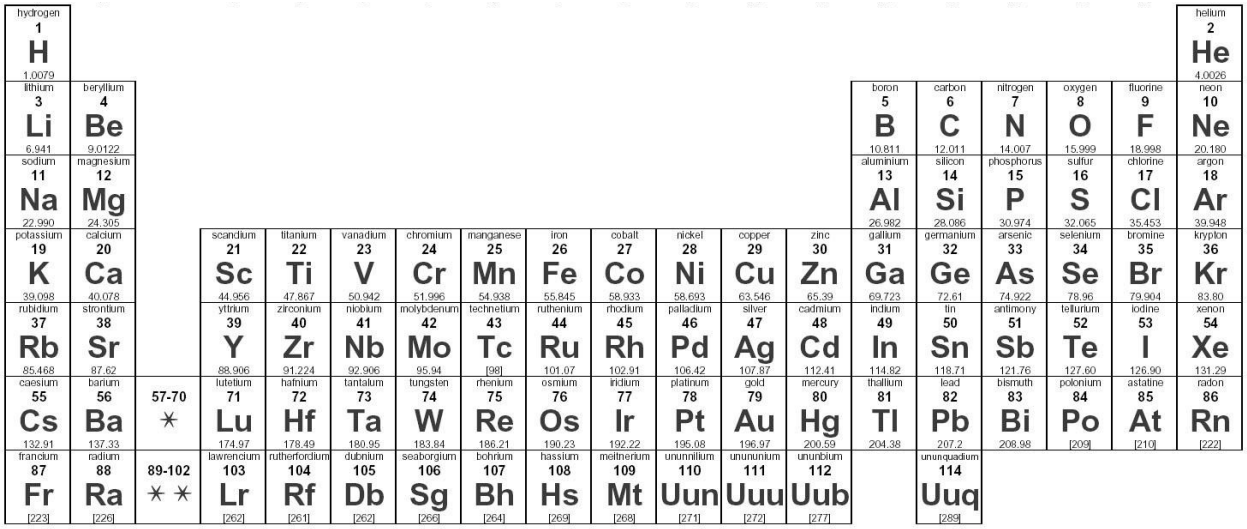
CH 335

Second Midterm Exam Thursday, February 27, 2014

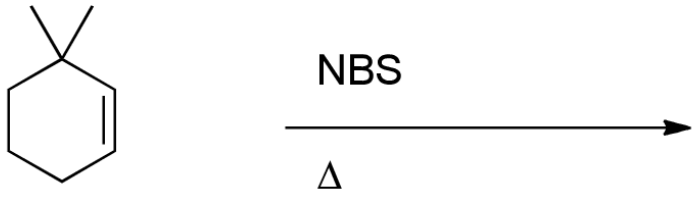
Name_____

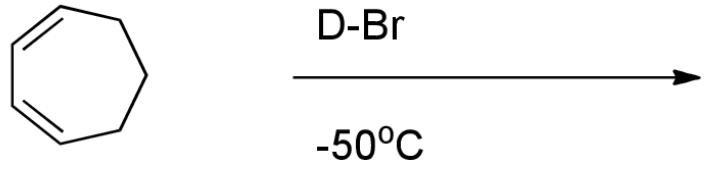
You may use model kits but no other material with chemical information without instructor approval.

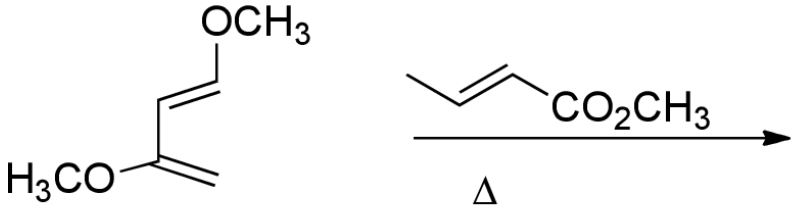
Please do not use ipods or other music players.

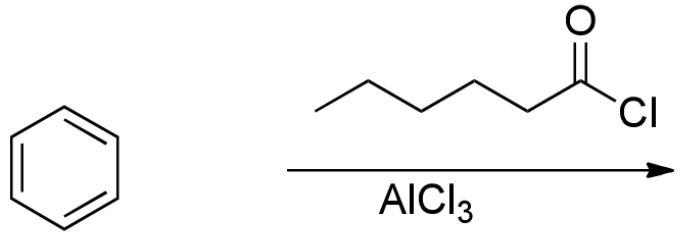


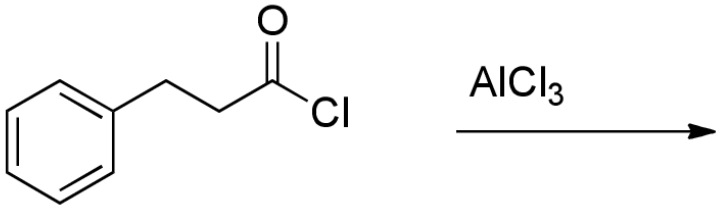
1. (30 points) Write the expected product(s) for each of the following reactions. Specify stereochemistry where appropriate, and include all expected products.

