

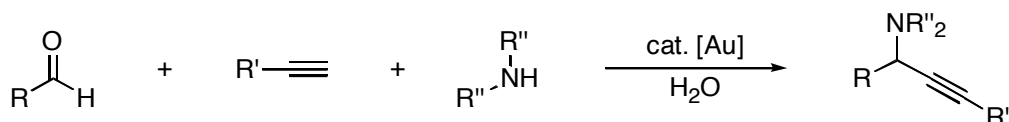
Homogeneous Gold Catalysis

Toste Group Problem Set

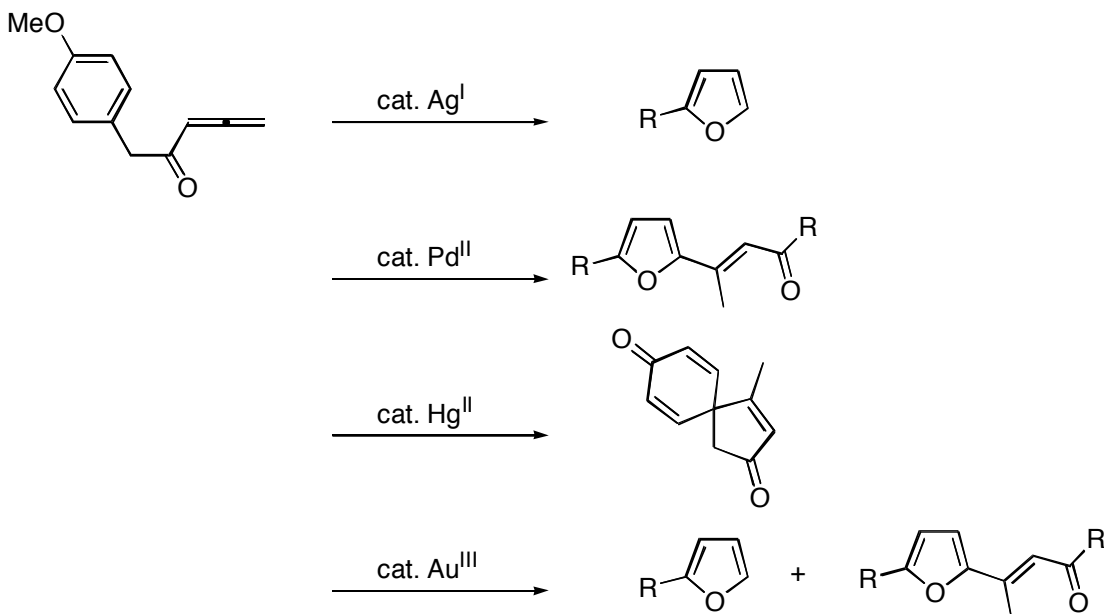
January 7th, 2004

1. C.J. Li and coworkers recently reported the following three component coupling reaction. The reaction proceeds in high yield with a variety of aldehydes, alkynes and amines. A variety of gold salts were effective in performing this coupling: AuCl, AuI, AuBr₃, AuCl₃. Au(0) was ineffective in this system.

Provide a catalytic cycle for this reaction.

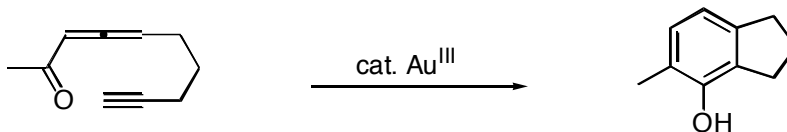


2. Allenyl ketones undergo a variety of transition metal-catalyzed reactions and rearrangements. The rearrangement to form furans in the presence of Ag(I) salts is known as the Marshall reaction. They can also participate in Heck reactions catalyzed by palladium. Mercury and gold function similarly in the addition of O-based nucleophiles to C-C multiple bonds. In the case of allenyl ketones, however, entirely different reactivity was observed (R = CH₂-4-(MeO)C₆H₄).

