CHEM 2OB3 Test 1 February 9, 2007 VERSION 1

Section 1 – Multiple Choice [1 $^{2}/_{3}$ marks for each].

Version 1
1 B
2 E
3 D
4 D
5 A
6 C
7 A
8 E
9 B
10 A
11 D
12 E
13 A
14 B
15 E

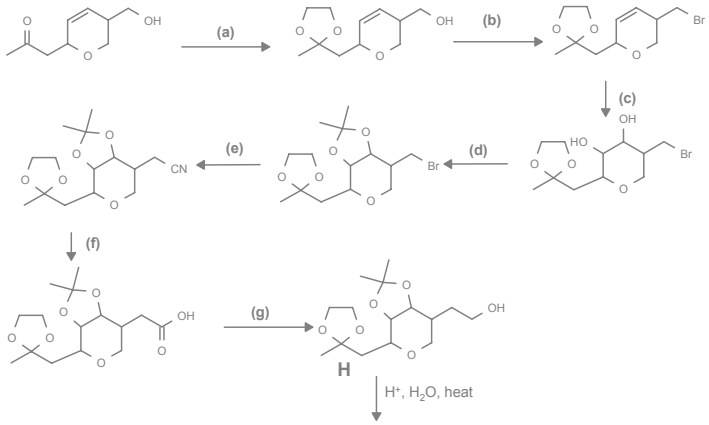
Version 2
1 C
2 A
3 E
4 E
5 A
6 B
7 C
8 A
9 A
10 D
11 E
12 E
13 A
14 E
15B

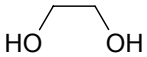
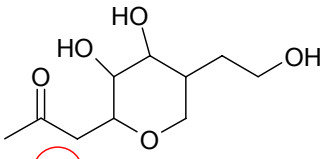
Section 2 – Short Answer

Question 16 [10 marks] The syntheses of certain antibiotics called pseudomonic acids include the following transformations.

(i) For the steps labelled (a) - (g), provide the reagents and conditions in the table below that will allow for each conversion.

(ii) The acidic hydrolysis of compound **H** results in three organic compounds: X, Y and Z. Provide the structures for these compounds in the box provided.



COMPOUND X	COMPOUND Y	COMPOUND Z
 0.5	 0.5	 2

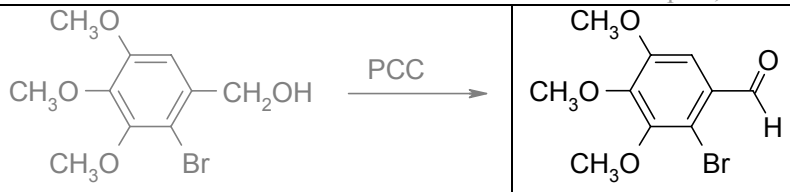
Reagents:

(a)  0.5, H^+ (any acid except H_3O^+) 0.5	(b) 1 PBr_3, ($SOBr_2$)
(c) OsO_4 or $KMnO_4$ 1	(d)  0.5, H^+ (any acid except H_3O^+) 0.5
(e) HCN or NaCN/H^+ or KCN/H^+ 1 or 0.5/0.5	(f) $NaOH/H_2O$ (any strong base) 1
(g) 1 $LiAlH_4$ or BH_3	

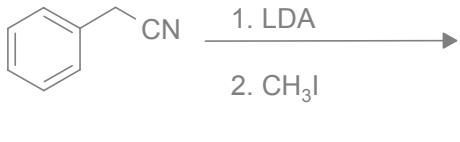
Question 17 [12 marks]

Each of the following reactions has been reported in the chemical literature and gives a predominance of a single product. Provide the MAJOR products necessary to complete TWELVE of the ~~FIFTEEN~~ FOURTEEN reactions below. If more than 12 are attempted, the first 12 will be marked.

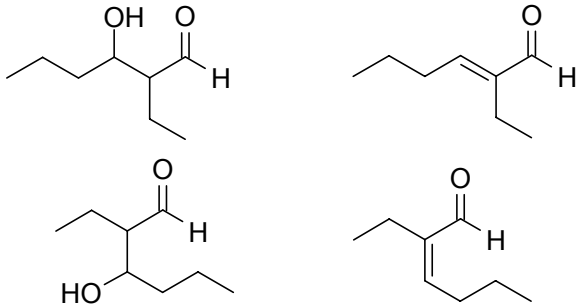
(a)



(b)

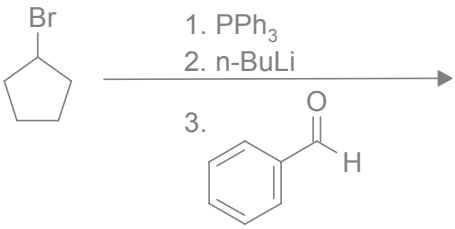


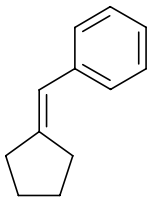
(c)



any one of these structures (two left structurese are the same as each other, as are two right structures)

