

HCl Addition to Dienes – Beyond Labz Virtual ChemLab Activity

Purpose: In this virtual experiment, you will be investigating the effect of temperature on the addition of hydrochloric acid to 1,3-butadiene. You will be comparing key signals in the ^{13}C NMR spectra of the reactant and product.

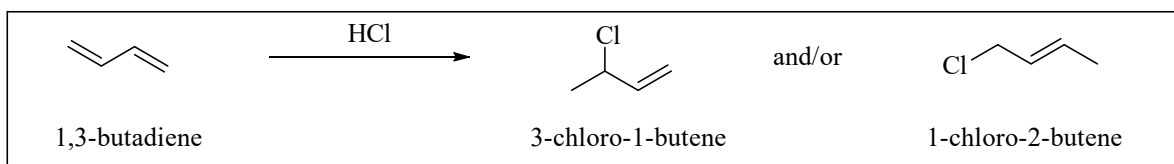


Figure 8.1 The addition of hydrochloric acid to 1,3-butadiene.

Introduction: The 1,3-butadiene (AKA buta-1,3-diene) starting material is a conjugated diene, meaning that the double bonds are separated by only one single bond. When conjugated dienes react with one equivalent of an electrophile, such as HCl, there are two possible addition products that can form. One possibility is that the hydrogen and chlorine can add to adjacent carbons in what is known as a 1,2-addition to form the 3-chloro-1-butene product. Another possibility is that the hydrogen adds to one end of the conjugated system and the chlorine adds to the other end in what is known as a 1,4-addition to form the 1-chloro-2-butene product. The numbers 1,2 and 1,4 refer to the carbons of the conjugated system.

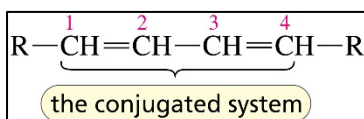


Figure 8.2 The numbered carbons of a conjugated diene.
(From *Organic Chemistry by Bruice, 8th Ed.*)

Examples of 1,2- and 1,4-additions to 1,3-butadiene, the starting material for this experiment, are shown in figure 8.3 below.

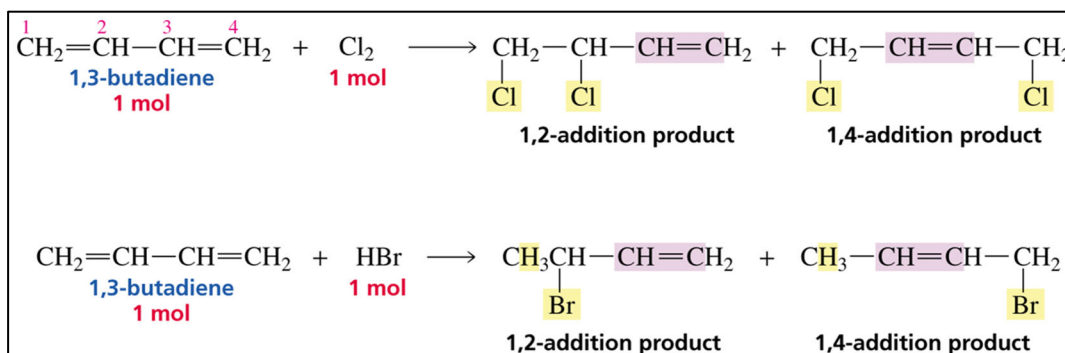


Figure 8.3 Examples of 1,2- and 1,4-additions to conjugated dienes.
(From *Organic Chemistry by Bruice, 8th Ed.*)

The reason why there are two possible products when an electrophilic reagent is added to a conjugated diene is because the initially formed carbocation is allylic, and the allylic cation has delocalized electrons. In the second step of the reaction, the nucleophile might add to either resonance form of the allylic cation. (Note: although we know that the actual structure of the allylic cation is the more accurately described by the resonance hybrid, drawing the individual resonance contributors makes it easier to see which carbon

atoms bear positive charge character, and to draw the curved arrow mechanism.) The mechanism for the reaction of hydrobromic acid with 1,3-butadiene is shown below (Figure 8.4). The mechanism for the reaction with hydrochloric acid is identical if you replace the “Br” with “Cl”.

