CHEM 330

Final Exam
December 5, 2014

Your name: _____

This a closed-notes, closed-book exam

The use of molecular models is allowed

This exam consists of 12 pages

Time: 2h 30 min

1. _____ / 30
2. _____ / 30
3. _____ / 30
4. _____ / 40
5. _____ / 40
6. _____ / 40
7. _____ / 40

TOTAL _____ / 250 = _____ / 100

This exam counts for 50% of your CHEM 330 final grade

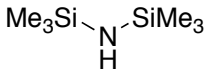
1. (30 pts.) Write a chemical equation and a brief sentence to illustrate each of the following mechanistic models:

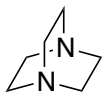
   a. Principle of vinylogy

   b. Fürst-Plattner rule

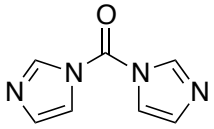
   c. Felkin-Ahn model

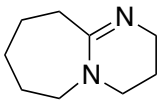
2. (30 pts.) Write a chemical equation to show an example of a reaction that involves the use of the following nitrogen-containing reactants (**do not** write mechanisms – just the reactions):

a. 

b. 

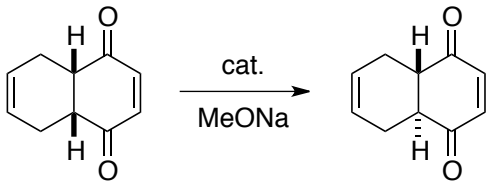
c. $H_2N-N(CH_3)_2$

d. 

e. 

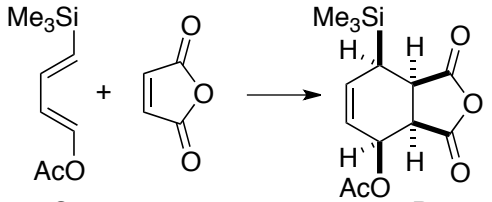
3. (30 pts.) Check the appropriate box to indicate whether the following statements are true or false:

a. Reaction of **A** with catalytic MeONa yields **B**: **true** ☐ **false** ☐



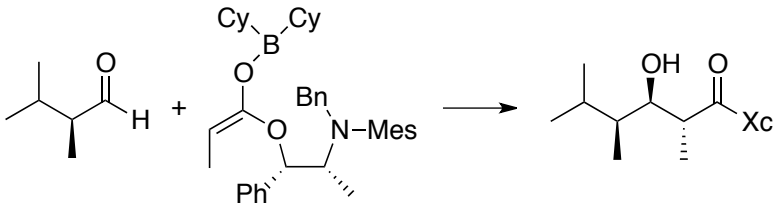
A **B**

b. Reaction of **C** with maleic anhydride yields **D**: **true** ☐ **false** ☐



C **D**

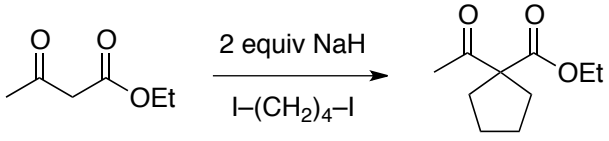
c. The reactants shown below are stereochemically matched: **true** ☐ **false** ☐



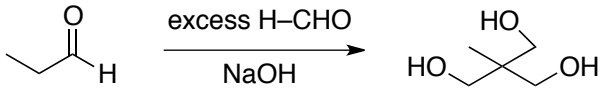
d. The copper atom undergoes oxidative addition in the course of the following reaction: **true** ☐ **false** ☐

$$CuCl_2 + 2\ LiCl \longrightarrow Li_2CuCl_4$$

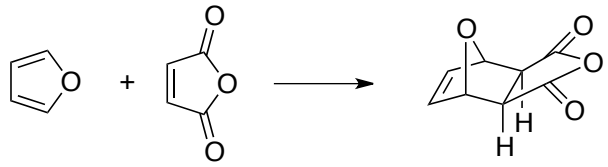
e. The following procedure is satisfactory for the preparation of the cyclic product shown **true** ☐ **false** ☐



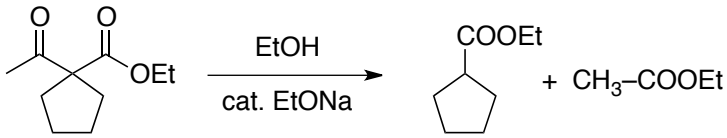
f. The following procedure is satisfactory for the synthesis of the triol shown **true** ☐ **false** ☐



