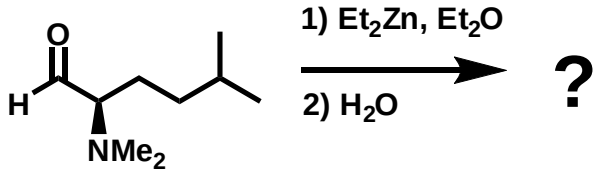
Dept. of Chemistry and Biochemistry

59-331/333 **Mar. 18, 2013**

Test #2 **Time: 53 minutes**

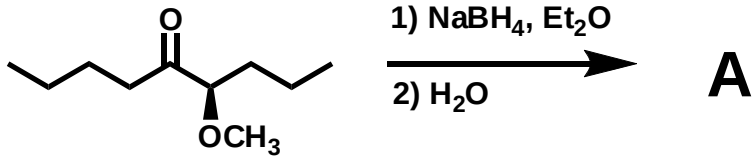
Answer all questions in the test booklet(s) provided. Show stereochemistry where relevant. Answers written in pencil will be marked, but cannot be returned for remarking.

1. Give the detailed rationale for the addition reaction of diethylzinc to the following aldehyde. The complete mechanism will include a drawing of the conformation through which the addition occurs, the appropriate trajectory of attack, the final product including stereochemistry, and the appropriate stereochemical descriptor for the product. (**10 marks**).

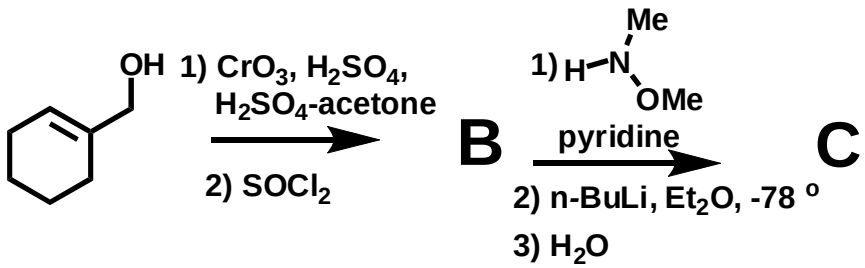


2. Indicate the structure of the expected major product from each of the following reactions. Include stereochemistry where it is relevant. Mechanisms are *not* necessary, but showing your work is likely to be a help. Cases with a * show definite stereochemical issues. (**5 for each letter, 40 marks total**)

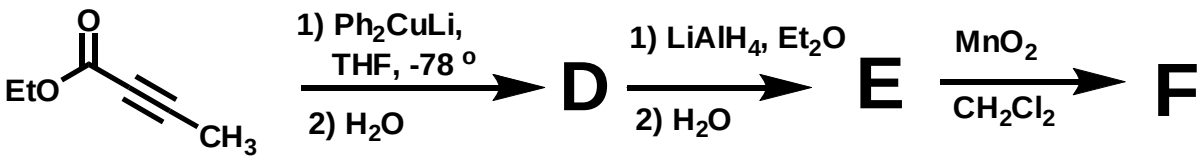
a)*



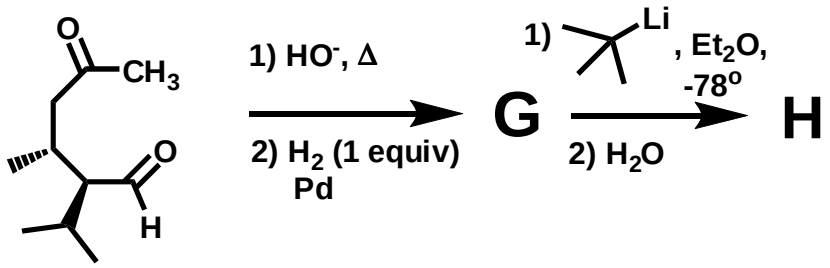
b)



c)

