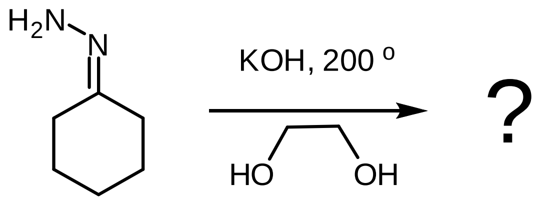
Dept. of Chemistry and Biochemistry

59-331/333 **Mar. 14, 2012**

Test #2 **Time: 55 minutes**

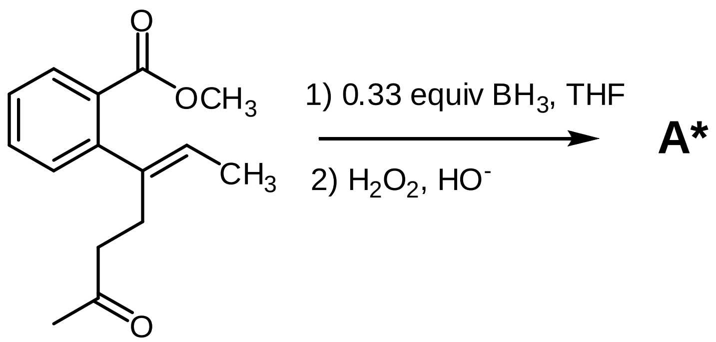
Answer all questions in the test booklet(s) provided. Show stereochemistry where relevant. Answers written in pencil will be marked, but cannot be returned for remarking.

1. Give the complete mechanism for the Wolff-Kischer reaction of the following hydrazone. (**10 marks**).

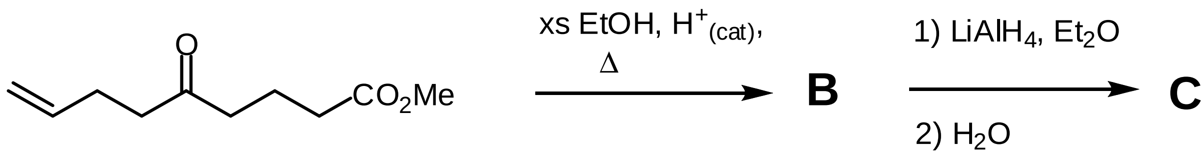


2. Indicate the structure of the expected major product from each of the following reactions. Include stereochemistry where it is relevant. Mechanisms are *not* necessary, but showing your work is likely to be a help. Cases with a * how definite stereochemical issues. (**5 for each letter, 40 marks total**)

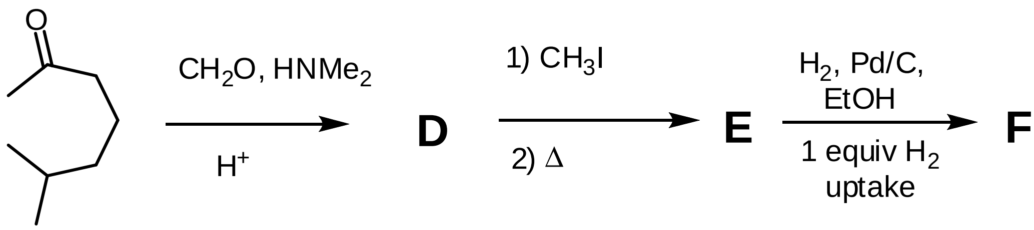
a)



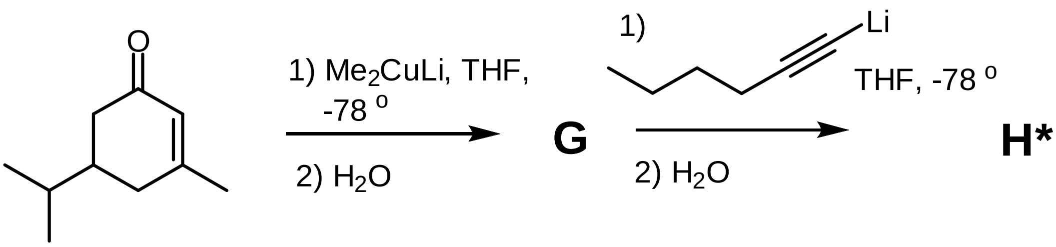
b)



c)

