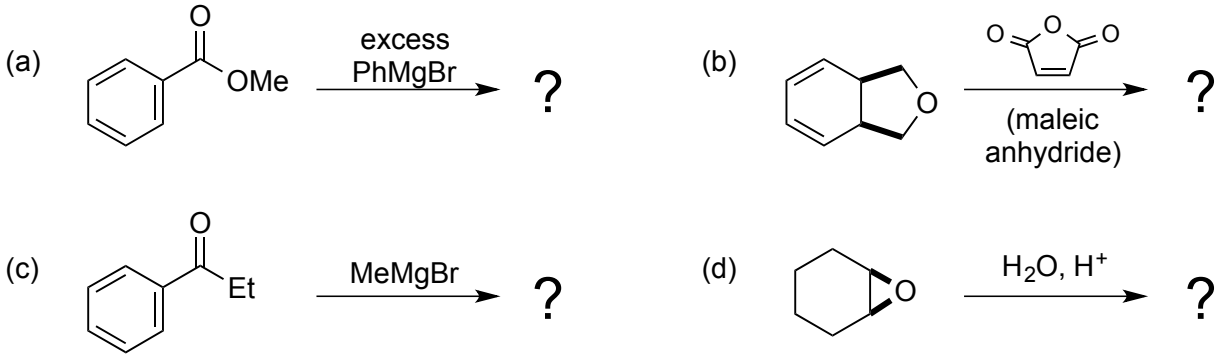
Dr James A. Bull **2.O1 Organic Synthesis**

Tutorial problems

It is essential to attempt these problems to reinforce your understanding of the material presented in the lectures. The stage at which the relevant material will be covered in lectures is indicated. Discuss your answers in tutorials with your organic tutor. Suggested answers will be available on blackboard after reading week.

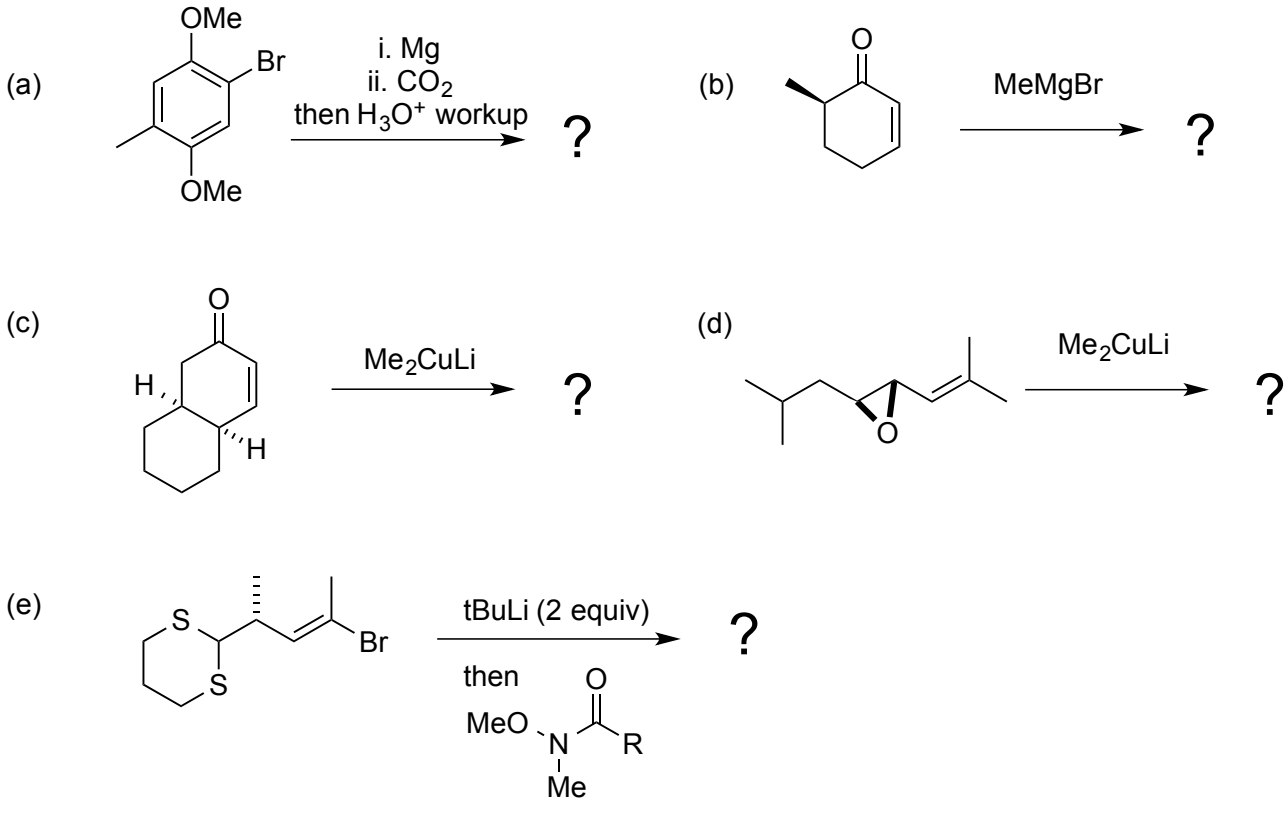
Before course / after lecture 1.

