

Name: Key

(Print your name clearly!)

Sametz: CHEM 322 Spring 2013

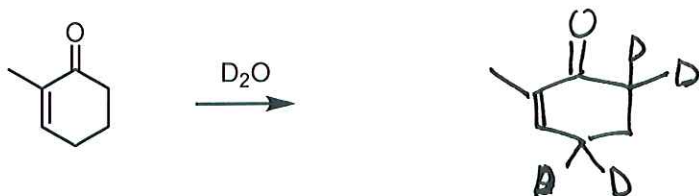
Organic Chemistry Exam 3

All answers should be written CLEARLY in the space provided. (If it's not clear, it's wrong).

																		1	2
																		He	
1	1																	10	
	H																	Ne	
2	2																	18	
	Li	Be																Ar	
3	3	4																18	
	Na	Mg																Ar	
4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
5	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
6	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	
	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
7	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	
	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt										
6	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	
	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu					
7	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	
	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr					

You may raise your hand to ask a question if you are unsure what a question is asking of you.

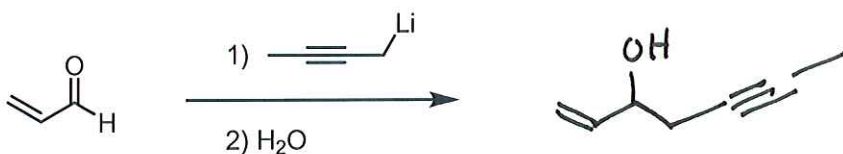
1. (4 points) The ketone below is partially deuterated when shaken with D_2O . This exchange is catalyzed by acid or by base. Draw the final product of this exchange, showing clearly where deuterium was incorporated into the molecule.



1 each
right - wrong

2. (44 points) Give the major organic product(s) for the following reactions.

a)

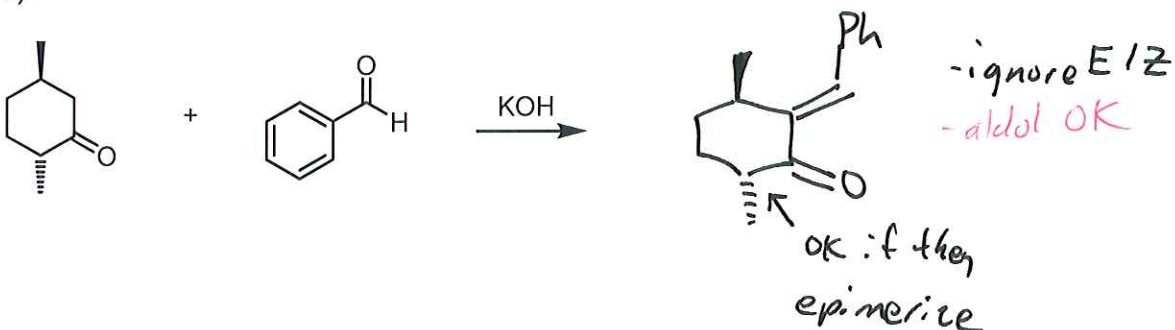


4 pts
each

b)

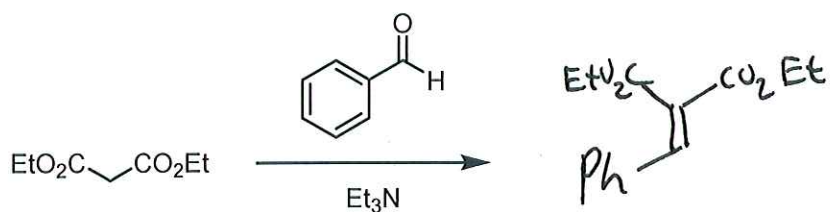


c)