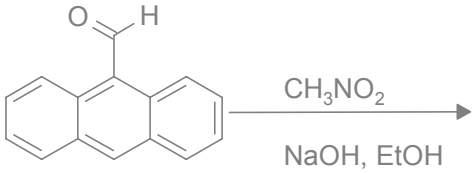
(d)

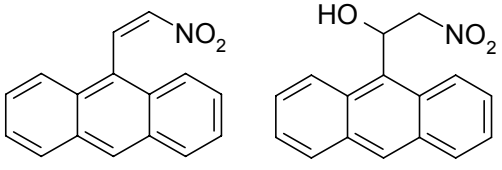




(E or Z isomers are OK)

(e)

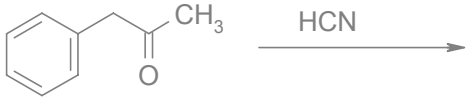


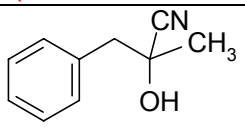


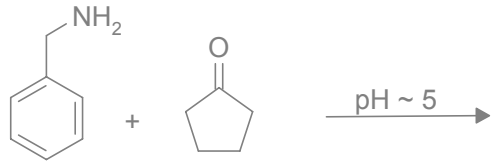
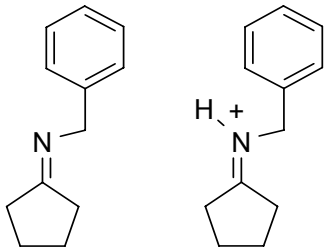
(preferred)

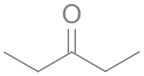
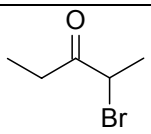
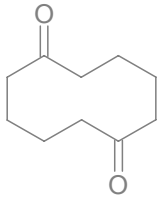
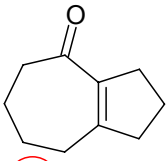
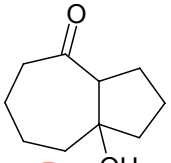
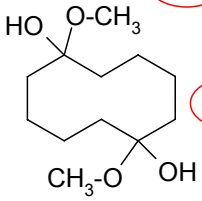
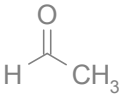
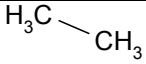
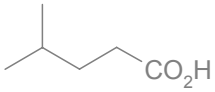
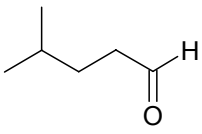
(either structure, E or Z isomers are OK)

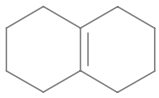
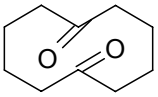
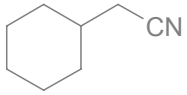
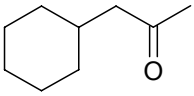
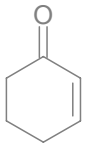
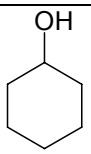
(f)





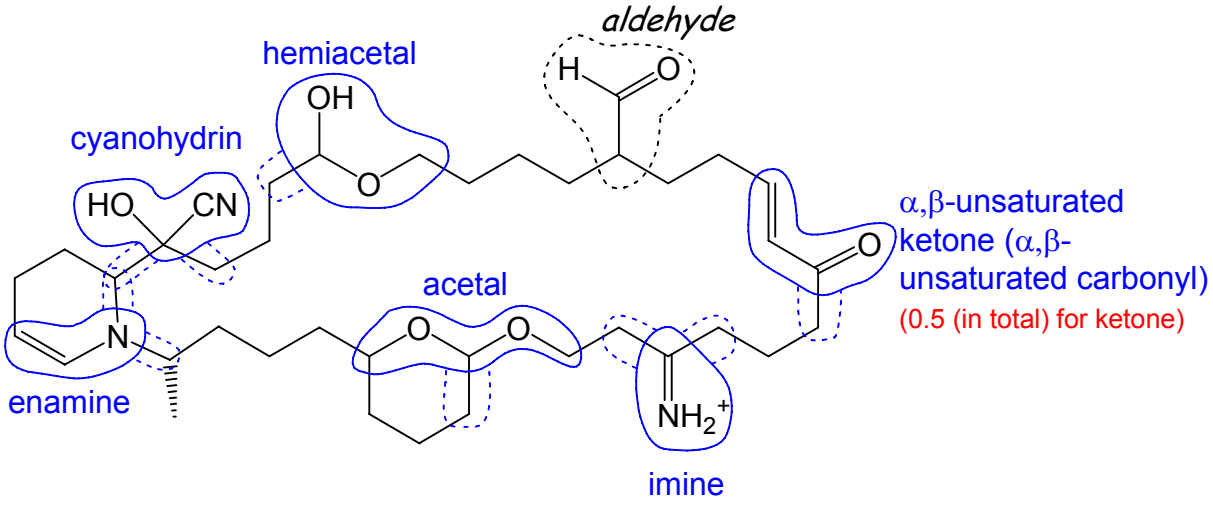
(g) 	 (protonated or unprotonated, E or Z isomer) (protonated form needs + charge, but its location is not important)

