UNIVERSITY OF WINDSOR
CHEMISTRY AND BIOCHEMISTRY

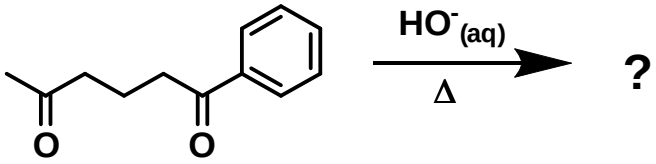
Chemistry 59-331/333 **Apr. 22, 2013**
Final Examination **Time: 3 hours**

Answer all questions in the exam booklet

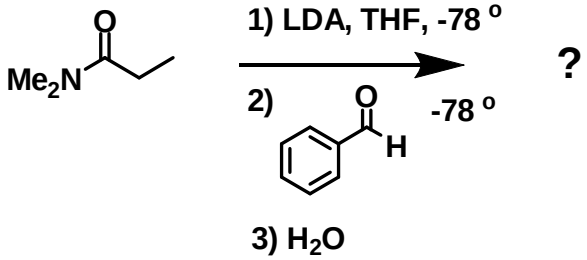
1. Do any eight (8). Total 40 marks

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 (*).

a)

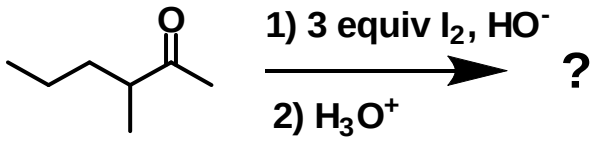


b)*

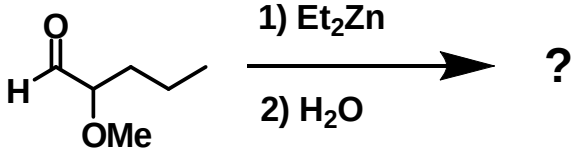


Note: amides tend to form (Z)- enolates

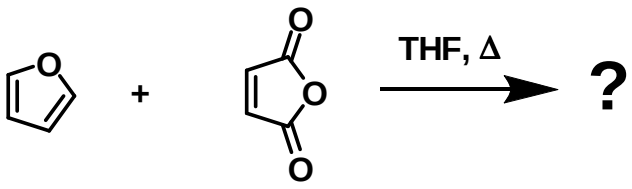
c)



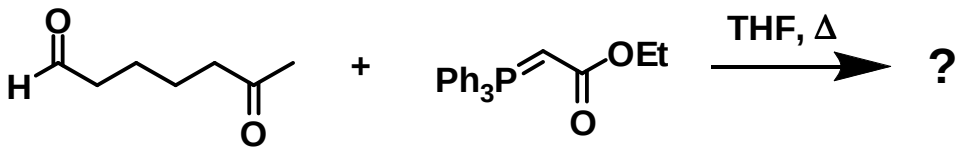
d)*



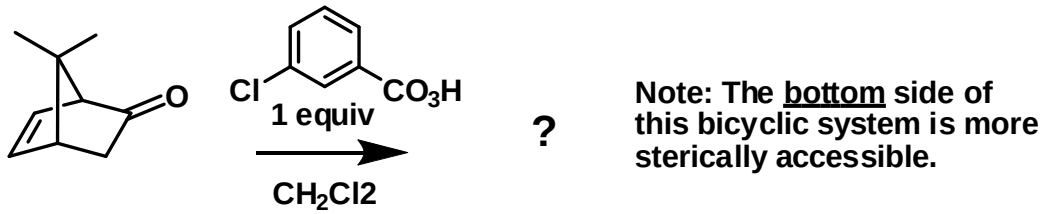
e)*



f)

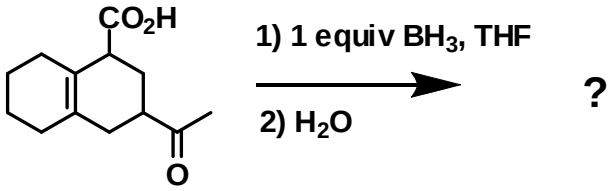


g)*

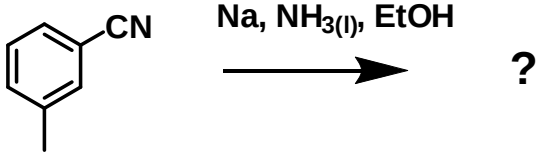


Note: The <u>bottom</u> side of this bicyclic system is more sterically accessible.

h)

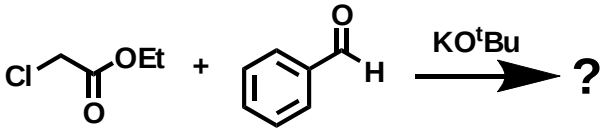


i)



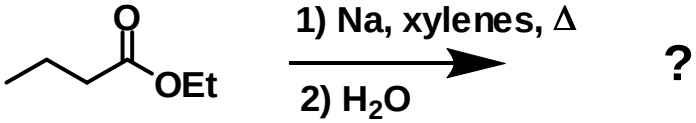
2. Total 20 marks

a) Draw the complete mechanism for the first part of the Darzens' condensation between benzaldehyde and ethyl chloroacetate. The full answer will show any small molecules which 'come off' during the reaction, the appropriate intermediates and final product, and whether each step is (practically speaking) reversible or irreversible.