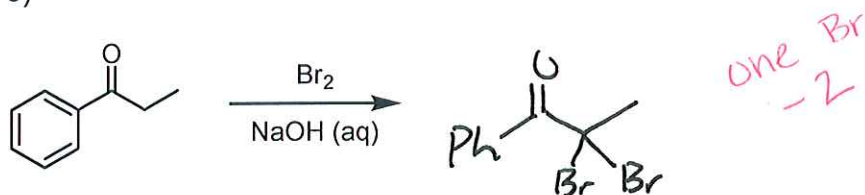


-ignore E/Z
-aldol OK

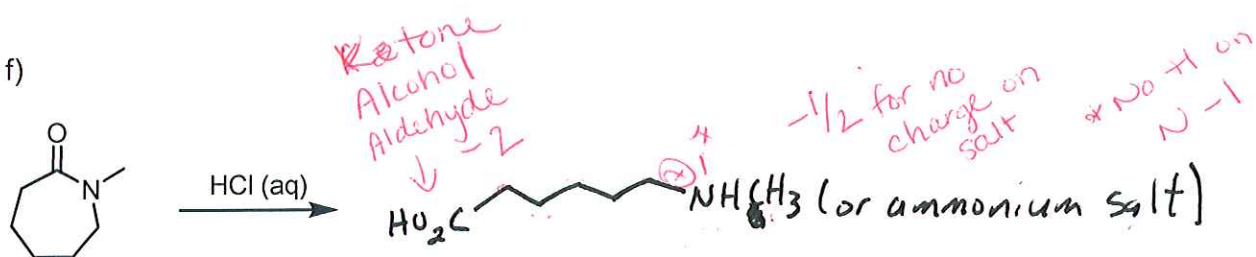
d)



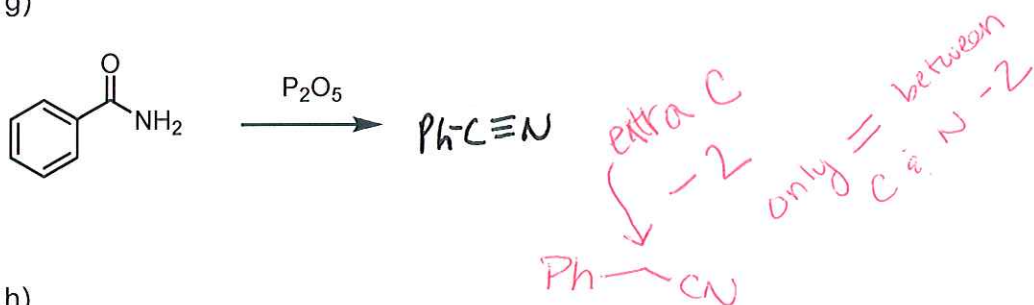
e)



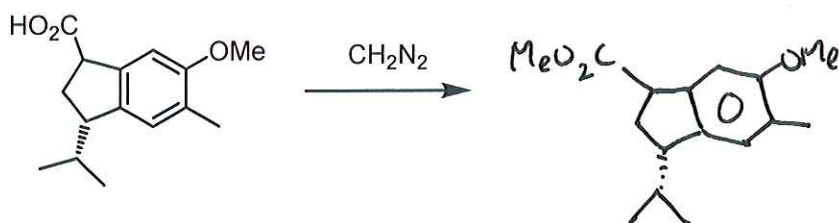
f)



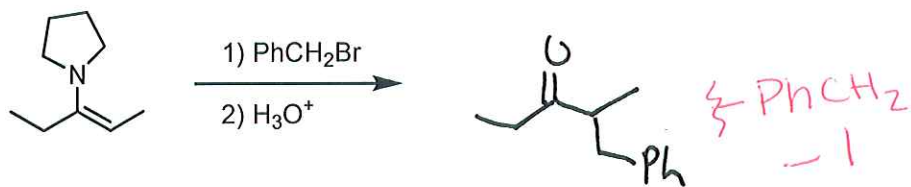
g)



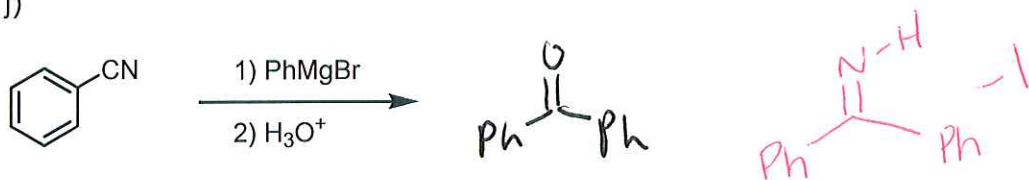
h)



