

10.5: HYDRATION OF ALKYNES FOR ANTI-MARKOVNIKOV PRODUCTS

Learning Objective

- predict the products and specify the reagents for the anti-Markovnikov-products of alkyne hydration

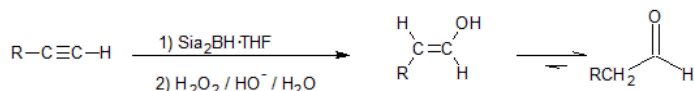
INTRODUCTION

The hydroboration-oxidation of alkynes is similar to the reaction with alkenes. However, there is one important difference. The alkyne has two pi bonds and both are capable of reacting with borane (BH_3). To limit the reactivity to only one of the pi bonds within the alkyne, a dialkyl borane reagent (R_2BH) is used. Replacing two of the hydrogens on the borane with alkyl groups also creates steric hindrance so that the hydroboration reaction produces the regioselective,

anti-Markovnikov product. Disiamylborane (Sia_2BH) and 9-borabicyclo[3.3.1]nonane (9-BBN) are two common reagents for the hydroboration step. Their structures are shown below.

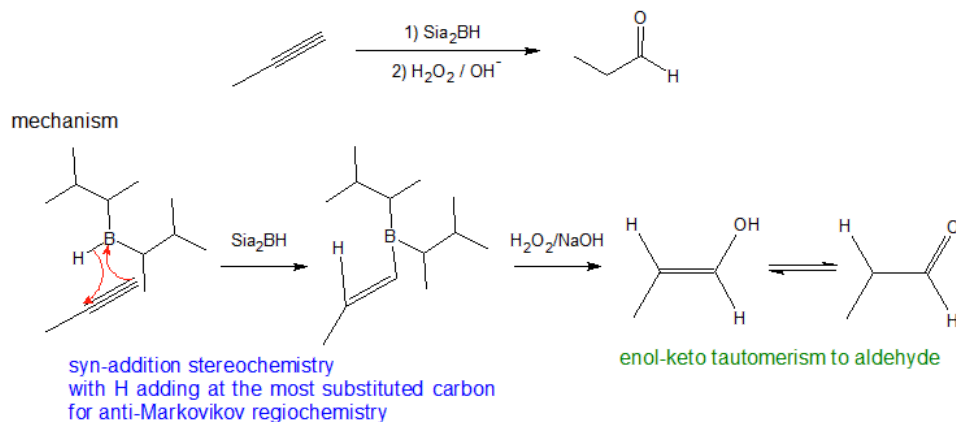


The oxidation reagents (a basic hydrogen peroxide solution) are the same for both alkenes and alkynes, The overall reaction is shown below.



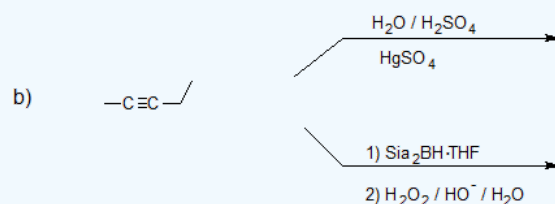
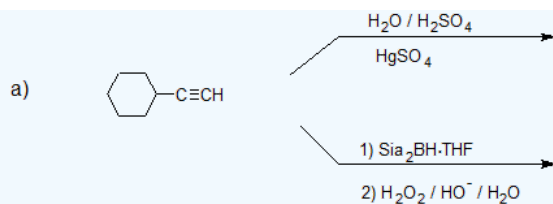
MECHANISM

The hydroboration reaction of alkynes has the same stereo- and regiochemistry as the alkene reaction. The primary difference is the steric hindrance of the two isoamyl groups of the dialkyl borane creates anti-Markovnikov regioselectivity. The hydrogen and boron bond with the same orientation to the alkyne carbon with syn-addition stereochemistry to form the enol. The enol immediately tautomerizes to the keto form which is an aldehyde for terminal alkynes. The hydration of 1-propyne is shown below along with the reaction mechanism.

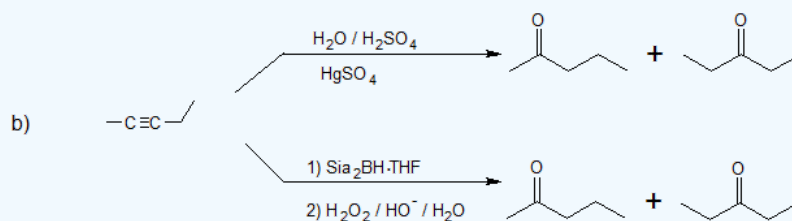
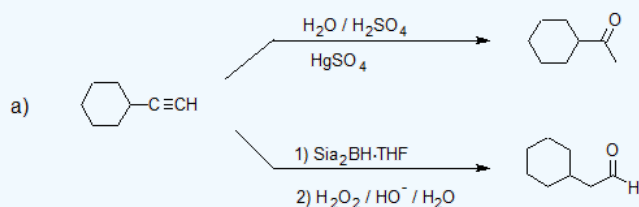


Exercise

- Draw the bond-line structure(s) for the product(s) of each reaction.



Answer



For internal alkynes, there is no difference in the reaction products.

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