UNIVERSITY OF WINDSOR
CHEMISTRY AND BIOCHEMISTRY

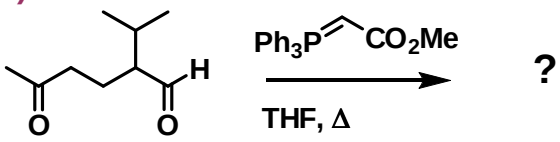
Chemistry 59-331/333 **Apr. 13, 2012**
Final Examination **Time: 3 hours**

Answer all questions in the exam booklet

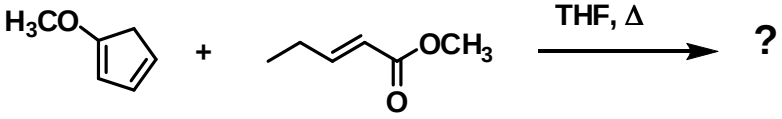
1. Do any eight (8). Total 40 marks

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 (*).

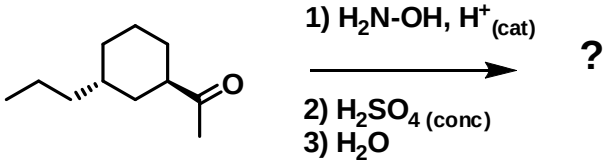
a)



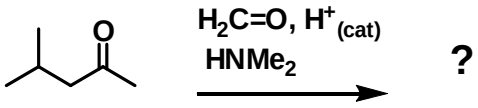
b)*



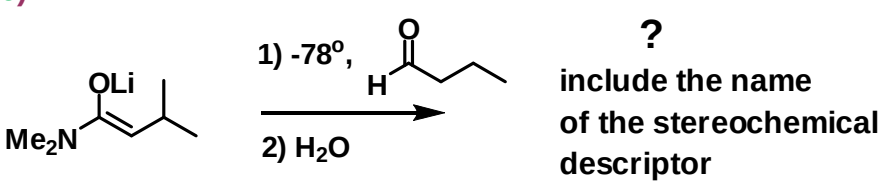
c)*



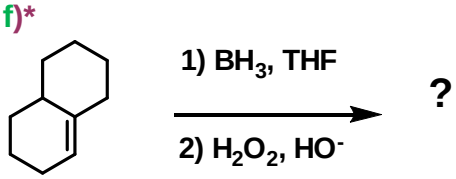
d)



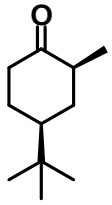
e)*



f)*



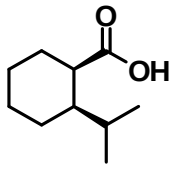
g)*



$NaBH_4$, EtOH

?

h)*



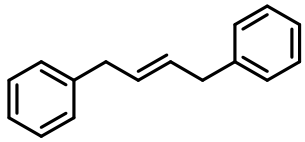
1) $SOCl_2$

2) CH_2N_2

3) Δ, H_2O

?

i)*



1) OsO_4

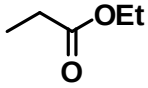
2) $Na_2SO_{3(aq)}$

(workup)

?

2. Total 20 marks

a) Draw the complete mechanism for the Claisen condensation between two molecules of ethyl propanoate. 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.

2 

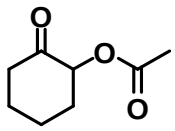
1) EtO^-, EtOH

2) H_3O^+ to pH 7

?

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

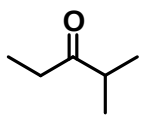
i) Show the complete mechanism for the metal reduction below. The stoichiometry of reaction is not implied by what is shown below; it should be apparent from your answer.



Zn, CH_3CO_2H

?

ii) Show the complete mechanism for the Beckmann rearrangement starting from 2-methyl-3-pentanone. The individual steps for the formation of the initial stable intermediate (step 1) from the ketone and hydroxylamine need not be shown, although its identity must be shown.



