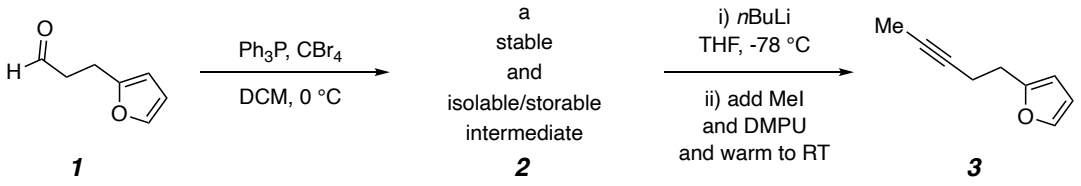
CHEM 8321/4321 **October 23, 2023**

Problem Set #7 **T. R. Hoye**

Due in class, Monday October 30, 2023

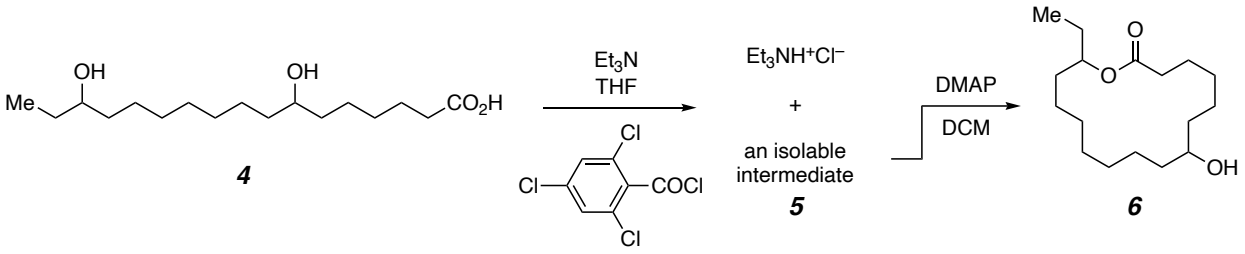
Detailed Mechanism Provide a detailed mechanism [i.e., *explicitly* show (using curly arrows) *EVERY* intermediate, formal charge (where relevant), equilibrium, and bond-making and -breaking step] to account for the following transformations:

a) Formation of the alkyne **3** from the aldehyde **1** via an intermediate dibromide **2**.



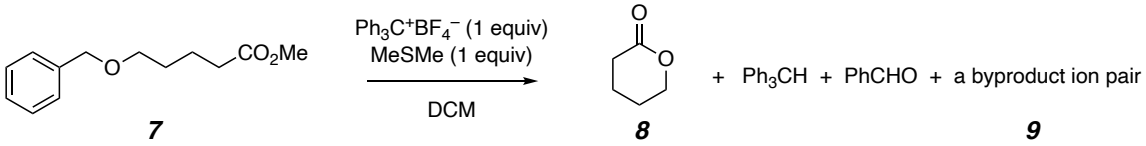
1 ***2*** ***3***

b) The formation of the lactone **6** from the diol acid **4** via **5** in a Yamaguchi esterification.



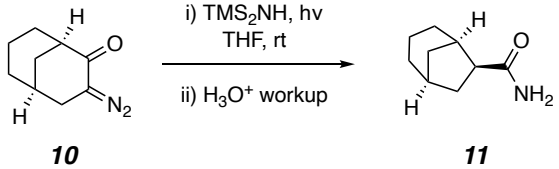
4 ***5*** ***6***

c) Formation of the valerolactone (**8**) from the benzylether ester **7** (*hint*: balance the equation; i.e. identify **9**).