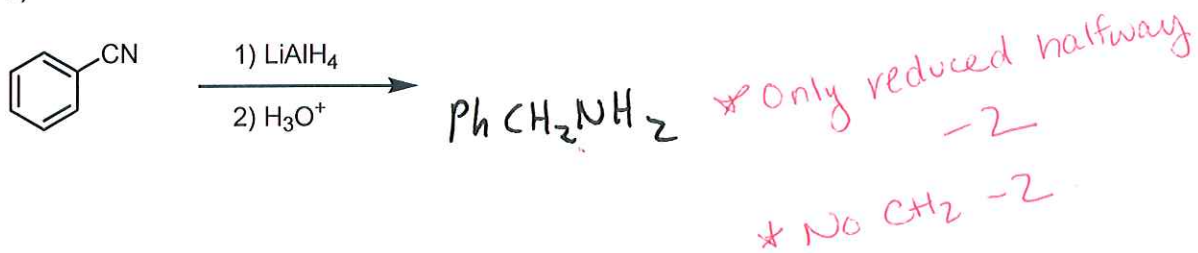
i)



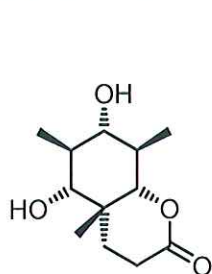
j)



k)



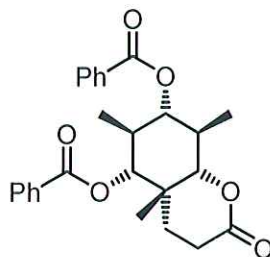
3. (15 points) Give reactants for 8 of the following 10 transformations. **CLEARLY INDICATE THE QUESTIONS THAT YOU DON'T WANT GRADED!** Otherwise, the first 8 questions that show work will be graded.



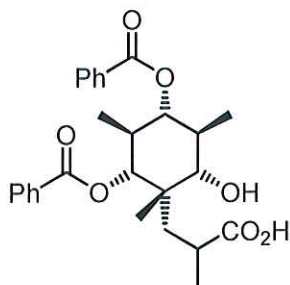
Best: $\text{Ph}-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-\text{Ph}$
or $\text{Ph}-\text{C}(=\text{O})-\text{Cl}$

(Et_3N , etc.
optional).

2/3 Fischer esterification:
lactone compatibility?

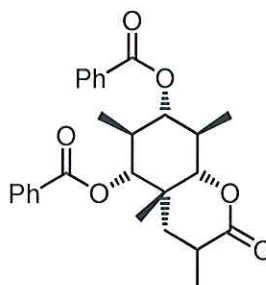


1) LDA
2) MeI

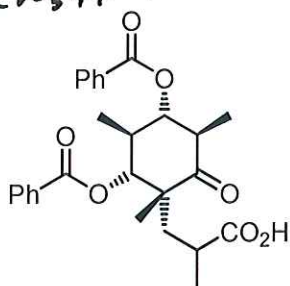


OH^-
(you can assume that
this is possible without
destroying the benzoate
esters)

(or H_3O^+ ;
literature was LiOH)