1) H_2N-OH, $H^+_{(cat)}$

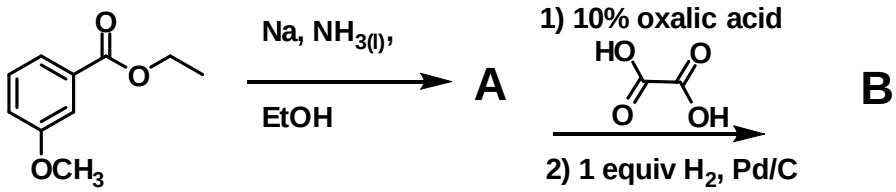
2) H_2SO_4 (conc)

3) H_2O

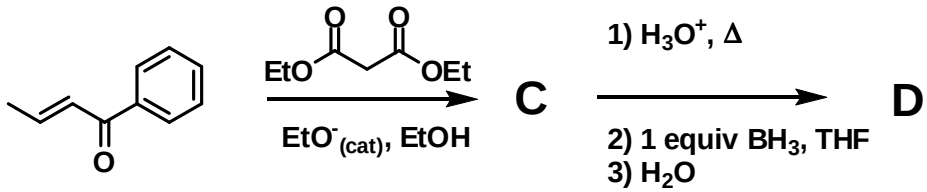
?

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 (*).

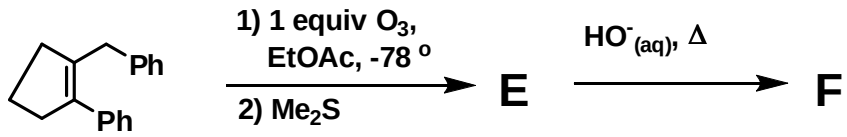
a)



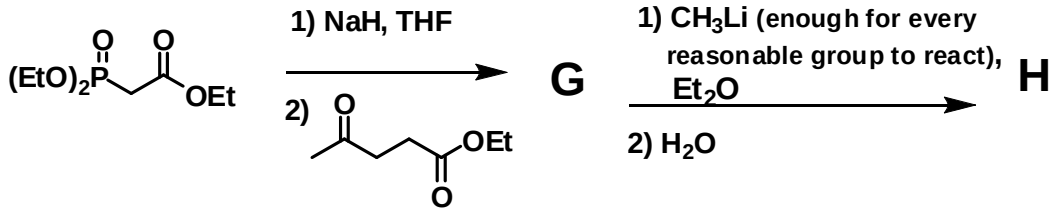
b)



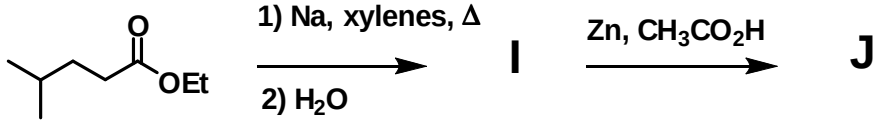
c)



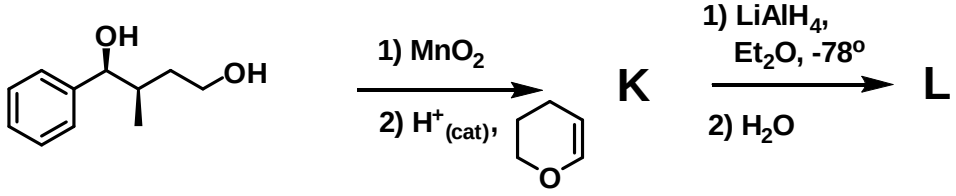
d)



e)



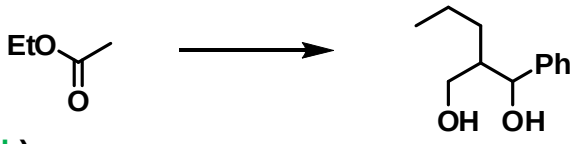
f)*



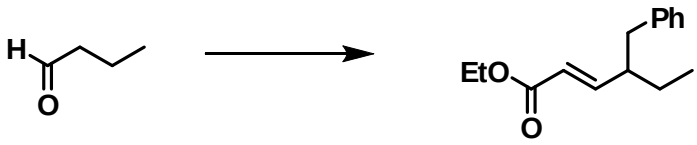
4. **Do any seven (7). Total 70 marks**

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.