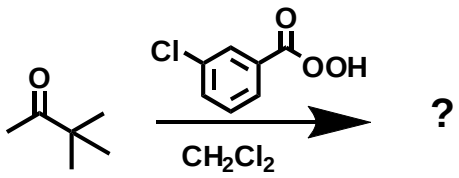


b) Do i) or ii), but not both

i) Show the complete mechanism for the acyloin condensation of ethyl butanoate. The stoichiometry of reaction is not implied by what is shown below; it should be apparent from your answer.

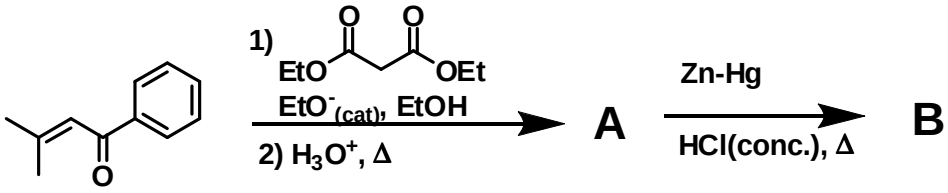


ii) Show the complete mechanism for the Baeyer-Villiger oxidation starting from 3,3-dimethyl-2-butanone.

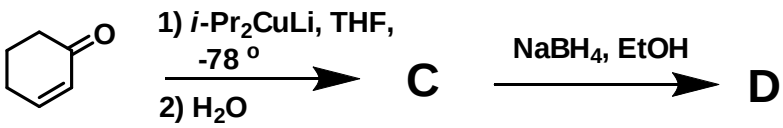


3. **Do any five (5) of the questions (a-f).** Mechanisms are not necessary, but showing your work may be a help. Include product stereochemistry where it applies (*).

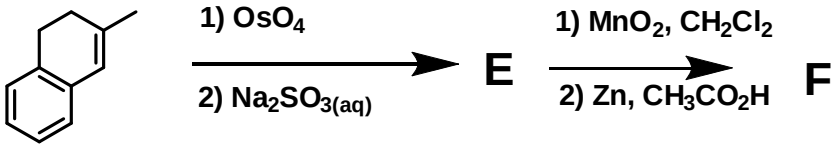
a)



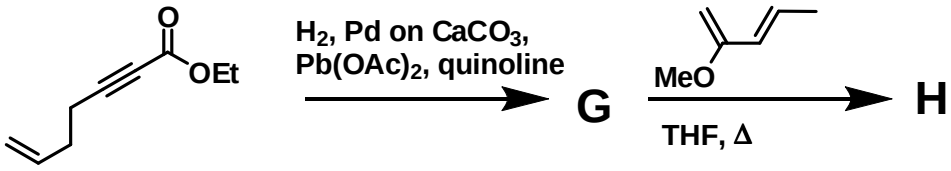
b)*



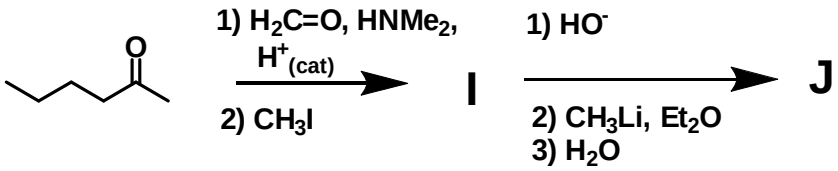
c)*



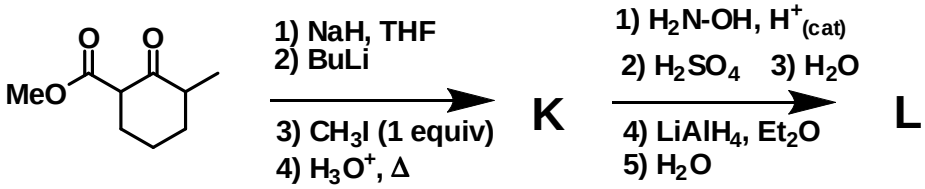
d)*



e)



f)

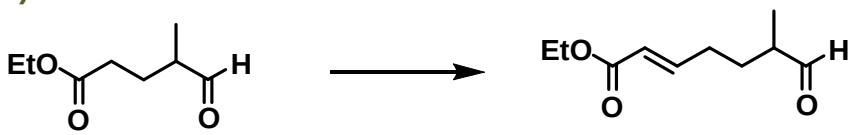


4. **Do any seven (7). Total 70 marks**

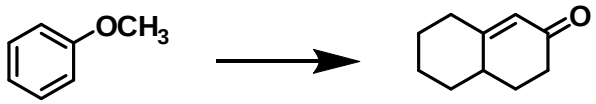
Show by equation how you would prepare the illustrated compounds below from the given starting material. You may use any other reagents you deem fit. Show all reagents, conditions, and isolable intermediates. Mechanisms are not

necessary, but showing your work may be a help. Indicate stereochemistry where it applies (*).