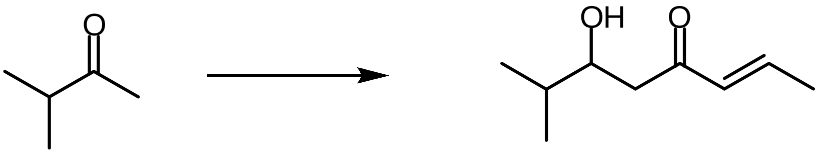


d)

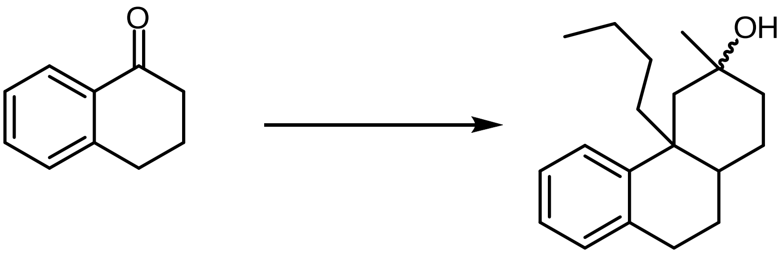


3. Show by equation how you would prepare the products illustrated below from the indicated starting material. Each requires >1 step. You may use *any* other reagents you deem to be fit. Show all reagents, conditions, and *intermediates that could be isolated.* Mechanisms are not necessary, but showing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

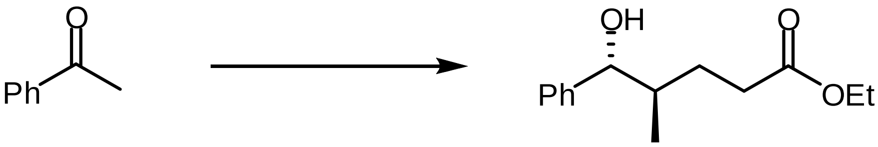
a)



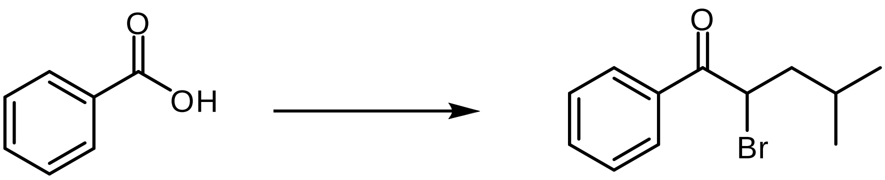
b)



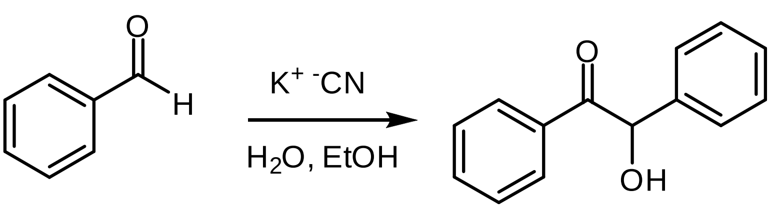
c)

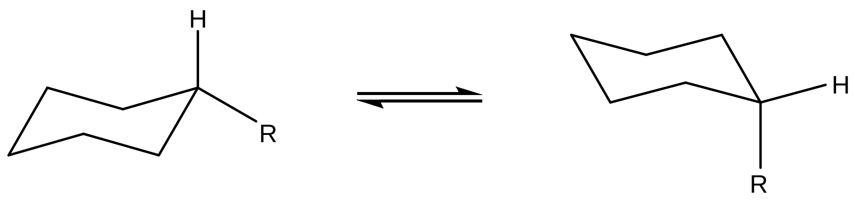


d)



Bonus (5 marks) In contrast to 1,3- and 1,5- dioxygenated compounds, 1,2-doxygenated compounds are much tougher to get access to. One way to do this, called the benzoin condensation, involves cyanide ion induced dimerization of aromatic aldehydes. It entirely uses principles that you have already seen, and *can* be catalytic. Can you propose a reasonable mechanism of this 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	OH, OCH_3. OCH_2CH_3, O-$C(CH_3)_3$	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