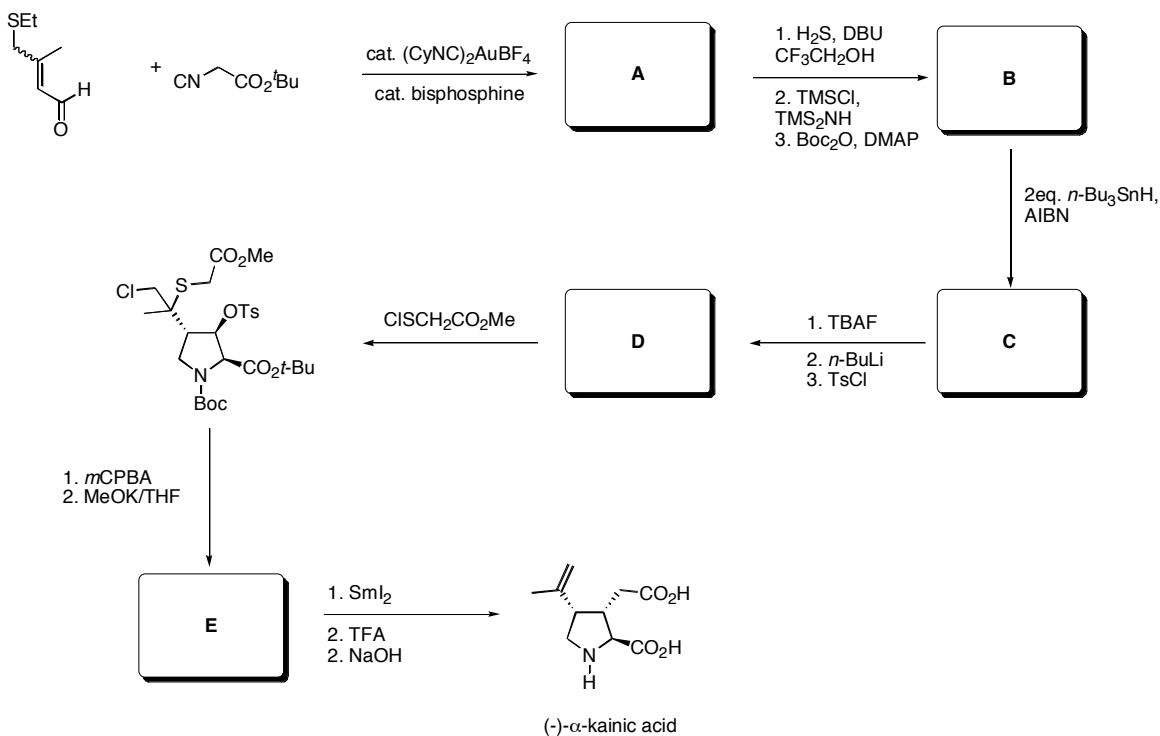


- Provide a mechanism for the Au(III) catalyzed reactions.
- Explain the difference in Hg(II) and Au(III) reactivity.
- Explain the difference in Ag(III) and Au(III) reactivity.

3. Based on some of the reactivity shown in #2, suggest a mechanism for this gold-catalyzed.

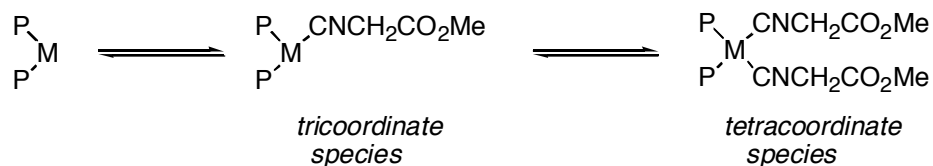


4. The gold-catalyzed asymmetric aldol reaction is probably the best-developed synthetic method involving a homogeneous gold species to date. Follow this short road map as you make your way back from vacation.



Explain the diastereoselectivity of the radical cyclization of **B** to afford **C**.

5. The asymmetric aldol reaction of isocyanoacetates has allowed some interesting comparisons between gold(I) and silver(I) catalysts, both of which have been optimized to provide excellent enantioselective reactions.



- IR studies indicate that gold(I) adopts a tricoordinate species at room temperature.
- IR studies indicate that silver(I) adopts a tetracoordinate species at room temperature.
- The enantioselectivity of the silver(I)-catalyzed aldol reaction increases at higher temperature.
- The enantioselectivity of the gold(I)-catalyzed aldol reaction is excellent at room temperature.

a) What conclusions about these systems can you draw?

b) How was the silver system altered to allow high enantioselectivities without increasing the temperature?