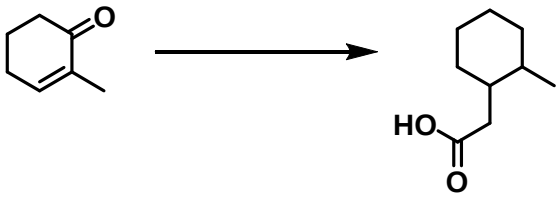
a)


EtO
O
Ph
OH
OH

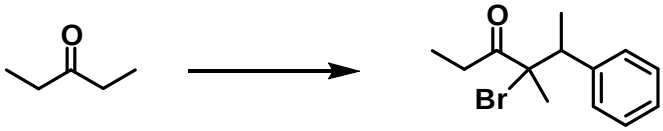
b)


H
O
Ph
EtO
O

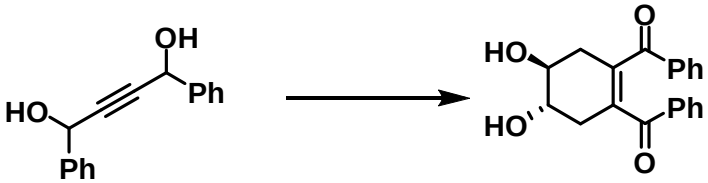
c)


O
HO
O

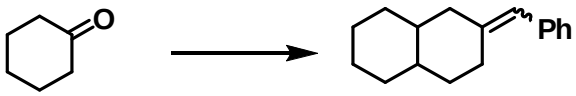
d)


O
O
Br

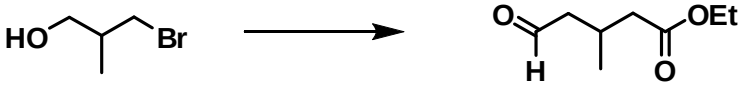
e)*


OH
HO
Ph
Ph
O
HO
Ph
HO
Ph
O

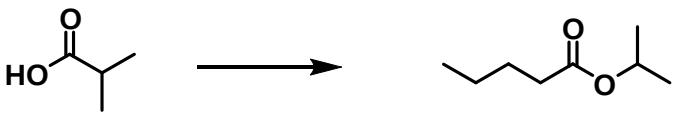
f)


O
Ph

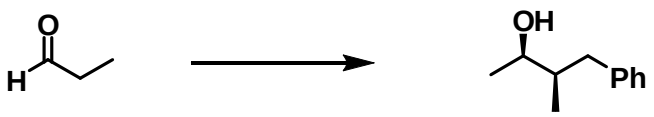
g)


HO
Br
O
H
OEt
O

h)

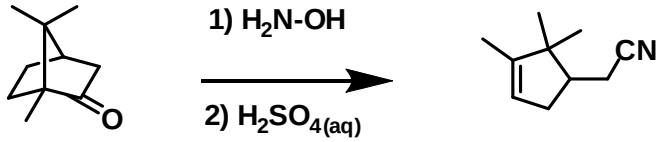

O
HO
O
O

i)*

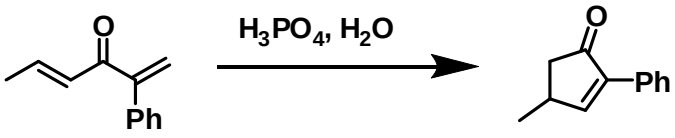

O
H
OH
Ph

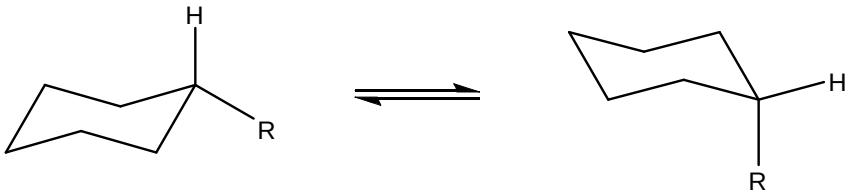
Bonus:

i**)** The Beckmann rearrangement sometimes goes ‘wrong’, especially when one of the substituents on the ketone is a tert-alkyl. In simple cases it may ‘look’ normal, but in other cases one gets a nitrile, like in the case below. Can you propose a reasonable mechanism for this abnormal Beckmann process?



ii) A reaction of much current interest is a cyclization reaction of a divinyl ketone called a Nazarov reaction. Can you propose a reasonable mechanism for the transformation?





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