant to help you remember how the reaction takes place:



Because the substrate (RX) reacts with the solvent, this reaction is sometimes called **solvolysis** as well.

Notes



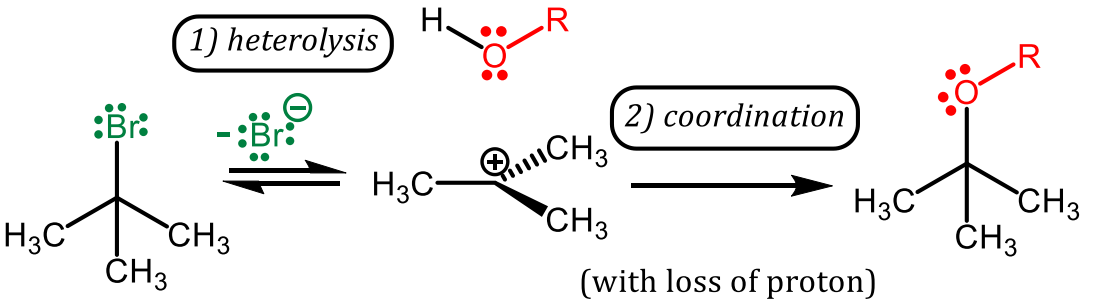
S_N1 is a two-step sequence of steps:

1) Heterolysis (lose a good **Leaving Group (LG)**)
2) Coordination (of a Nucleophile)

Heterolysis occurs: B

A "good" leaving group (LG) is: C

Notes



S_N1 = 1) Heterolysis, 2) Coordination. **Fill in the curved arrows to show the flow of electrons**

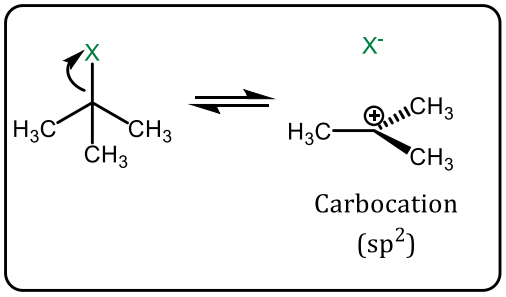
R in HOR can be: **A**

Rate-Limiting Step: **B**

Rate Law: **C**

Notes

Rate-Limiting Step for S_N1



The rate-limiting step leads to a leaving group (here X-) and a carbocation as products. Substrates that produce more stable products react faster by S_N1.

Substrate trend:

CH_3X < 1° RX < [ ] < [ ]

Too unstable; will not work for S_N1!

REACTIVITY →

Leaving group (LG) trend:

R-F < [ ] < [ ] < [ ]

Generally difficult for S_N1!

Notes

A

Solvent can stabilize cations

B

Solvent can stabilize anions
(we saw this for bases)

Stronger attractive intermolecular forces are more stabilizing, so the solvents in which the S_N1 reaction is the fastest are:

C

Notes

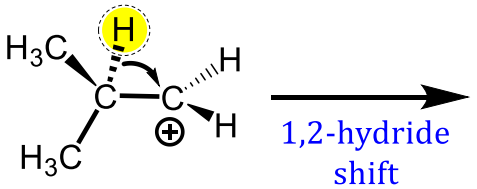
Thermodynamically favorable reactions will occur spontaneously when they are kinetically and mechanistically accessible. In **Lecture Topic I.8** we saw that carbocations can rearrange.

Carbocations will always

A

The rate at which the carbocation rearranges is:

B

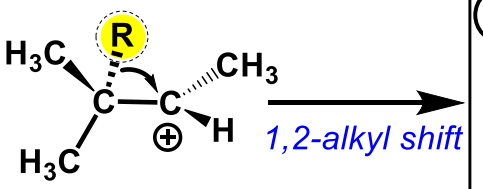


Primary Carbocation

C

Notes

Alkyl groups can also migrate to create a more stable species. This *usually* only happens when there are no hydride units to shift. A notable exception is when rearrangement leads to relief of ring strain (given as an Example in the Reaction Guide).



Secondary Carbocation

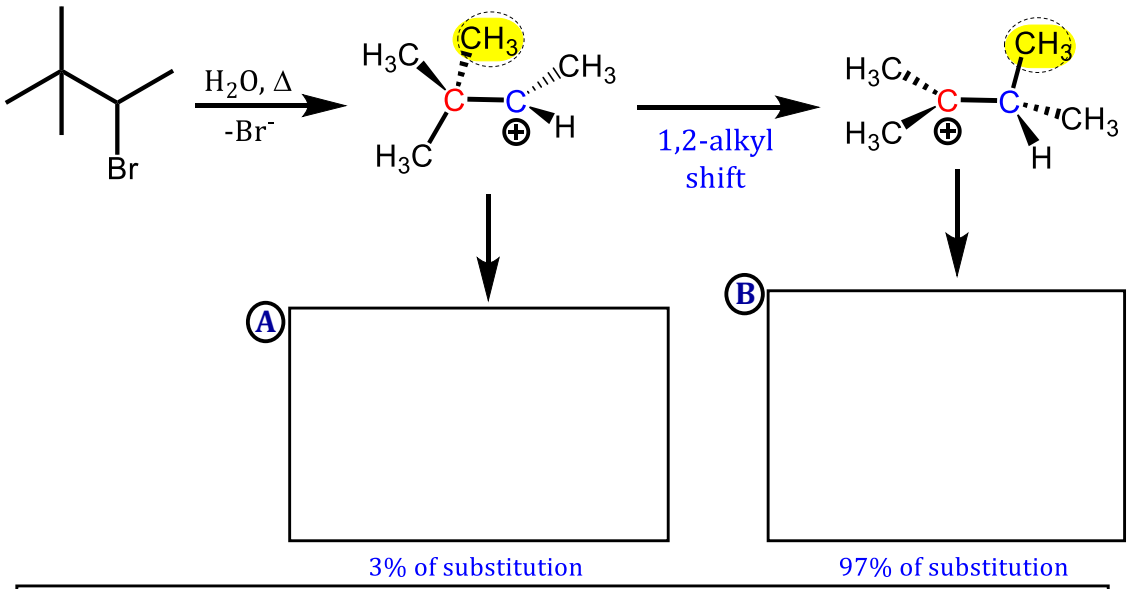
A

Because a carbocation forms as an intermediate in the S_N1 reaction:

B

Notes

Lecture Topic II.3: The S_N1 Mechanism
The Major S_N1 Product derives from the Most Stable Carbocation



C The Major Product:

Notes