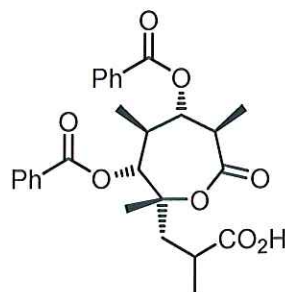


suitable
 Cr^{VI} reagent
e.g. $\text{K}_2\text{Cr}_2\text{O}_7/\text{pyr}$



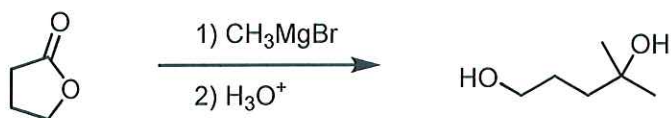
RCO_3H

e.g. $\text{CF}_3\text{CO}_3\text{H}$
mCPBA

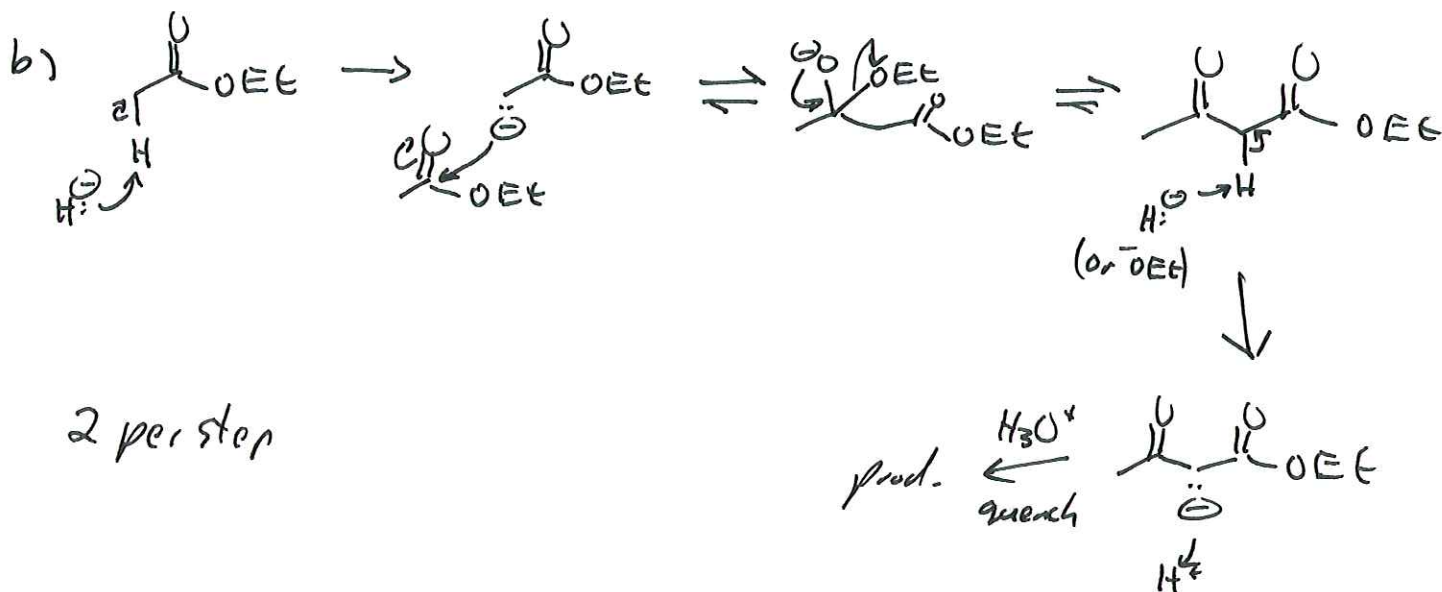
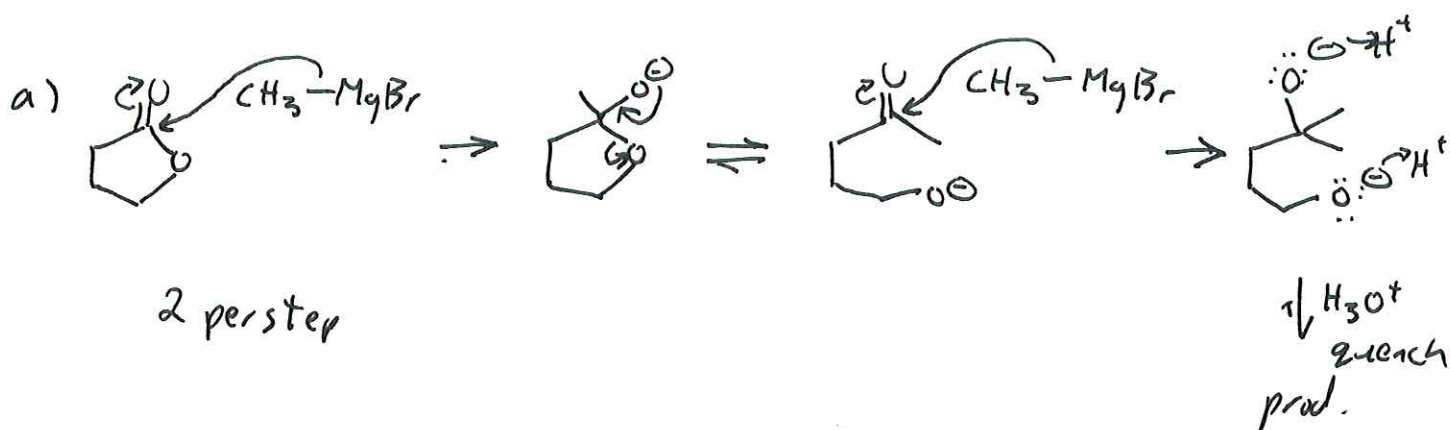
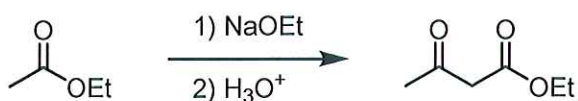


4. (10 points) Give a complete reaction mechanism for **one** of the following two reactions. If you show work on both, **CLEARLY** indicate which of the two you wish to be graded; if it's not clear to the grader, they will choose one to grade.