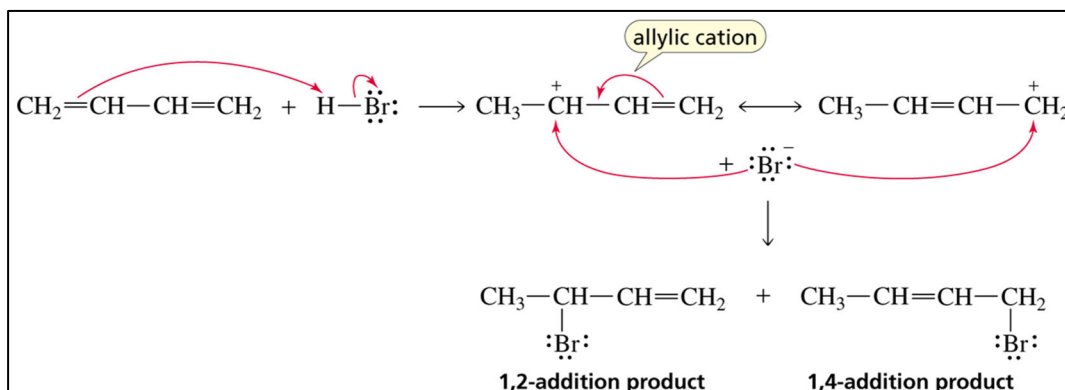


Figure 8.4 The mechanism for the reaction of a conjugated diene with HBr.
(From *Organic Chemistry by Bruice, 8th Ed.*)

For a reaction that can produce more than one product, the product that is formed the fastest is known as the **kinetic product**. The product that is the most stable is known as the **thermodynamic product**. As a general rule, *lower temperatures favor the formation of the kinetic product*, and *higher temperatures favor the formation of the thermodynamic product*. If the product that is formed the fastest is also the most stable product, then the major organic product would be the same regardless of temperature.

NMR spectroscopy:

Any nuclei that contain an odd number of protons or an odd number of neutrons can be studied by nuclear magnetic resonance (NMR) spectroscopy, but organic chemists tend to focus on carbon and hydrogen. You will use the Beyond Labz virtual platform to record the ^{13}C NMR spectrum for the buta-1,3-diene starting material and the ^{13}C NMR spectrum for the chloro-butene products. Where the signals appear in the ^{13}C NMR spectrum indicates the type of carbon atom.

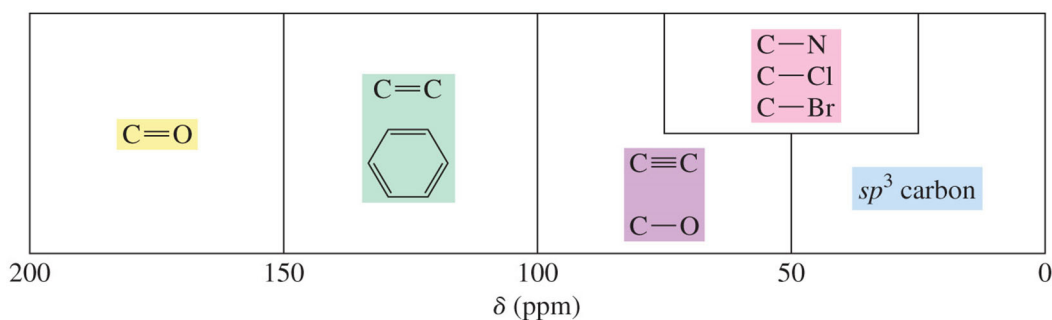


Figure 8.5 Approximate ^{13}C NMR chemical shifts. (From *Organic Chemistry by Bruice, 8th Ed.*)

