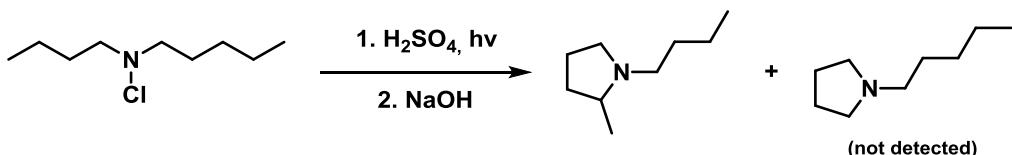


Tutorial Questions

Lisa Barbaro - Nov 2014

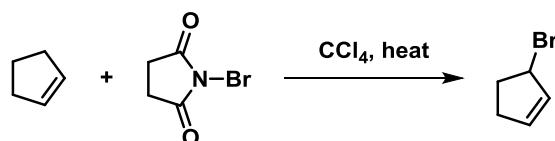
Part 1 – Radical Reactions

1. What is the name of the following reaction? Give the mechanism.



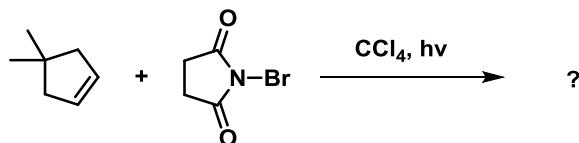
What is the reason for the observed selectivity?

2. Give the mechanism of the following addition to cyclopentene

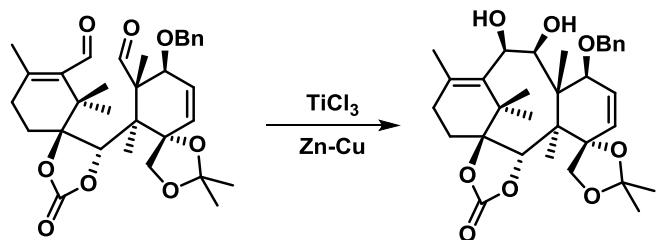


Why is NBS (N-bromosuccinimide) often used as the Br source in radical-brominations rather than Br_2 directly?

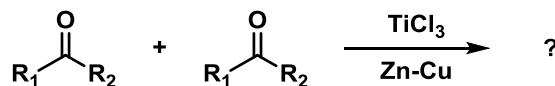
What results from the addition to 4,4-dimethylcyclopentene?



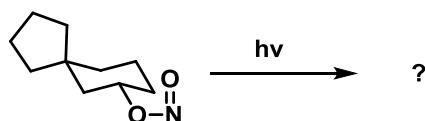
3. An important ring closing step in the total synthesis of Taxol is shown below. What is the name of this coupling reaction? Draw the mechanism.



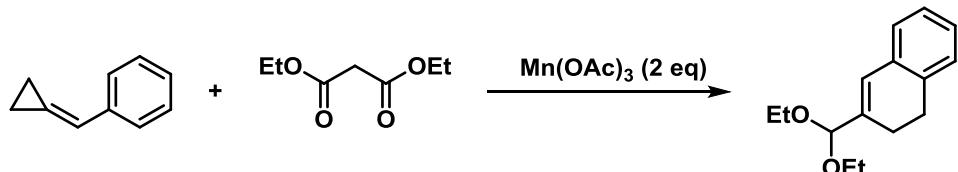
This is in fact an unusual example of this type of coupling. What would be the typical product formed using two identical carbonyl groups under these conditions?



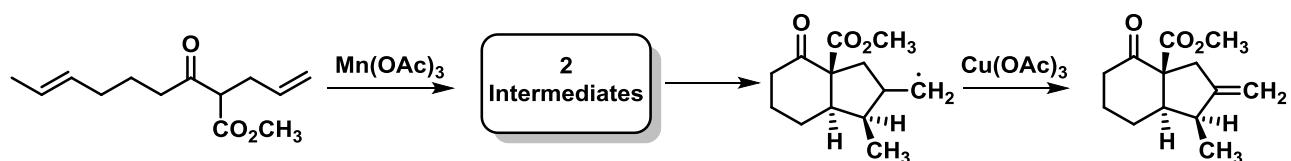
4. What is the product formed in this reaction?



