ORGANIC CHEMISTRY 2 LECTURE GUIDE 2019

BY RHETT C. SMITH, PH.D.

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Executive Editor: Rhett C. Smith, Ph.D. You can reach him through our office at:
IQ@protonguru.com

Cover photo courtesy of William C. Dennis, Jr.

Printed in the United States of America

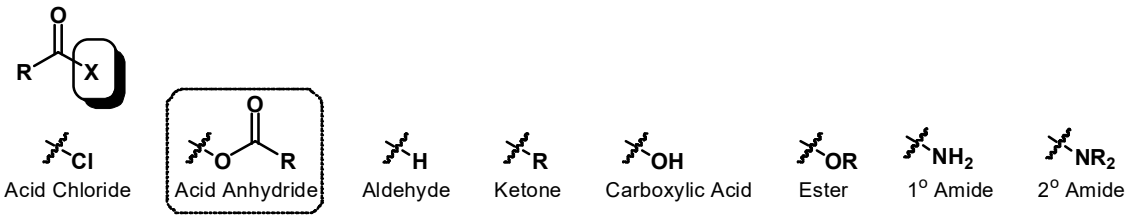
10 9 8 7 6 5 4 3 2 1

ISBN 978-0578415017 (IQ-Proton Guru)

Lesson VI.4. Relative Rates of Nucleophilic Attack on Carbonyl Functional Groups

Carbonyl reactivity depends on sterics and electronics

Because each of the various carbonyl-containing functional groups has a different substituent, their reactivities to the initial nucleophilic addition vary as well:



Less electron density (more positive charge) on the carbonyl C will increase susceptibility to nucleophilic attack:

A

Notes

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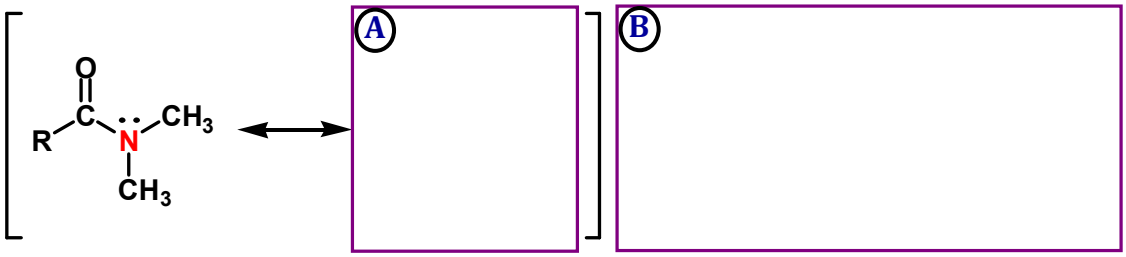
Carbonyl reactivity depends on sterics and electronics

Drawing out the contributing resonance structures can help us assess the electron-density at the carbonyl unit:



Resonance contributors *Resonance hybrid*

Esters will have similar resonance structures wherein an O lone pair moves

Acid (or metal coordination) can increase the reactivity of a carbonyl:

Notes

Lesson VI.4. Relative Rates of Nucleophilic Attack on Carbonyl Functional Groups

Carbonyl reactivity depends on sterics and electronics

More steric encumbrance slows down the rate of nucleophilic attack (just like we saw for S_N2 reactions, 1° > 2° > 3°):

Aldehyde versus ketone:

A

Carboxylic acid versus ester:

B

A similar case can be made for comparison of primary and secondary amides.

Notes