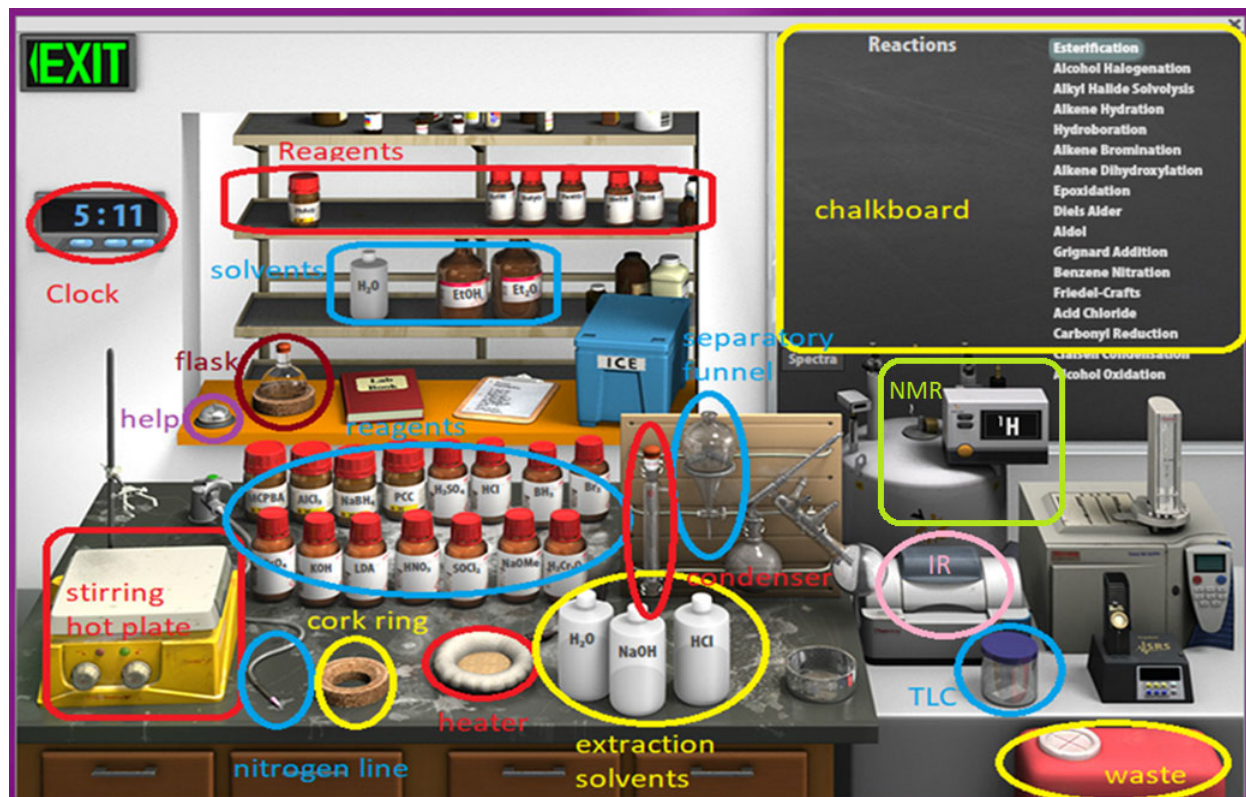


Figure 8.6 Synthesis virtual lab.

Virtual Lab Instructions (video instructions also available). Help is available by clicking on the bell on the stockroom counter.

Part 1: Collecting the ^{13}C NMR spectrum of the starting material

1. To load the synthesis lab, under “Organic Worksheets”, select “Diene Reactions” and then “VCL 3-1: Diene Halogenation-1”. *Note: The available reagents are the same for experiments VCL 3-1 & VCL 3-3 so we will just use the same virtual synthesis lab for both.*
2. On the chalkboard (top right) mouse over “Alkene Bromination”, and you will see the available chemicals. You will notice that there are 3 different alkenes, and 1 diene available from the “stockroom”, so be sure to select the correct starting diene to record the ^{13}C NMR spectrum. *Note: this really should be labelled alkene halogenation since we are adding a chlorine and not bromine.*
3. Clicking and dragging adds reagents into the flask. Click on the buta-1,3-diene and drag it into the flask.
4. Check to see that only buta-1,3-diene has been added to the flask by hovering your mouse over the flask. The contents of the flask will display on the chalkboard.
5. Drag the flask over to the clamp above the stirring hot plate.
6. By default, the NMR is set to record ^1H - change to ^{13}C by clicking the window on the NMR spectrometer. Record the ^{13}C NMR spectrum of the buta-1,3-diene by clicking on the NMR spectrometer and dragging the sample tube to the flask. This will display the ^{13}C NMR spectrum on the screen. You can type the name of the compound on the spectrum and click save to save it to your lab notebook. To view the chemical shift values (in ppm) mouse over each peak- the first number is the chemical shift. Click ok to close the spectrum.
7. Reset the synthesis lab by clicking on the waste container to “clear lab”.

