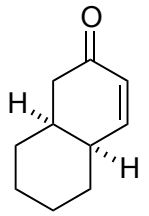
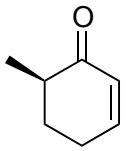
Tutorial problems

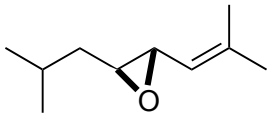
1. Give the products for the reactions shown below with mechanisms. Explain the observed selectivity.

(a) 

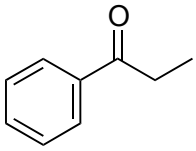
Me_2CuLi

(b) 

MeMgBr

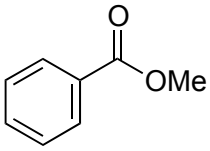
(c) 

Me_2CuLi

(d) 

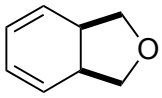
LDA, then

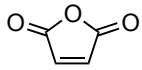
BuCHO

(e) 

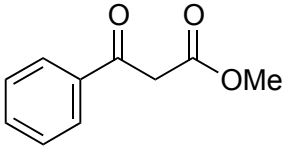
excess

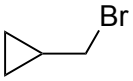
PhMgBr

(f) 

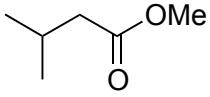


(maleic anhydride)

(g) 

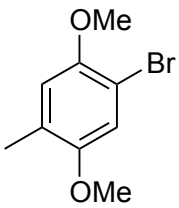
1. NaH, DMF, then add 

2. H_3O^+, heat

(h) 

LDA;

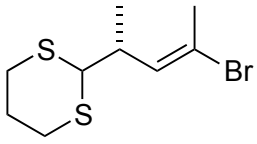
then Me_3SiCl

(i) 

i. Mg

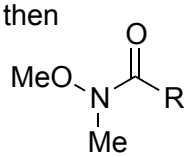
ii. CO_2

then H_3O^+ workup

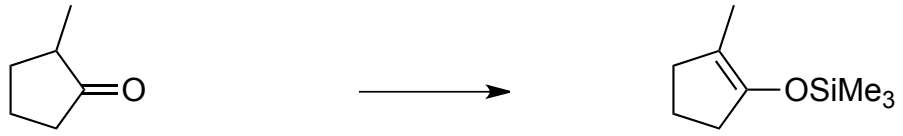
(j) 

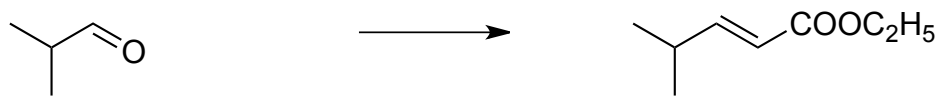
tBuLi (2 equiv)

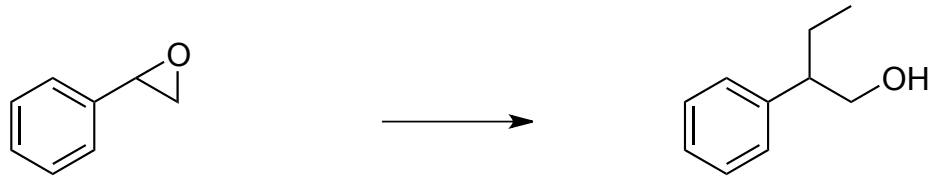
then

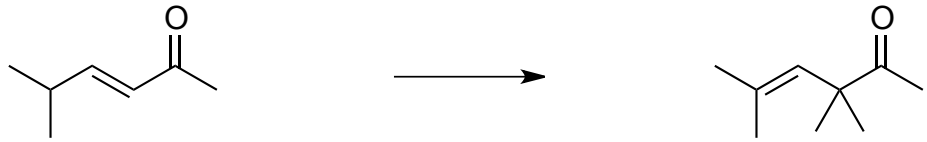


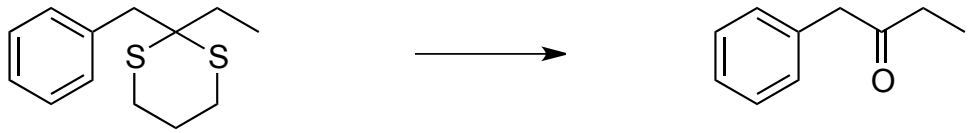
2. State how you would carry out the transformations shown below and provide mechanisms. Identify the required selectivity considerations where appropriate.