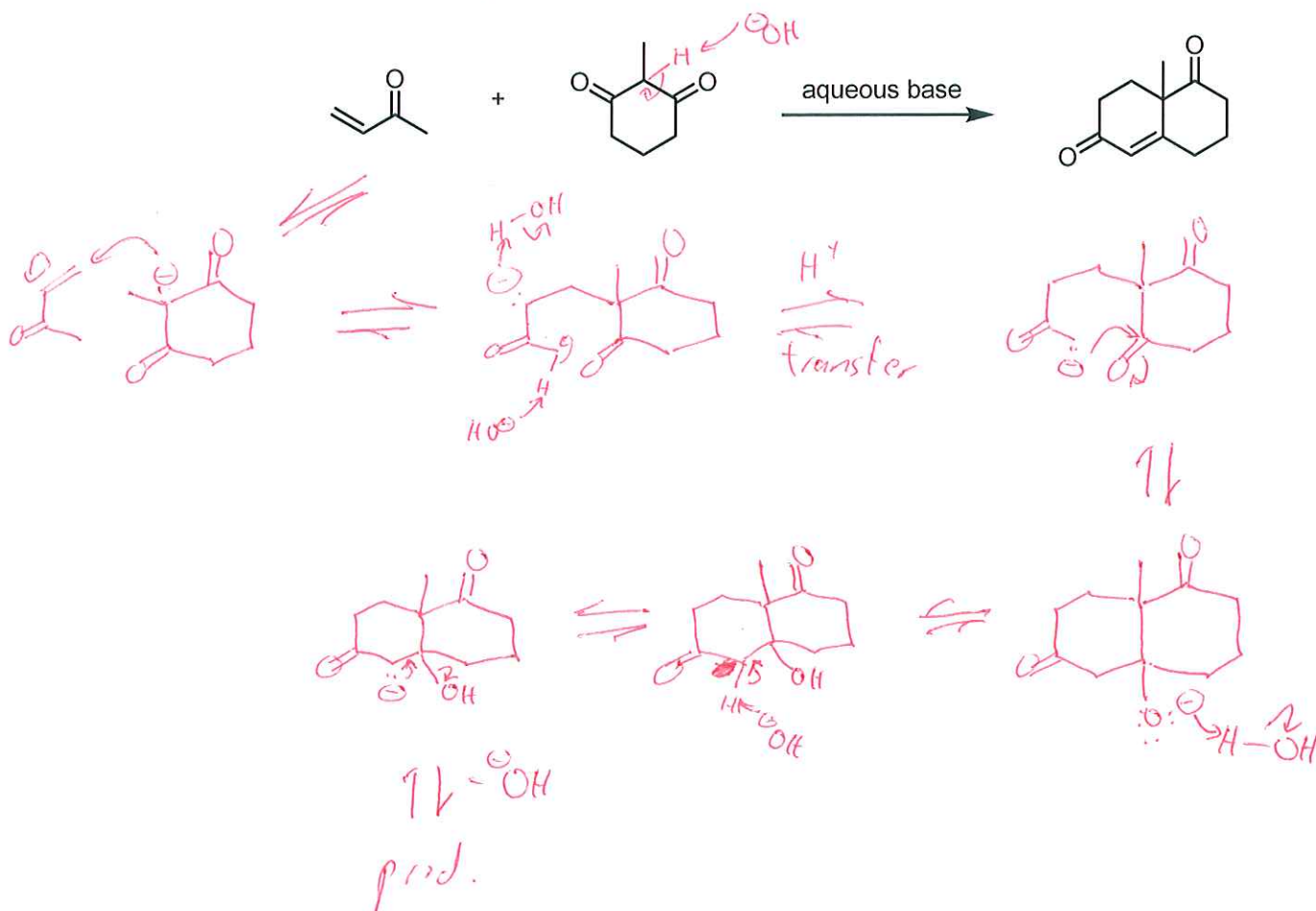
a)



b)



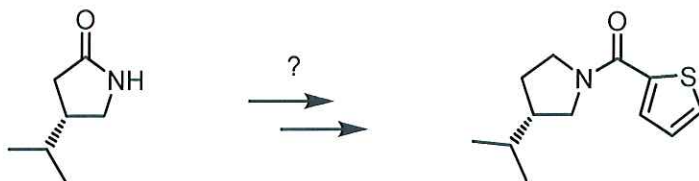
5. (7 points) The Wieland-Miescher ketone has been used as a starting material in the synthesis of many natural products. Its synthesis via Robinson annulation is shown below. Give a reasonable reaction mechanism for this reaction.