1. Review some fundamental material: give the products for the reactions shown below and the mechanism reaction.

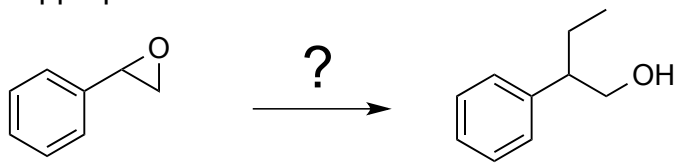


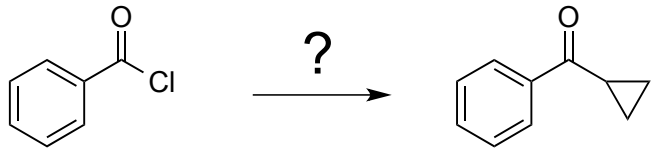
After lecture 2

2. Give the products for the reactions shown below with mechanisms.
Explain the observed selectivity (regio-, chemo- or stereo-selectivity) where appropriate.



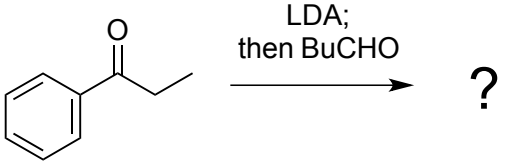
3. State how you would carry out the transformations shown below and provide mechanisms using the reagents you suggest. Identify the required selectivity considerations where appropriate.

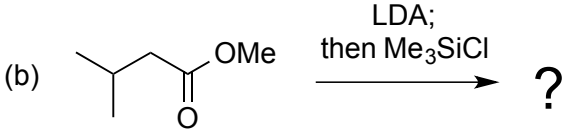
(a) 

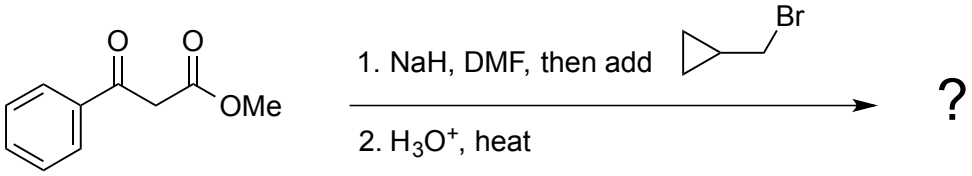
(b) 

After lectures 3-5

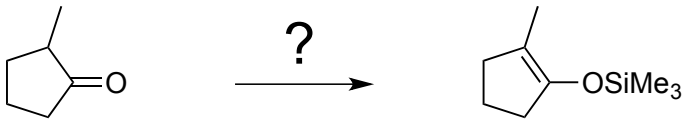
4. Give the products for the reactions shown below, with mechanisms. Explain the observed selectivity.

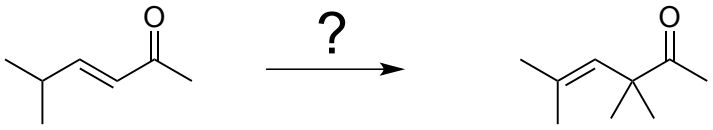
(a) 

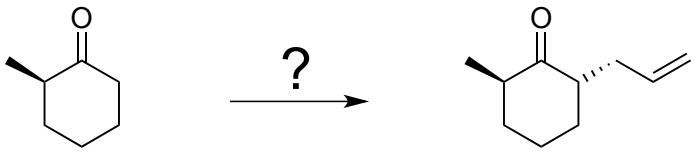
(b) 

(c) 

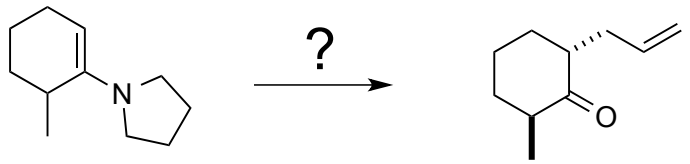
5. State how you would carry out the transformations shown below and provide mechanisms. Identify the required selectivity considerations where appropriate.