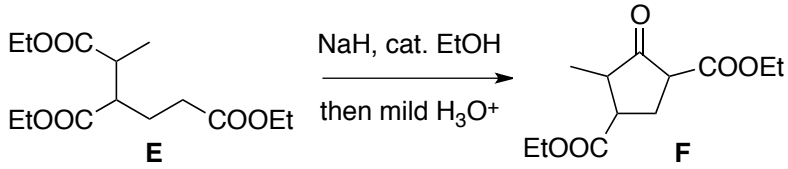
g. The Diels-Alder reaction of furan with maleic anhydride gives the exo-adduct due to a lack of secondary orbital interactions **true** ☐ **false** ☐



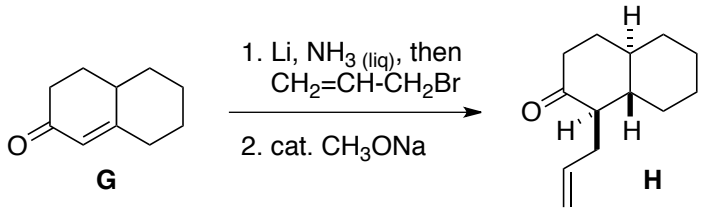
h. The process shown below is a reverse Claisen condensation: **true** ☐ **false** ☐



i. Treatement of **E** with NaH / cat. EtOH, followed by mild H_3O^+, will produce **F**: **true** ☐ **false** ☐

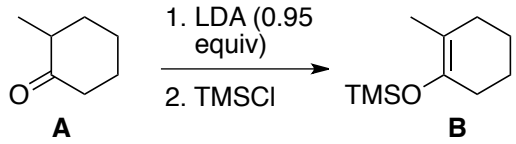


j. Treatment of **G** with Li in liquid NH_3, followed by allyl bromide and then catalytic MeONa, will produce **H** **true** ☐ **false** ☐

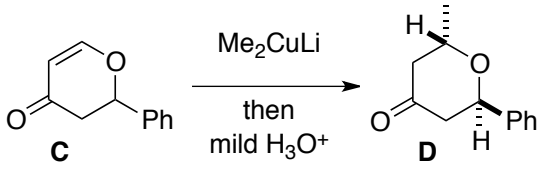


4. (40 pts.) Provide a succinct explanation for the following experimental observations:

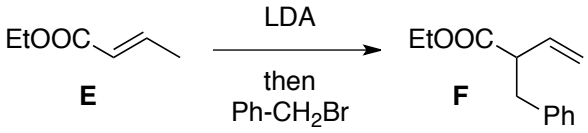
a. Deprotonation of ketone **A** with 0.95 equiv of LDA, followed by reaction with TMS-Cl, produces silyl enol ether **B**, **BECAUSE**:



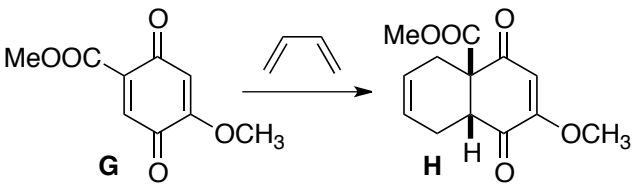
b. Reaction of compound **C** with Me_2CuLi, followed by mild H_3O^+, selectively yields **D**, **BECAUSE**:



c. Treatment of compound **E** with LDA, followed by benzyl bromide, selectively yields **F**, **BECAUSE**:

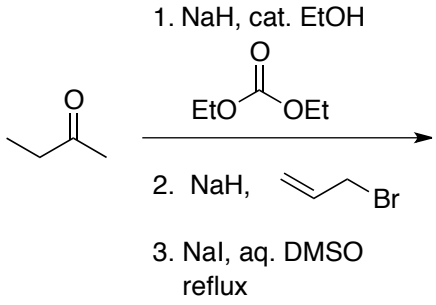


d. Benzoquinone **G** undergoes Diels-Alder reaction selectively at the double bond bearing the COOMe group, **BECAUSE**:

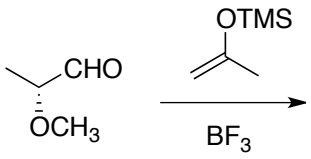


5. (40 pts.) Predict the structure of the major product expected from the following reactions. Notes: **(i) it is not necessary to draw mechanisms; (ii) aqueous workups at appropriate stages are understood.**

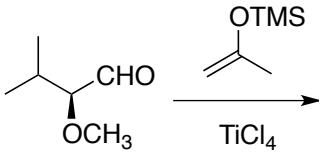
a.