(h)  Br_2 acetic acid	
(i)  $NaOCH_3$, MeOH heat	 1 or  0.5 or  0.5 (**0** marks for acetals)
(j)  1. H^+, HS SH 2. Raney Ni	
(k)  1. $SOCl_2$ 2. $LiAlH(O^tBu)_3$, Et_2O -78C	

(l)  1. O_3 → 2. Zn , HOAc	
(m)  1. MeMgI → 2. H_3O^+	
(n)  H_2 → nickel, high pressure	

Question 18 [6 marks]

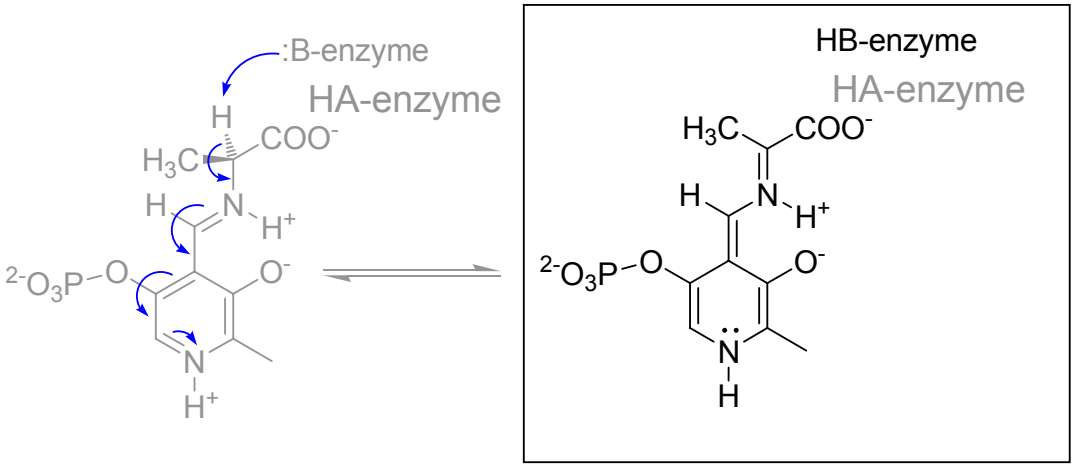
Circle and name all the functional groups in this molecule (there are **seven**, one of which is already identified). Circle the minimum number of atoms that are required to define each functional group.



1 for each {name + correctly circled atoms}
- circling the atoms inside the dotted lines is OK, more than that is not
- smaller functional groups - no marks (except ketone, as above)

Question 19 [4 marks]

Pyridoxal phosphate is a cofactor in the alanine racemase-catalyzed epimerization of alanine. Starting from the external aldimine with L-alanine (shown), show the mechanism for the next step of the reaction. Draw arrows as appropriate on the structure shown, and draw the next structure. (Only the next step, not the whole reaction.)

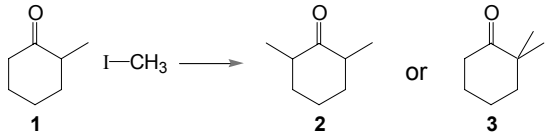


1 for getting the arrows completely correct on the left hand side
1 for doing the correct chemical step (deprotonating Cα)

2 for getting the right hand structure completely correct

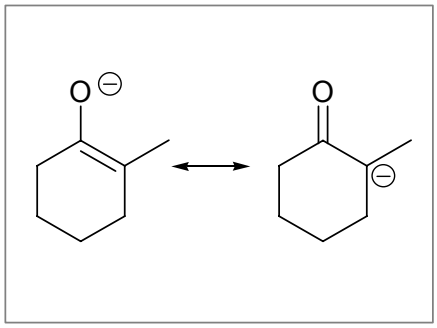
Question 20 [5 marks]

In order to make dimethylcyclohexanones (**2** or **3**) from 2-methylcyclohexanone (**1**) and CH_3-I, it is necessary to form the enolate using either Na^+ ^-OEt or LDA.

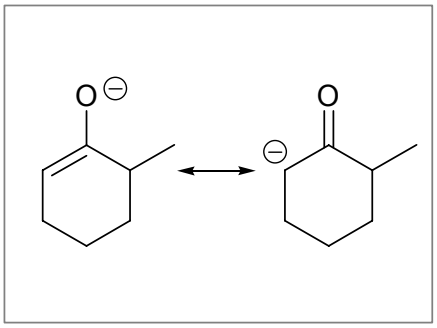


(a) Which base would give the thermodynamic enolate? $Na^{+-}OEt$ or NaOEt (1)

(b) Draw the thermodynamic and kinetic enolates:



thermodynamic



kinetic

4 - only one resonance form is required for each
- (2) marks (total) if the only mistake is mixing up thermodynamic & kinetic

---

THE END