

## 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

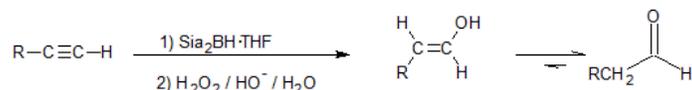
### INTRODUCTION

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.

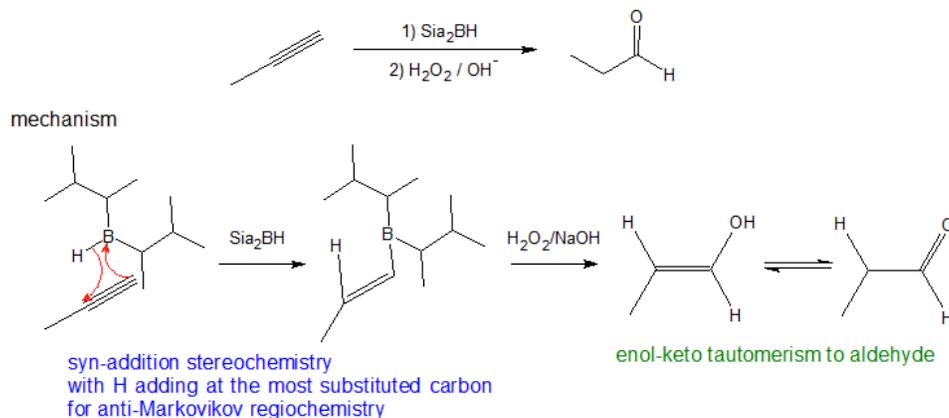


The oxidation reagents ( a basic hydrogen peroxide solution) are the same for both alkenes and alkynes, The overall reaction is shown below.



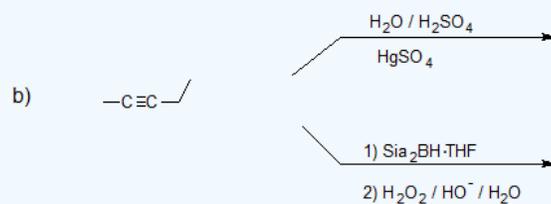
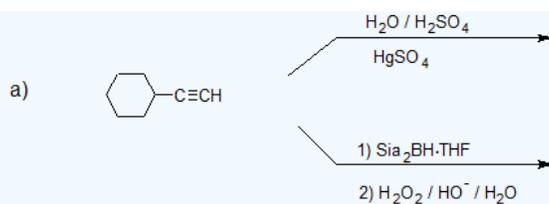
### MECHANISM

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.

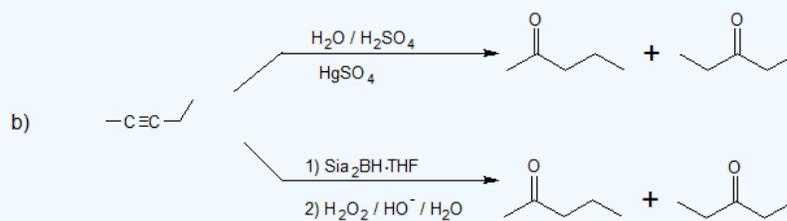
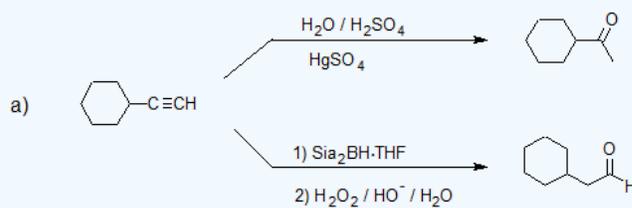


### Exercise

- 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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