Part 2: Diene Halogenation at Low Temperature

8. On the chalkboard (top right) mouse over “Alkene Bromination”, and you will see the available chemicals. You will notice that there are three different alkenes, and one diene available from the “stockroom”, so be sure to select the correct starting diene for the reaction.
9. Clicking and dragging adds reagents into the flask. Click on the buta-1,3-diene and drag it into the flask.
10. Click on the diethyl ether and add it to the flask, assume that a volume of ~10.0 mL was added.
11. Check to see that the reagent and the solvent have been added to the flask by hovering your mouse over the flask. The contents of the flask will display on the chalkboard.
12. Drag the flask over to the clamp above the stirring hot plate.
13. This first experiment will be conducted at low temperature. Click and drag an **ice-water bath** to place it below the flask.
14. Add the hydrochloric acid by clicking and dragging from the reagent bottle (red cap) labeled HCl. Assume that exactly one equivalent of HCl was added.
15. Check the chalkboard and verify that your flask contains the correct diene, the diethyl ether, and the HCl solution.
16. Start the reaction by clicking the right knob on the stirring hotplate.
17. Stir the reaction for 4 hours and 10 minutes. (Advance the clock 4 hours and 10 minutes and be very grateful that this is a virtual experiment!). The reaction should now be complete - check the chalkboard for disappearance of the starting material and add more time if necessary.
18. Remove the ice-water bath by clicking and dragging to the waste container.
19. Stop the reaction by dragging the separatory funnel over to the flask. The chalkboard will display what is in the flask, which should be the product, and the diethyl ether.
20. Add water to the separatory funnel.
21. Recall that the less dense ether layer (“organic layer”) will float on top of the aqueous layer. If you hover your mouse over the layers, it will display if the layer is organic or aqueous and the chalkboard will display the chemicals contained within the layer.
22. Remove the lower aqueous layer by clicking and dragging to the cork ring support. Double check that it just contains water, and you did not accidentally grab the organic layer! If it is just water, drag the flask to the waste container.
23. Drag the organic layer to the cork ring. This step assumes that you evaporated the solvent using a rotatory evaporator, leaving you with just the product in the flask.
24. By default, the NMR is set to record ^1H - change to ^{13}C by clicking the window on the NMR spectrometer. Record the ^{13}C NMR spectrum of the product by clicking on the NMR spectrometer and dragging the sample tube to the flask. This will display the ^{13}C NMR spectrum on the screen. You can type the name of the compound on the spectrum and click save to save it to your lab notebook. To view the chemical shift values (in ppm) mouse over each peak - the first number is the chemical shift. Click ok to close the spectrum.
25. Reset the synthesis lab by clicking on the waste container to “clear lab”.