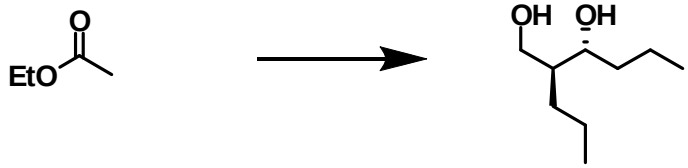
a)



b)

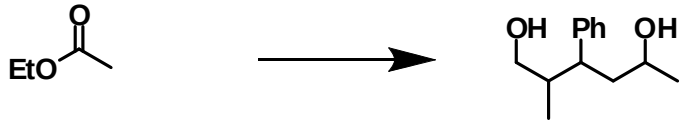


c)*

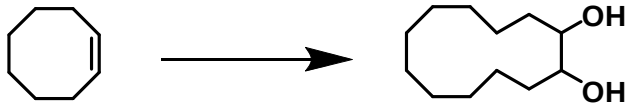


Note: esters normally form (E)- kinetic enolates

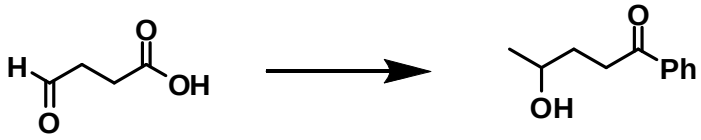
d)



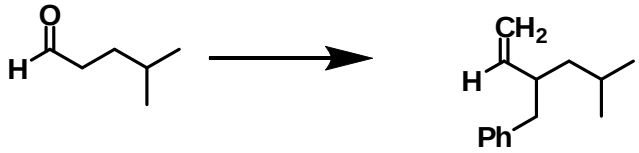
e)



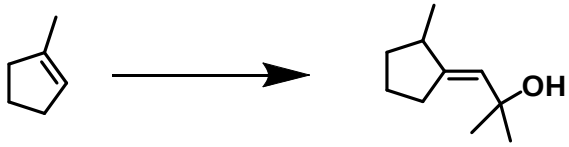
f)



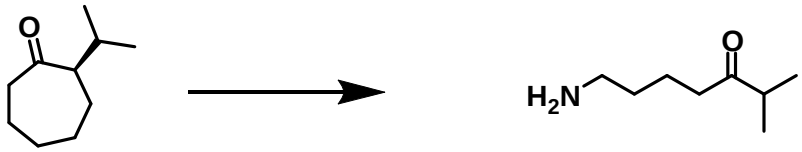
g)



h)

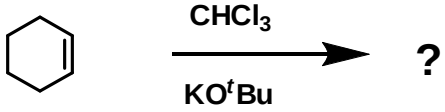


i)*

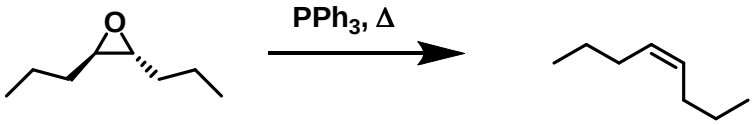


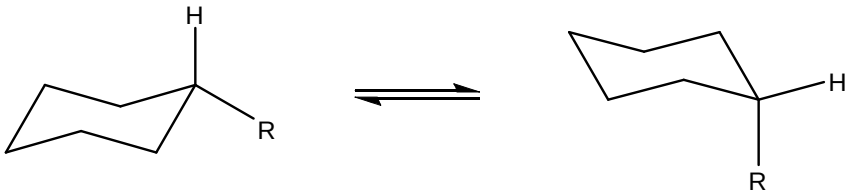
Bonus:

i**)** Given that we didn't get to the Arndt-Eistert synthesis in any substantive way, a related question follows. Give a reasonable pathway for the following reaction of chloroform, base, and an alkene. By the way, this should serve as a warning that great caution should be taken before adding chloroform and strong bases.



ii) One of the methods for inverting the stereochemistry of an alkene is to convert to an epoxide and then subjecting that epoxide to triphenylphosphine. Can you suggest how this reaction occurs?





Common Conformational 'A' Values

R	A value	R	A value
H	0	F	0.3
CH_3	1.7	Cl, Br, I	ca. 0.5
CH_2CH_3	1.8 (also $CH_2CH_2CH_3$, etc)	OH, OCH_3. OCH_2CH_3, $O\text{-}C(CH_3)_3$	0.6-0.9
$CH(CH_3)_2$	2.15	-C≡CH	ca. 0.45
NMe_2	2.1	$-CH=CH_2$	ca. 1.5
Ph	2.9	CO_2R	1.2-1.35
$C(CH_3)_3$	4.8	$SiMe_3$	2.5