(a) 

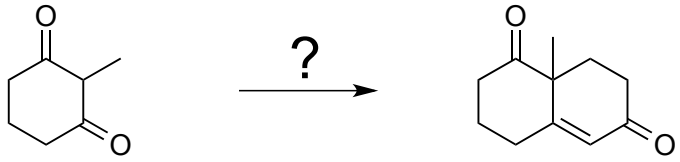
(b) 

(c) 

(d)



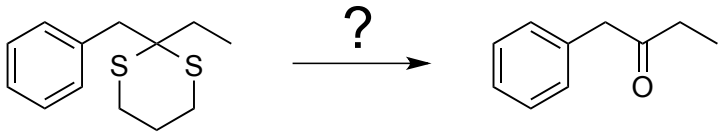
(e)



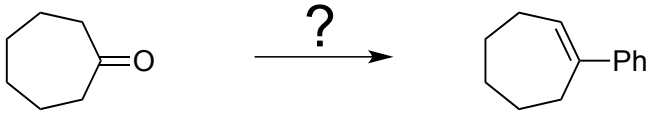
After lectures 6-7

6. State how you would carry out the transformations shown below and provide mechanisms. Identify the required selectivity considerations where appropriate.

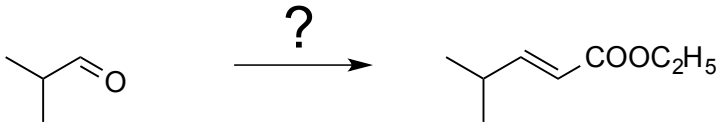
(a)



(b)

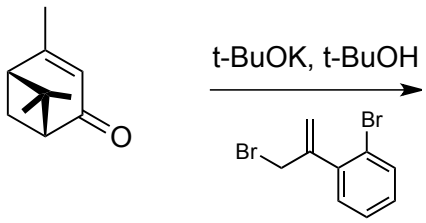


(c)



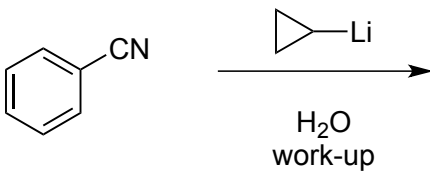
7. Predict the products **A** and **B** of the reactions (i) and (ii) below.

(i)



A
(contains 2 alkene protons)

(ii)



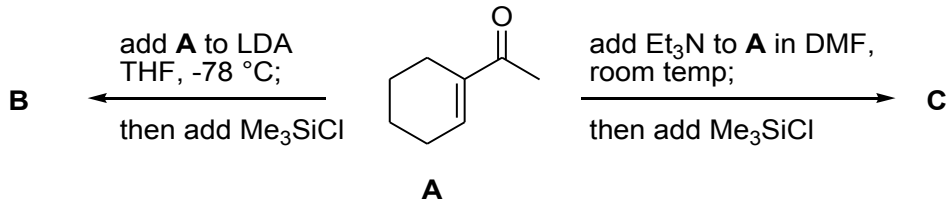
B
(does not contain nitrogen)

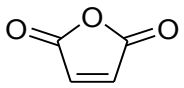
Additional questions/revision questions

8. In an experiment, compound **A** was added to a solution of lithium diisopropylamide (LDA) in tetrahydrofuran (THF) at –78 °C. To this mixture was then added chlorotrimethylsilane, Me_3SiCl. A product **B** was formed; ^1H NMR analysis of **B** indicated the presence of three alkene protons in addition to other signals.

   In a second experiment, **A** was treated with triethylamine in DMF, followed by chlorotrimethylsilane. A product **C** was formed. Compound **C** was isomeric with **B**, and ^1H NMR analysis showed the presence of two alkene protons in addition to other signals. Closer examination of the ^1H NMR spectrum of **C** showed that it consisted of two isomers, each having two alkene protons.

   Identify **B** and **C**, and provide mechanisms for their formation under the conditions described. Explain why **C** exists as two isomers. Subjection of a mixture of **B** and **C** to Diels–Alder reaction with maleic anhydride **D** showed that only one of the isomeric compounds **B** and **C** reacted; which one was reactive with **D**, and why?





D: maleic anhydride

9. Identify the lettered intermediates in the scheme below. Give a mechanism for the conversion **B**→**C**. What is the driving-force for step 3 in the conversion **D**→**E**?