Part 3: Diene Halogenation at High Temperature

26. On the chalkboard (top right) mouse over “Alkene Bromination”, and you will see the available chemicals. You will notice that there are 3 different alkenes, and 1 diene available from the “stockroom”, so be sure to select the correct starting diene for the reaction.
27. Clicking and dragging adds reagents into the flask. Click on the buta-1,3-diene and drag it into the flask.
28. Click on the diethyl ether and add it to the flask, assume that a volume of ~ 10.0 mL was added.
29. Check to see that the reagent and the solvent have been added to the flask by hovering your mouse over the flask. The contents of the flask will display on the chalkboard.
30. Drag the flask over to the clamp above the stirring hot plate.
31. Add the hydrochloric acid by clicking and dragging from the reagent bottle (red cap) labeled HCl. Assume that exactly one equivalent of HCl was added.
32. Check the chalkboard and verify that your flask contains the correct diene, the diethyl ether, and the HCl solution.
33. This second experiment will be conducted at high temperature. Click and drag the **heating mantle** below the flask.
34. To prevent the solvent from evaporating, add a **reflux condenser** to the flask.
35. Notice that the top of the condenser is sealed with a rubber septum. If we heat a closed system, it will explode! Click and drag the nitrogen line to the top of the condenser.
36. Start the reaction by clicking the right knob on the stirring hotplate.
37. Reflux the reaction for 2 hours. (Advance the clock 2 hours). The reaction should now be complete.
38. Stop the reaction by dragging the separatory funnel over to the flask. The chalkboard will display what is in the flask, which should be the product, and the diethyl ether.
39. Remove the lower aqueous layer by clicking and dragging to the cork ring support. Double check that it just contains water, and you did not accidentally grab the organic layer! If it is just water, drag the flask to the waste container.
40. Drag the organic layer to the cork ring. This step assumes that you evaporated the solvent using a rotatory evaporator, leaving you with just the product in the flask.
41. Double check that the NMR is still set to ^{13}C . If not, click the window on the NMR spectrometer to do so. Record the ^{13}C NMR spectrum of the product by clicking on the NMR spectrometer and dragging the sample tube to the flask. This will display the ^{13}C NMR spectrum on the screen. You can type the name of the compound on the spectrum and click save to save it to your lab notebook. To view the chemical shift values (in ppm) mouse over each peak - the first number is the chemical shift. Click ok to close the spectrum.
42. Reset the synthesis lab by clicking on the waste container to “clear lab”.

Part 4: Diene Halogenation at Room Temperature

43. On the chalkboard (top right) mouse over “Alkene Bromination”, and you will see the available chemicals. You will notice that there are 3 different alkenes, and 1 diene available from the “stockroom”, so be sure to select the correct starting diene for the reaction.

44. Clicking and dragging adds reagents into the flask. Click on the buta-1,3-diene and drag it into the flask.
45. Click on the diethyl ether and add it to the flask, assume that a volume of ~ 10.0 mL was added.
46. Check to see that the reagent and the solvent have been added to the flask by hovering your mouse over the flask. The contents of the flask will display on the chalkboard.
47. Drag the flask over to the clamp above the stirring hot plate.
48. Add the hydrochloric acid by clicking and dragging from the reagent bottle (red cap) labeled HCl. Assume that exactly one equivalent of HCl was added.
49. Check the chalkboard and verify that your flask contains the correct diene, the diethyl ether, and the HCl solution.
50. This third experiment will be conducted at room temperature, so there is no need to add any other items to the reaction set-up.
51. Start the reaction by clicking the right knob on the stirring hotplate.
52. Let the reaction stir for 2 hours. (Advance the clock 2 hours). The reaction should now be complete.
53. Stop the reaction by dragging the separatory funnel over to the flask. The chalkboard will display what is in the flask, which should be the product, and the diethyl ether.
54. Remove the lower aqueous layer by clicking and dragging to the cork ring support. Double check that it just contains water, and you did not accidentally grab the organic layer! If it is just water, drag the flask to the waste container.
55. Drag the organic layer to the cork ring. This step assumes that you evaporated the solvent using a rotatory evaporator, leaving you with just the product in the flask. Notice that there are two different organic products in the flask!
56. Double check that the NMR is still set to ^{13}C . If not, click the window on the NMR spectrometer to do so. Record the ^{13}C NMR spectrum of the product by clicking on the NMR spectrometer and dragging the sample tube to the flask. This will display the ^{13}C NMR spectrum on the screen. You can type the name of the compound on the spectrum and click save to save it to your lab notebook. To view the chemical shift values (in ppm) mouse over each peak - the first number is the chemical shift. Click ok to close the spectrum.
57. You now have two products in the flask. To separate these two products, you will need to perform a distillation.
58. Drag the flask containing the organic products back to the clamp above the stirring hot plate.
59. Click and drag the distillation apparatus over to the flask.
60. Click and drag the nitrogen line to the distillation apparatus.
61. Start the distillation by clicking the right knob on the stirring hotplate. Mouse over the thermometer and record the temperature (this is the starting temperature).
62. Advance the clock for 10 minutes, mouse over the thermometer again and record the temperature (this is the collection temperature).
63. Distilling for 30 more minutes (advance the clock 30 minutes) should remove the lower boiling alkene product, leaving the higher boiling alkene in the flask.
64. Stop the distillation by clicking and dragging the collection flask (containing the product) to the cork ring support.