7 ***8*** ***9***

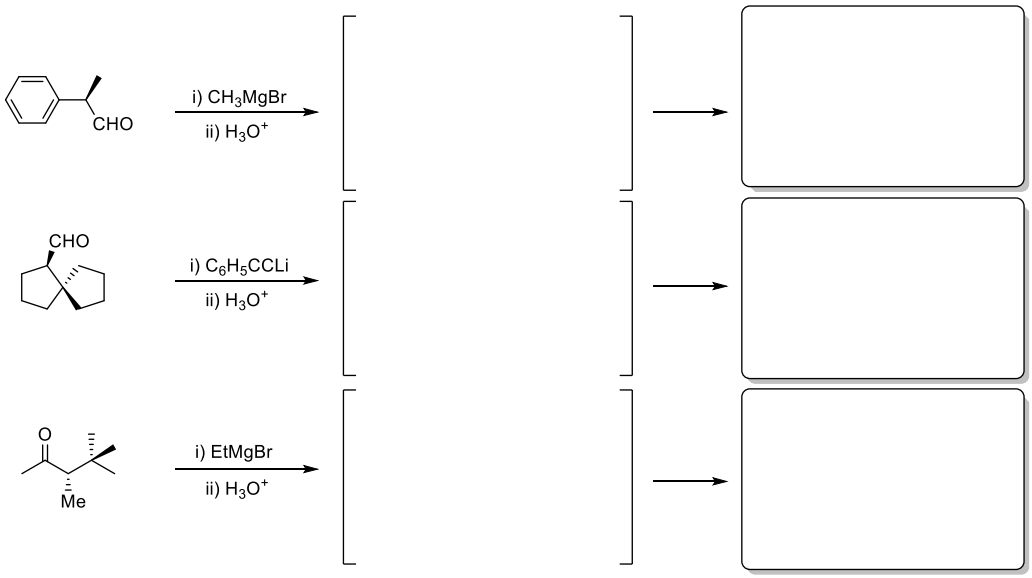
d) The conversion of the diazoketone **10** to the amide **11**. (*hint*: dinitrogen is liberated in stage i))



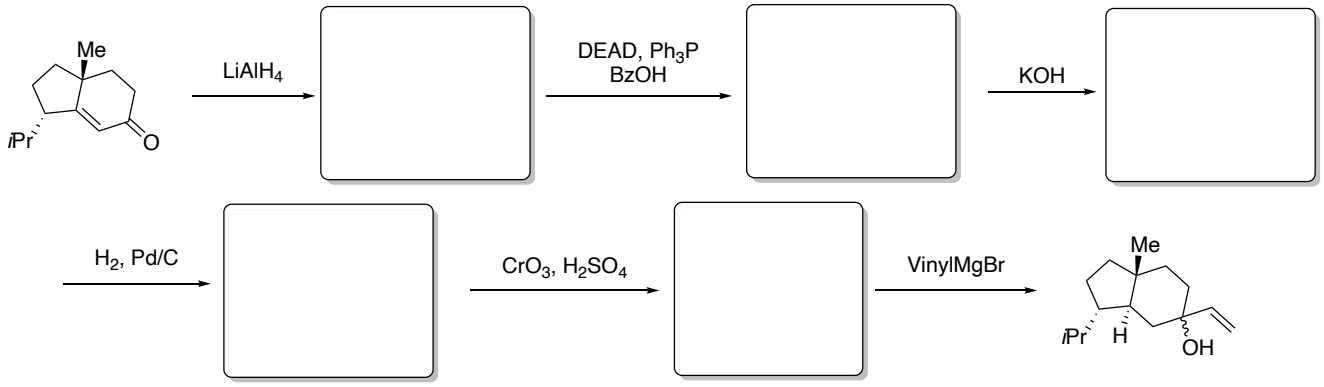
10 ***11***

Other Questions

1. In the box, provide the structure of the major diastereomer formed in each of these 1,2-addition reactions. In brackets, show the Felkin-Ahn model that accounts for that outcome.



2. Deduce the products. (*hint:* the second step is a Mitsunobu reaction, done to affect the diastereoselectivity of the hydrogenation reaction)



2. Reaxys Database Search

a) How many benzoyl peroxide derivatives (all possible substitutions on each of the two phenyl rings; single phenyl rings, not fused as in, e.g., naphthalene) are in the Reaxys database?

b) According to Reaxys, how many cinnamic ester derivatives have been isolated from natural sources? *Hint:* in the Query Builder under "Other," select "isolated from natural source."