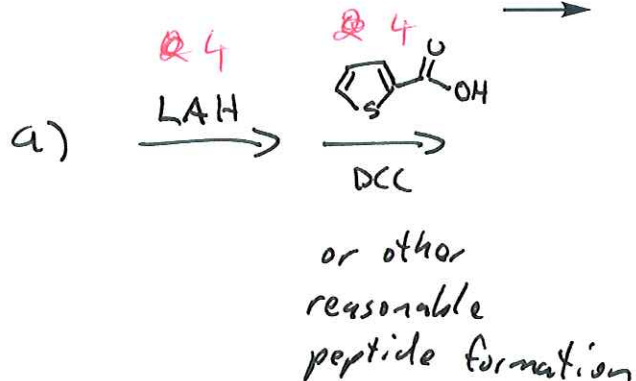
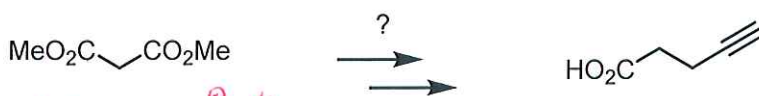
1 per step
(if final elimination done E2,
give them the points)

6. (8 points) Provide a synthesis for **one** of the following two products on the right from the indicated starting material(s) on the left. If you show work on both, **CLEARLY** indicate which of the two you wish to be graded; if it's not clear to the grader, they will choose one to grade.

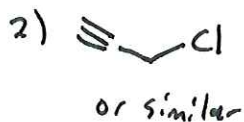
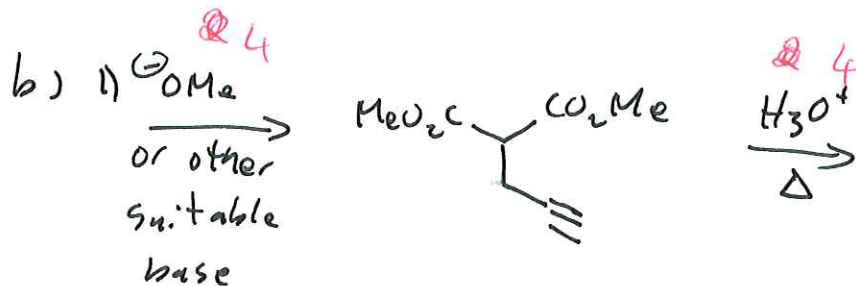
a)



b)

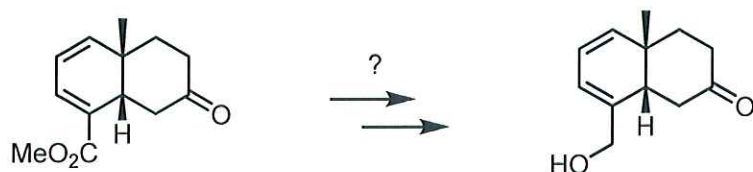


4 pts per step

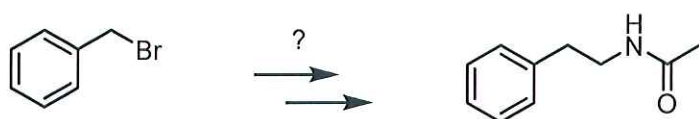


7. (12 points) Provide a synthesis for **one** of the following two products on the right from the indicated starting material(s) on the left. If you show work on both, **CLEARLY** indicate which of the two you wish to be graded; if it's not clear to the grader, they will choose one to grade.

a)



b)



a) MeOH, H^+ ⁴ $\xrightarrow{\text{acetal}}$ LAH ⁴ $\xrightarrow{\text{1}^\circ \text{alcohol}}$ H_3O^+ ⁴ 4 pts. per stop
 or $\text{HO}-\text{CH}_2-\text{OH}, \text{H}^+$

also possible: NaBH_4 ; LAH ; 1° protect ; oxidize ; 1° deprotect

b) CN^- ⁴ $\xrightarrow{\text{LAH}}$ ⁴ $\xrightarrow{\text{DCC}}$ ⁴ peptide coupling
 or other
 ($\text{R}-\text{COCl} / \text{Et}_3\text{N}$ etc.)