65. The distillation of the higher boiling alkene is continuing. Before you forget, record the boiling point of this alkene.
66. Double check that the NMR is still set to ^{13}C . If not, click the window on the NMR spectrometer to do so. Record the ^{13}C NMR spectrum of the lower boiling alkene in the flask on the cork ring by clicking on the NMR spectrometer and dragging the sample tube to the flask. This will display the ^{13}C NMR spectrum on the screen. You can type the name of the compound on the spectrum and click save to save it to your lab notebook. To view the chemical shift values (in ppm) mouse over each peak - the first number is the chemical shift. Click ok to close the spectrum.
67. Discard the lower boiling alkene product by dragging its flask to the waste container.
68. Determine if the distillation has concluded by checking if the higher boiling alkene product is now in the collection flask, and that nothing is left in the distillation flask. If not, distill for 10 more minutes (advance the clock 10 minutes).
69. Stop the distillation by clicking and dragging the collection flask (containing the higher boiling product) to the cork ring support.
70. Double check that the NMR is still set to ^{13}C . If not, click the window on the NMR spectrometer to do so. Record the ^{13}C NMR spectrum of the higher boiling alkene in the flask on the cork ring by clicking on the NMR spectrometer and dragging the sample tube to the flask. This will display the ^{13}C NMR spectrum on the screen. You can type the name of the compound on the spectrum and click save to save it to your lab notebook. To view the chemical shift values (in ppm) mouse over each peak - the first number is the chemical shift. Click ok to close the spectrum.
71. Your virtual experiment is complete!

Prelab Questions

Before working with compounds in the laboratory, it is important to look up key physical properties and hazards for the chemicals that you are working with. For the 1,3-butadiene, 3-chloro-1-butene, and 1-chloro-2-butene look up the formula weight (FW), boiling point (b.p.), density, and hazards and complete the table below.

	FW (g/mol)	b.p. (°C)	Density (g/mL)	Hazards
1,3-butadiene				
3-chloro-1-butene				
1-chloro-2-butene				

1. The reaction of 1,3-butadiene with HCl often results in a mixture of the two possible products listed in the table above. If you obtained a such a mixture, would recrystallization be a suitable method for purifying the product? Explain why or why not.

Results and Observations

^{13}C NMR results Report the ^{13}C NMR signals by numbering them from left to right (the highest chemical shift is peak 1), match each peak to the appropriate carbon atom and answer any questions.

^{13}C NMR	Peak	Chemical Shift (δ , approx. ppm)
	1	
	2	

1,3-butadiene (draw structure & label C atoms)

2. Why are there only 2 signals in the ^{13}C NMR spectrum for the 1,3-butadiene?

¹³ C NMR	Peak	Chemical Shift (δ , approx. ppm)
	1	
	2	
	3	
	4	

3-chloro-1-butene (draw structure & label C atoms)

3. Is 3-chloro-1-butene described as the “1,2-product” or the “1,4-product”? Explain.

¹³ C NMR	Peak	Chemical Shift (δ , approx. ppm)
	1	
	2	
	3	
	4	

1-chloro-2-butene (draw structure & label C atoms)

4. Is 1-chloro-2-butene described as the “1,2-product” or the “1,4-product”? Explain.

Distillation Observations: Record the collection temperatures for the two distillations.

	Lower-boiling alkene	Higher-boiling alkene
Product Name		
Collection Temperature (°C)		

Lab Report Questions

5. Compare the boiling points of the two possible products and the collection temperatures recorded from the distillations. Can these temperatures be used to identify the product of each reaction? Explain your response.

6. Identify (by giving the structure and the name) of the product of the reaction at low temperature. Is this the expected product (1,2-addition vs. 1,4-addition)? Explain your response.

7. Identify (by giving the structure and the name) of the product of the reaction at high temperature. Is this the expected most stable product? Explain your response by comparing the stability of the two possible products. (*hint: alkene stability is related to the number of alkyl substituents*).

8. Explain what happened to the reaction at room temperature, and why this occurred. Did you find this outcome surprising? Explain your reasoning.

Optional/bonus: How could DEPT ^{13}C NMR be used to assign the carbon signals in the starting diene?