### UNIVERSITY OF WINDSOR CHEMISTRY AND BIOCHEMISTRY

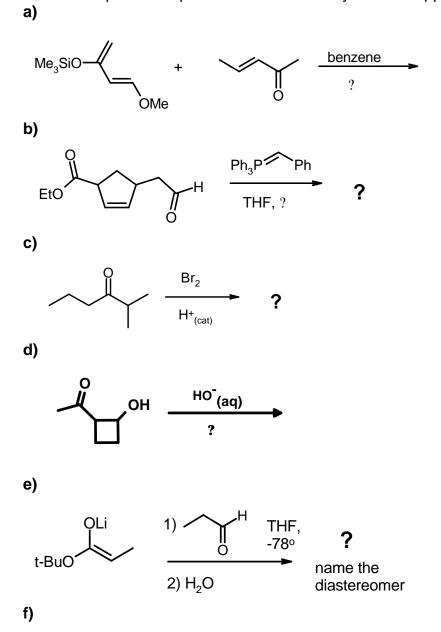
Chemistry 59-331/333 Final Examination Apr. 23, 2001 Time: 3 hours

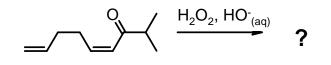
## Answer all questions in the exam booklet

#### 1. Do any eight (8). Total 40 marks

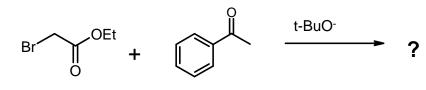
Indicate the structure of the expected major product from each of the following transformations. Mechanisms are not necessary, but showing your work may be a help. Include product stereochemistry where it applies.

?

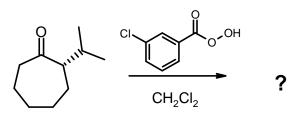




g)



h)



i)

# $EtO_2C \xrightarrow{O} 1) \text{ excess MeLi, Et}_2O$

#### 2. Total 20 marks

**a)** Draw the complete mechanism for the Claisen condensation between two molecules of ethyl acetate. The complete answer will show any small molecules which 'come off' during the reaction, the appropriate intermediates and final product, and whether each step is reversible or irreversible.

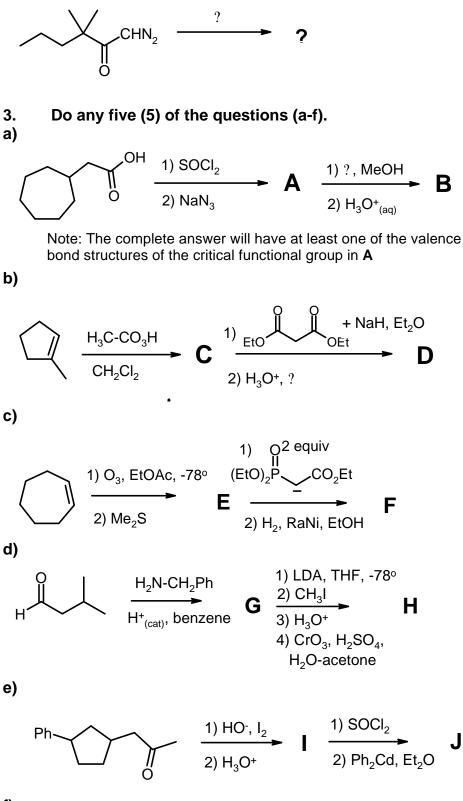
$$2 \qquad \stackrel{O}{\longrightarrow} OEt \qquad \stackrel{1) \text{ EtO}^-, \text{ EtOH}}{2) \text{ H}_3 \text{O}^+ \text{ to pH 5}} \qquad \textbf{?}$$

## b) Do i) or ii), but not both

i) Show the complete mechanism for the Birch reduction of toluene. The stoichiometry of reaction is not implied by what is shown below; it should be apparent from your answer.

$$\begin{array}{c} \overbrace{}^{CH_3} \\ \hline \\ EtOH \end{array} \xrightarrow{} \begin{tabular}{c} Na^\circ, NH_{3(l)} \\ \hline \\ \hline \\ EtOH \end{array} \begin{tabular}{c} P \\ \hline \\ \end{tabular}$$

ii) Show the complete mechanism for the rearrangement part of the Arndt-Eistert synthesis. The complete answer will show at least one reasonable valence bond structure for the reactive functional group. Again, show any molecules given off during the reaction. Note that the final trapping step of this synthesis is *not* included in this question.



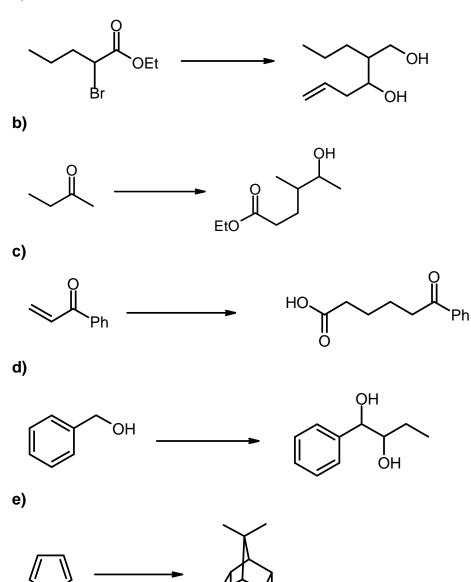
f)

$$\underbrace{(1) \text{ Na}^{\circ}, i \text{PrOH}, \text{NH}_{3(l)}}_{2) 10\% \text{ HCl}_{(aq)}} \text{ K } \underbrace{(1) \text{ Ph}_2\text{CuLi}, \text{Et}_2\text{O}}_{2) \text{ Zn}(\text{Hg}) \text{ amalgam}, \text{ L}}_{\text{HCl}_{(conc)}} \text{ L}$$

## 4. Do any seven (7). Total 70 marks

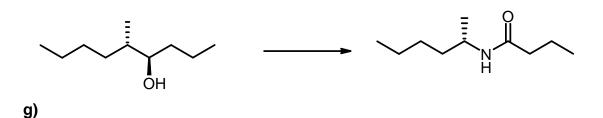
Show by equation how you would prepare the illustrated compounds below from the given starting material. You may use any other reagents you deem fit. Show all reagents, conditions, and isolable intermediates. Mechanisms are not necessary, but showing your work may be a help.

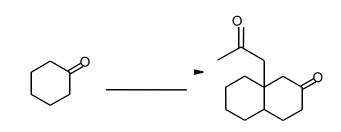
a)

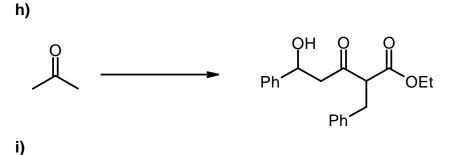


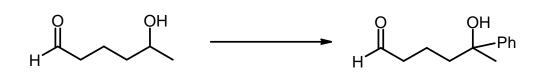
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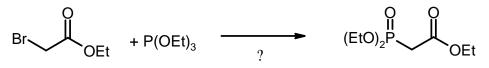






#### Bonus:

I) As mentioned in class, the phosphonate esters used in the Wadsowrth-Horner-Emmons modification of the Wittig reaction are prepared by the Arbuzov reaction, shown below. Provide a reasonable mechanism for this reaction



**ii)** Sulphur ylides are quite closely related to phosphorus ylides. They react with carbonyls, yet tend to give different products in which the oxygen atom is retained. Keeping in mind that the reactivity of sulphur ylides is *somewhat* like those of phosphorus, predict the product (and show the mechanism) of....

$$(H_3C)_2S^+-CH_2^-$$
 ??