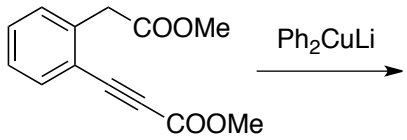
b.



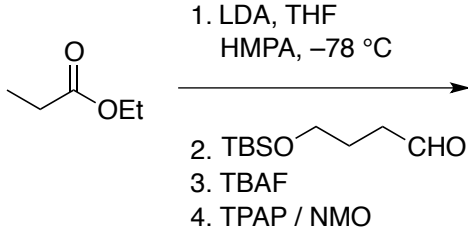
c.



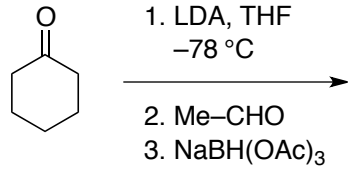
d.



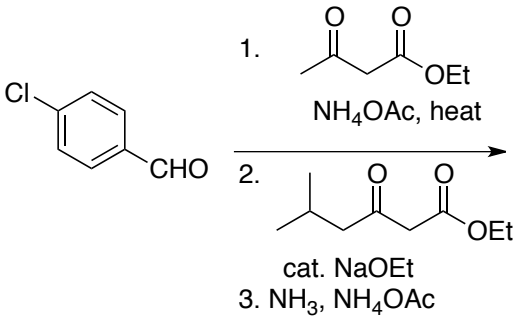
e.



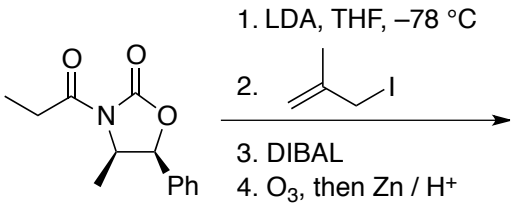
f.


1. LDA, THF
–78 °C
2. Me–CHO
3. NaBH(OAc)3

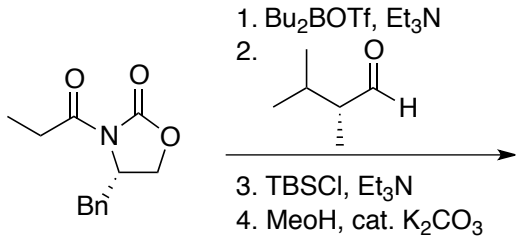
g.


Cl
CHO
1.
OEt
NH4OAc, heat
2.
OEt
cat. NaOEt
3. NH3, NH4OAc

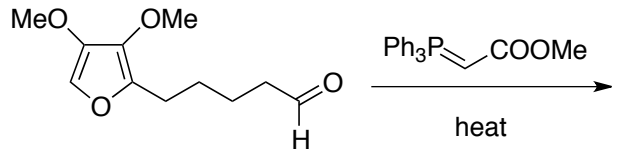
h.


1. LDA, THF, –78 °C
2.
I
3. DIBAL
4. O3, then Zn / H+
Ph

h.


1. Bu2BOTf, Et3N
2.
H
3. TBSCl, Et3N
4. MeoH, cat. K2CO3
Bn

j.


MeO
OMe
Ph3P
COOMe
heat
H

6. (40 pts.) Complete the following equations by indicating all the reagents that are necessary to effect the transformations shown. Provide your answers as a numbered list of reagents, in the correct order, written over/under the reaction arrows. **Note**: aqueous workups are understood and do not need to be included in your answers.

a.

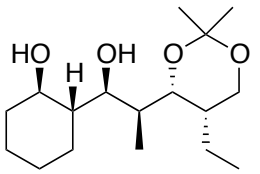
b.

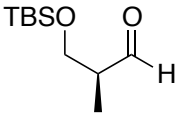
c.

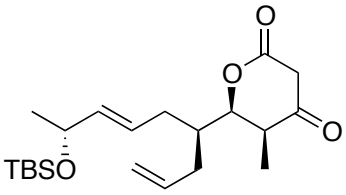
d.

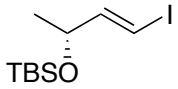
7. (40 pts.) Propose a method to achieve the enantioselective synthesis of the molecules shown below starting with the suggested compounds plus any additional building blocks that might be required (simple carbonyl compounds, alkyl halides,…). Be careful about protecting groups and configurations of stereocenters. Assume the availability of all needed reagents, auxiliaries, etc. Present your answer as a **clear** flowchart.

It is not necessary to draw mechanisms or to indicate aqueous workups.

a. 

starting with 

b. 

starting with 

Happy Holidays !