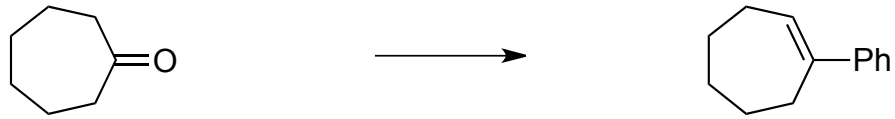
(a) 

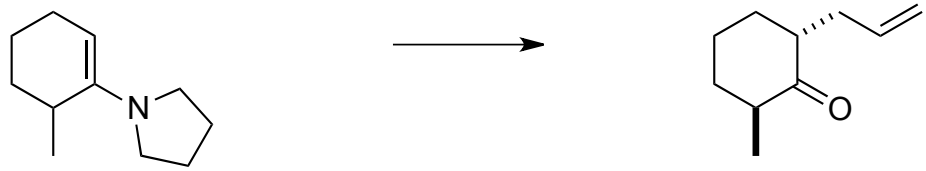
(b) 

(c) 

(d) 

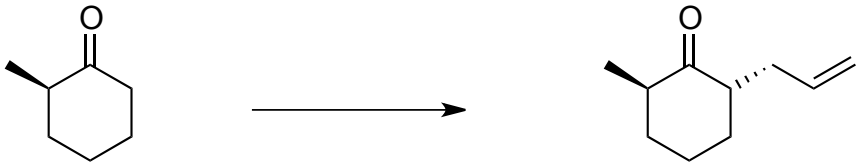
(e) 

(f) 

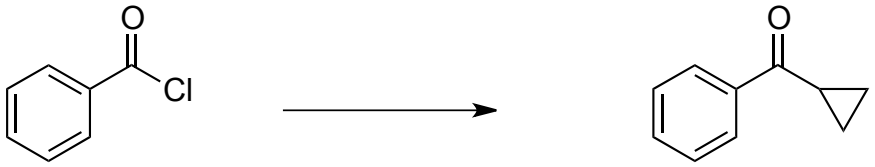
(g) 

3. State how you would carry out the transformations shown below

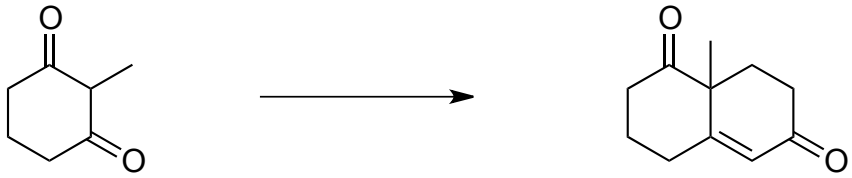
(a)



(b)



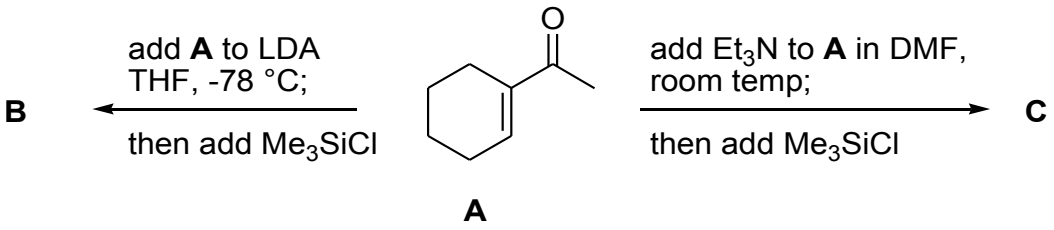
(c)

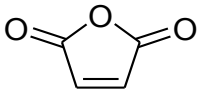


4. In an experiment, compound **A** was added to a solution of lithium diisopropylamide (LDA) in tetrahydrofuran (THF) at –78 °C. To this mixture was then added chlorotrimethylsilane, Me_3SiCl. A product **B** was formed; ^1H NMR analysis of **B** indicated the presence of three alkene protons in addition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