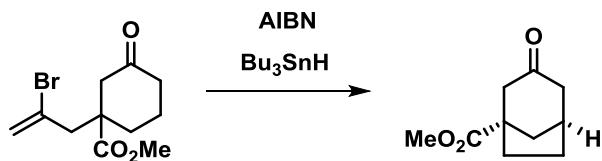
5. What is the role of $\text{Mn}(\text{OAc})_3$ in the following reaction? Draw the mechanism (there are several intermediates).



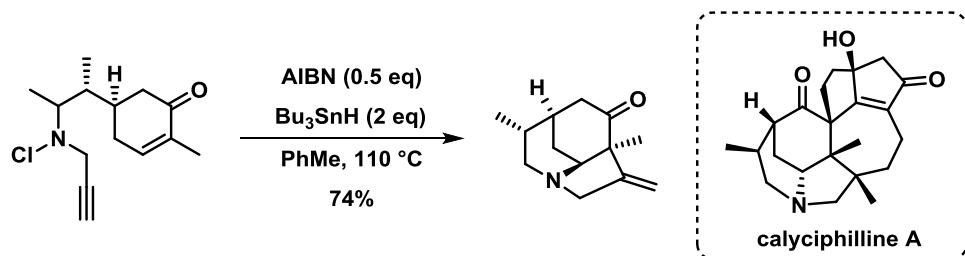
6. Please complete the following sequence, and the associated mechanism



7. Propose a mechanism for this reaction, and account for the selectivity



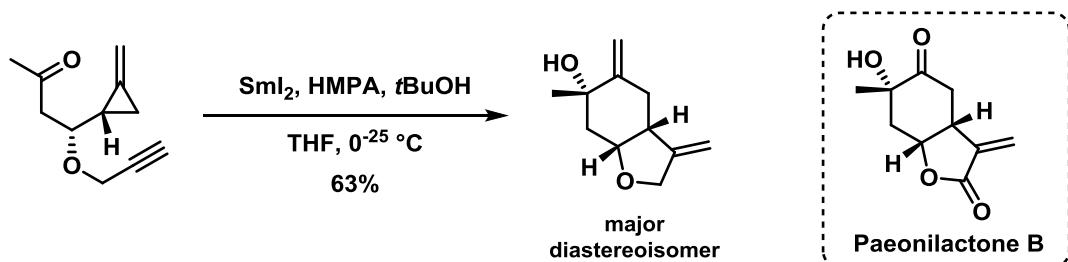
8. A key step in the total synthesis of calyciphylline A by Stockdille *et al*, exploits the radical cascade reaction below to access the core structure. Provide a mechanism for the product of this step.



9. Draw a mechanism for the following radical cyclisation



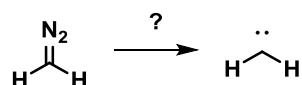
10. The following cascade reaction is featured in Kilburn's stereoselective synthesis of paeonilactone B. Indicate the mechanism, and label all ring closing reactions using Baldwin's rules. How is stereoselectivity achieved?



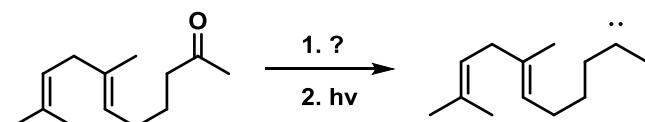
Part 2 – Carbenes

11. The following reactions detail various methods in which carbenes are generated (note that many of these are not actually isolated). Indicate any missing reagents/methods where needed, and draw the associated mechanisms.

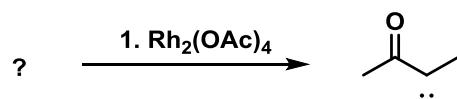
a)



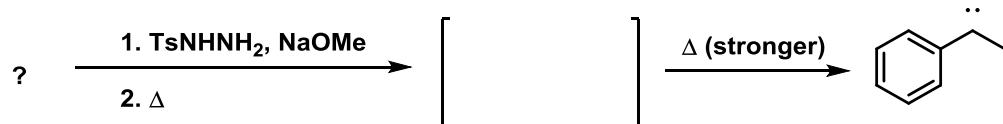
b)