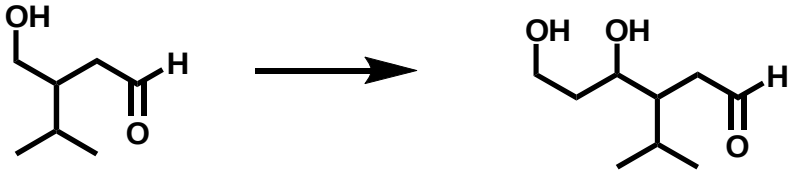


d)*

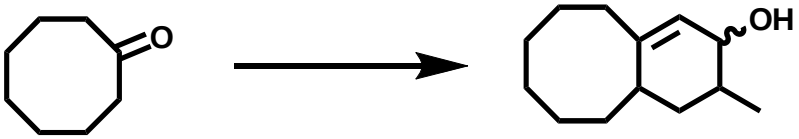


3. Show by equation how you would prepare the products illustrated below from the indicated starting material. Each requires >1 step. You may use *any* other reagents you deem to be fit. Show all reagents, conditions, and *intermediates that could be isolated.* Mechanisms are not necessary, but showing your work may be a help. ***DO ANY THREE*** **(10 each, 30 total)**

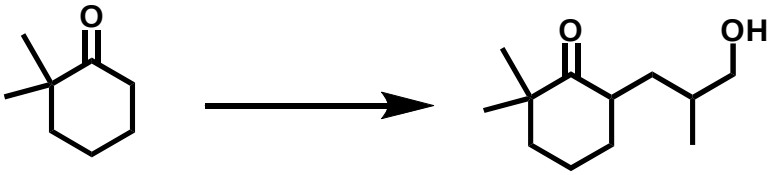
a)



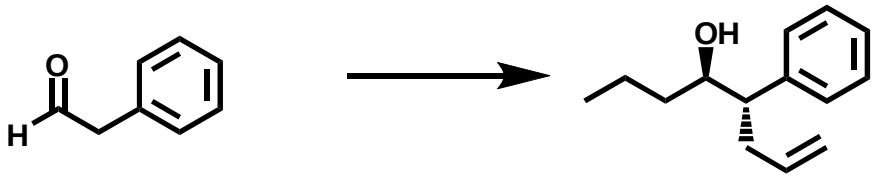
b)



c)

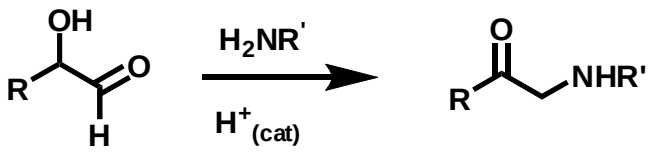


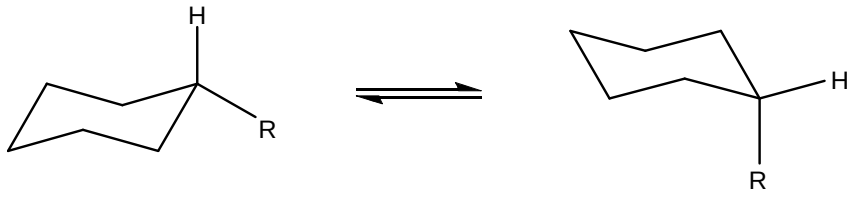
d)*



including stereochemistry -in terms of size,
Ph > CH_2-CH=CH_2

Bonus (5 marks) The Amadori rearrangement is a well-known organic chemical reaction that is seen heavily in carbohydrate chemistry. The reaction can be acid (which I'm showing) or base catalyzed, and below is the reaction stripped to its essentials. Can you give a plausible mechanism for this?





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	OH, OCH_3. OCH_2CH_3, $O\text{-}C(CH_3)_3$	0.6-0.9
$CH(CH_3)_2$	2.15 (*i*-Pr)	-C≡CR	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 (*t*-Bu)	$SiMe_3$	2.5