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

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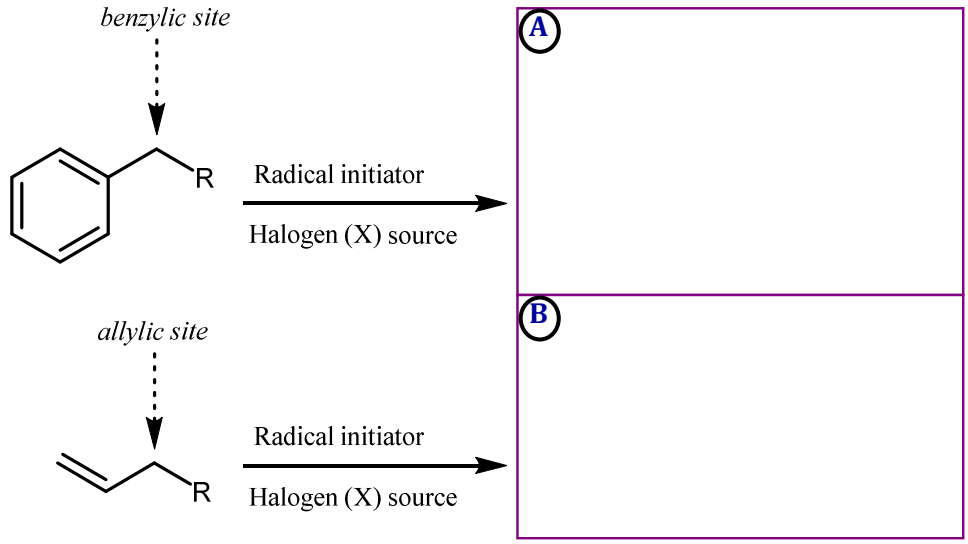
Lesson IV.15. Radical Halogenation of Allylic and Benzylic Compounds

Radicals abstract hydrogen atoms to make the most stable radical possible

The radical intermediate of radical halogenation is very stable for an allylic or benzylic substrate, but high concentration of halogens can lead to electrophilic addition of X_2 to the double bond in an allylic case. For this reason, special reagents (i.e., NBS) capable of producing only a low concentration of halogen are typically used in such cases:

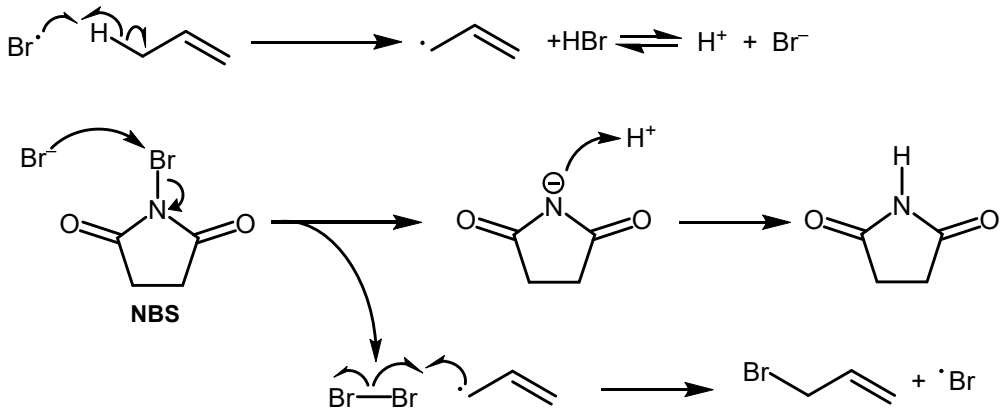


Notes

Lesson IV.15. Radical Halogenation of Allylic and Benzylic Compounds

NBS is a source of dilute bromine

When *N*-bromosuccinimide (NBS) is heated, a low concentration of Br_2 is generated. The initial radicals are generated by heating benzoyl peroxide $(PhC(O))_2$. These radicals go on to initiate formation of bromine radicals. Once bromine radicals are generated, they can propagate further reaction:



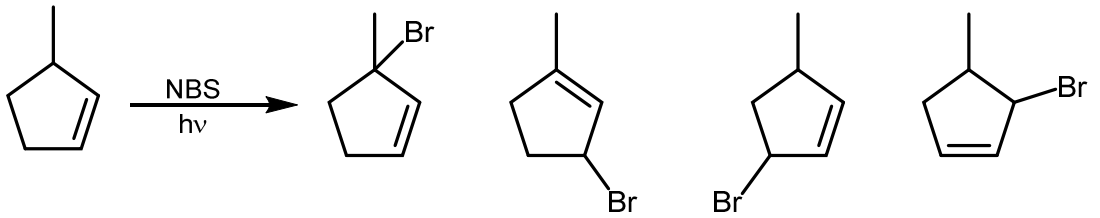
This reaction works if the $-C(H)=CH_2$ is replaced with an arene ring as well.

Notes

Lesson IV.15. Radical Halogenation of Allylic and Benzylic Compounds

Radical bromination practice

Remember that allylic radicals have more than one resonance contributor, such that the actual molecule (hybrid) has radical character at two carbons; the situation becomes even more complicated when there are two allylic sites from which to choose in the starting material:



How does one account for all of these products?

A	B

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