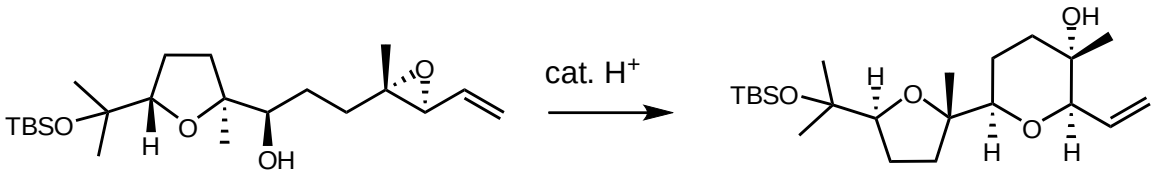
Problem 5



Ref.: H. Hioki, M. Motosue, Y. Mizutani, A. Noda, T. Shimoda, M. Kubo, K. Harada, Y. Fukuyama and M. Kodama, Org. Lett., 2009, 11, 579-582.

1. Draw all of the bonds at the reactive atoms in the starting materials

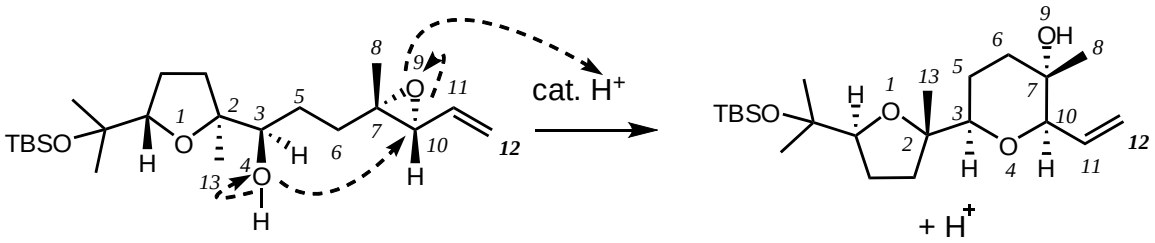
2. Draw all of the H-atoms at or near the reactive sites of the starting materials and the products

3. Balance the equation

4. Number the non-H atoms

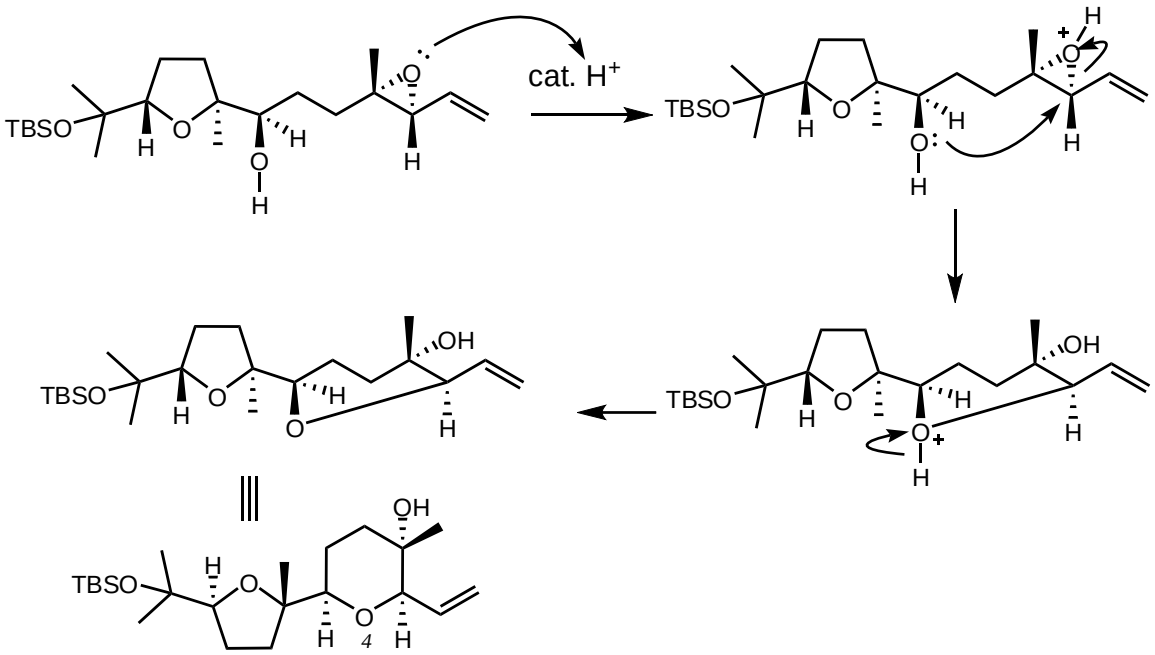
5. Identify bonds made and broken

Bonds made: 4-10, 9-H
Bonds broken: H-4, 10-11.



6. Conditions
Acidic (does not generate strong bases)

Mechanism

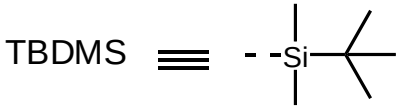


Discussion

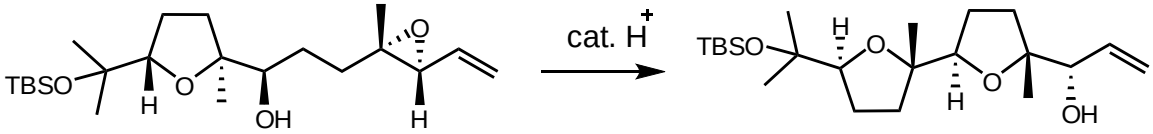
1. Catalysts (cat.) are often used in the first step of a mechanism.

2. The last step of the mechanism shows the deprotonation without the indication of any specific base. This is an acceptable practice and it will be used in this book when drawing mechanisms under acidic conditions. The same step can also be shown with the help of a species that can act as a base. If more than one such compound is available then the specie that will produce the weakest conjugate acid should be used. In the above example, it could be another molecule of the starting material or the conjugate base of the proton (H^+, as such, is not used in organic synthesis. The specie is always attached to some conjugate base. For example, H_3O^+ is one common source of H^+ and its conjugate base is H_2O).

3. The group TBS is also known as TBDMS. The abbreviation stands for tertiary butyldimethylsilyl. The TBDMS group is a common protective group for alcohols in organic synthesis. A protective group temporarily blocks a functional group. As such, a chemical reaction can be carried out selectively on another functional group present in the same compound. In the above case, the TBS is blocking the reaction on the alcohol. As a result, the other alcohol can react selectively.



Now try the following mechanism:



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