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

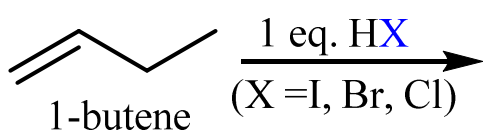
10 9 8 7 6 5 4 3 2 1

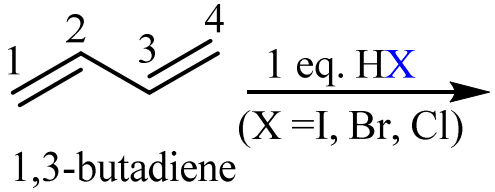
ISBN 978-0578415017 (IQ-Proton Guru)

Lesson IV.2. Addition Reactions of Conjugated Dienes

Differing Reactivity

If a C=C bond is π-conjugated, its reactivity may differ from that of a C=C in an isolated alkene:



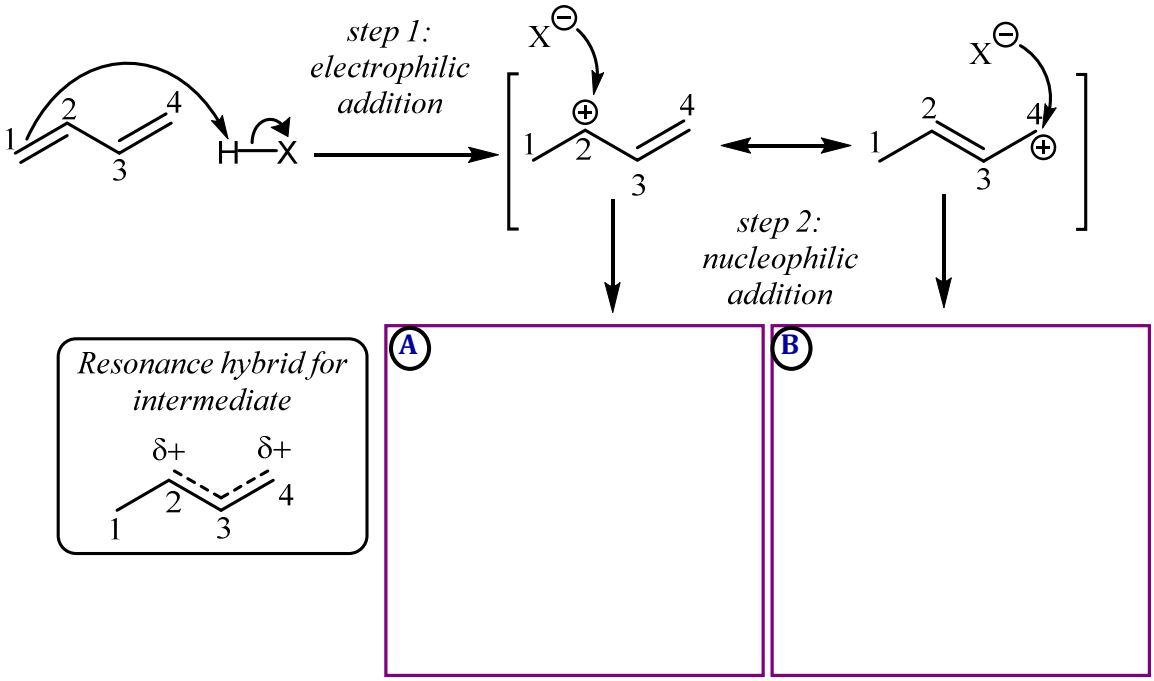


Notes

Lesson IV.2. Addition Reactions of Conjugated Dienes

Identifying Electrophilic Sites

Let us study the process by which the two products form in the case of the conjugated diene:



Notes

Lesson IV.2. Addition Reactions of Conjugated Dienes

1,2-Addition vs. 1,4-Addition

The 1,2-addition is faster (lower energy of activation, $E_{a1,2}$ in the figure below) because the halide is closer to C2 when it is produced. This is known as a:

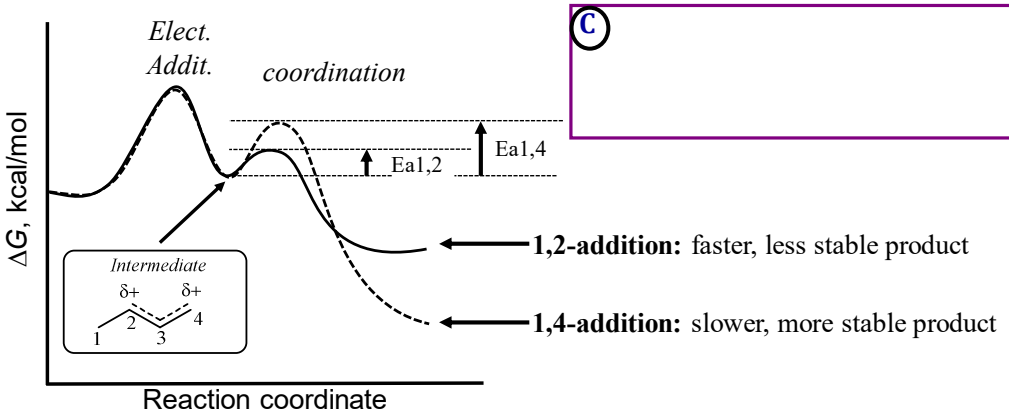
A

The result of this is that the

B

product is formed faster – it is the

C



Notes

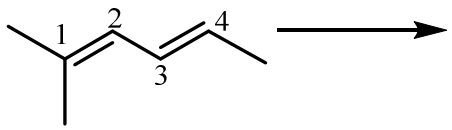
Lesson IV.2. Addition Reactions of Conjugated Dienes

Thermodynamic Products versus Kinetic Products

The 1,2-addition product is always the kinetic product. However, the

A

Is always the **thermodynamic product**. It may result from 1,4-addition (as we saw for 1,3-butadiene), or 1,2-addition, like this:



A

Notes

Lesson IV.2. Addition Reactions of Conjugated Dienes

Thermodynamic Control versus Kinetic Control

To reach equilibrium, you need more energy, because the reaction must be able to go from product back to the carbocation intermediate (higher energy barrier than from intermediate to product!).

If the reaction is done at low temperature (i.e., –77 °C) there is not enough thermal energy in the system to reach equilibrium.

At a higher temperature (*i.e.*, 50 °C) equilibrium can be reached.

Low T: A

High T: B

Notes