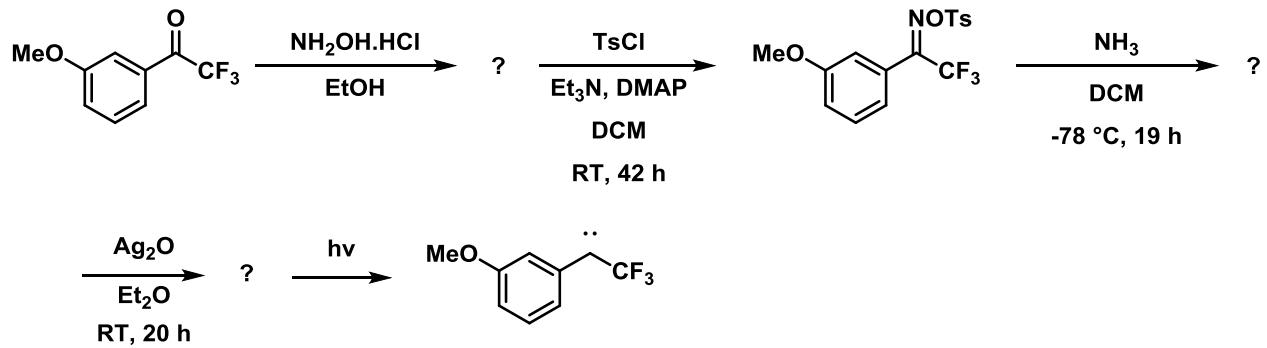
c)



d)

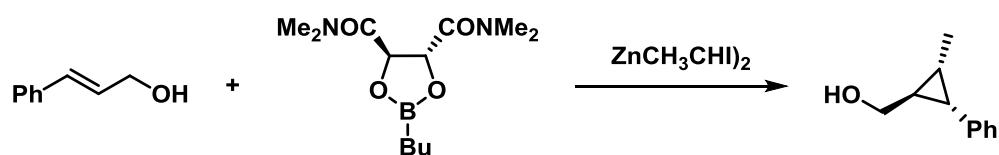


e)

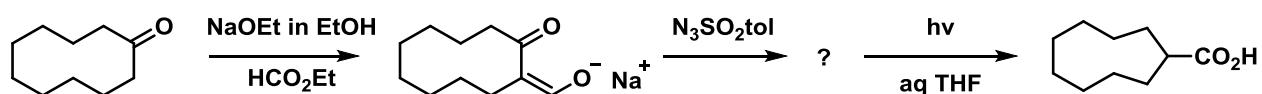


12. Please give the names of the following reactions and indicate the mechanisms:

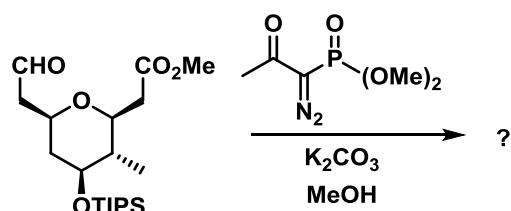
a)



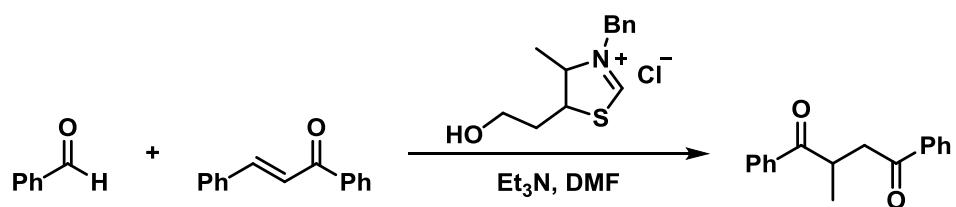
b)



c)



d)



The first step involves the reaction between the active catalyst with the aldehyde. What is the name of the key intermediate formed in this step?

The product is formed through a 1,4-addition of the intermediate to the α,β -unsaturated ketone, however another pathway is possible at this stage. What is this pathway and why isn't this alternate product observed?

13. Oxidised phospholipids are an important class of biomolecules which are generated in humans (as well as other higher level organisms) by reaction with reactive oxygen species. Oxophospholipids have been shown to exhibit pro-inflammatory biological activity associated with such diseases as rheumatoid arthritis, emphysema and atherosclerosis.

The following reactions describe a fragment of a series of oxidised phospholipids, synthesised by the Carreira group.

Please fill in the blanks and indicate the mechanisms for each step.