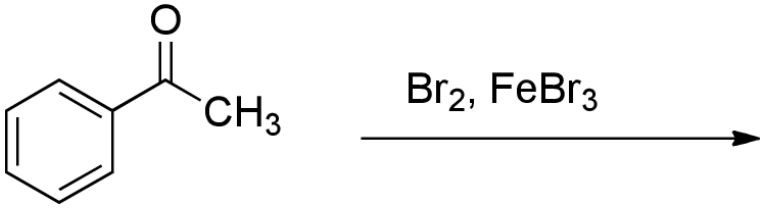
A. 

B. 

C. 

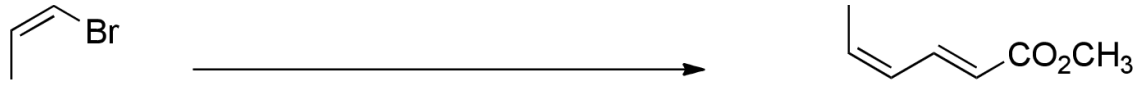
D. 

E. 

F. 

2. (25 points) Write (over the arrow) the reagents and/or conditions needed to accomplish the following transformations.

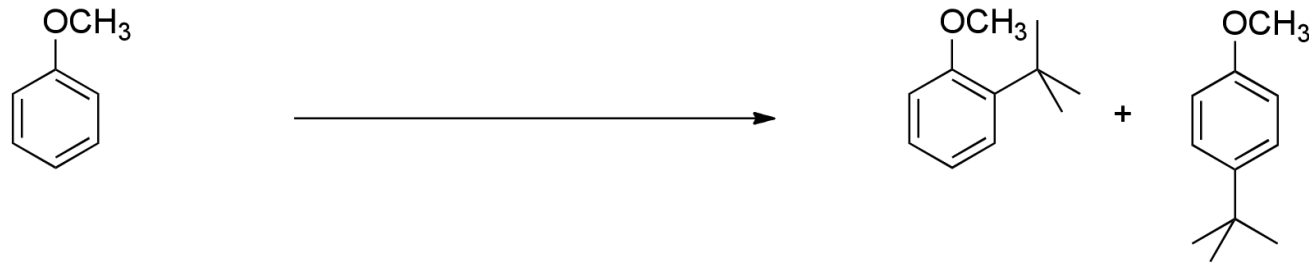
A.



B.

C.

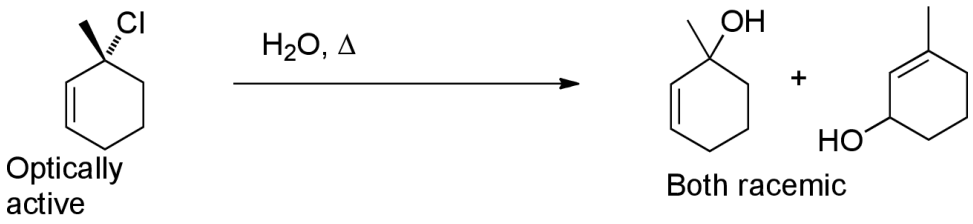
D.



E.

3. (20 points) Write multistep mechanisms (using the correct electron-pushing formalism, and as many steps as needed) for each of the following transformations. Be sure to draw resonance structures for any intermediate so stabilized.

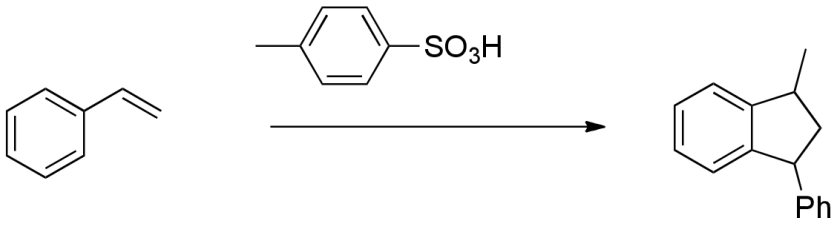
A.



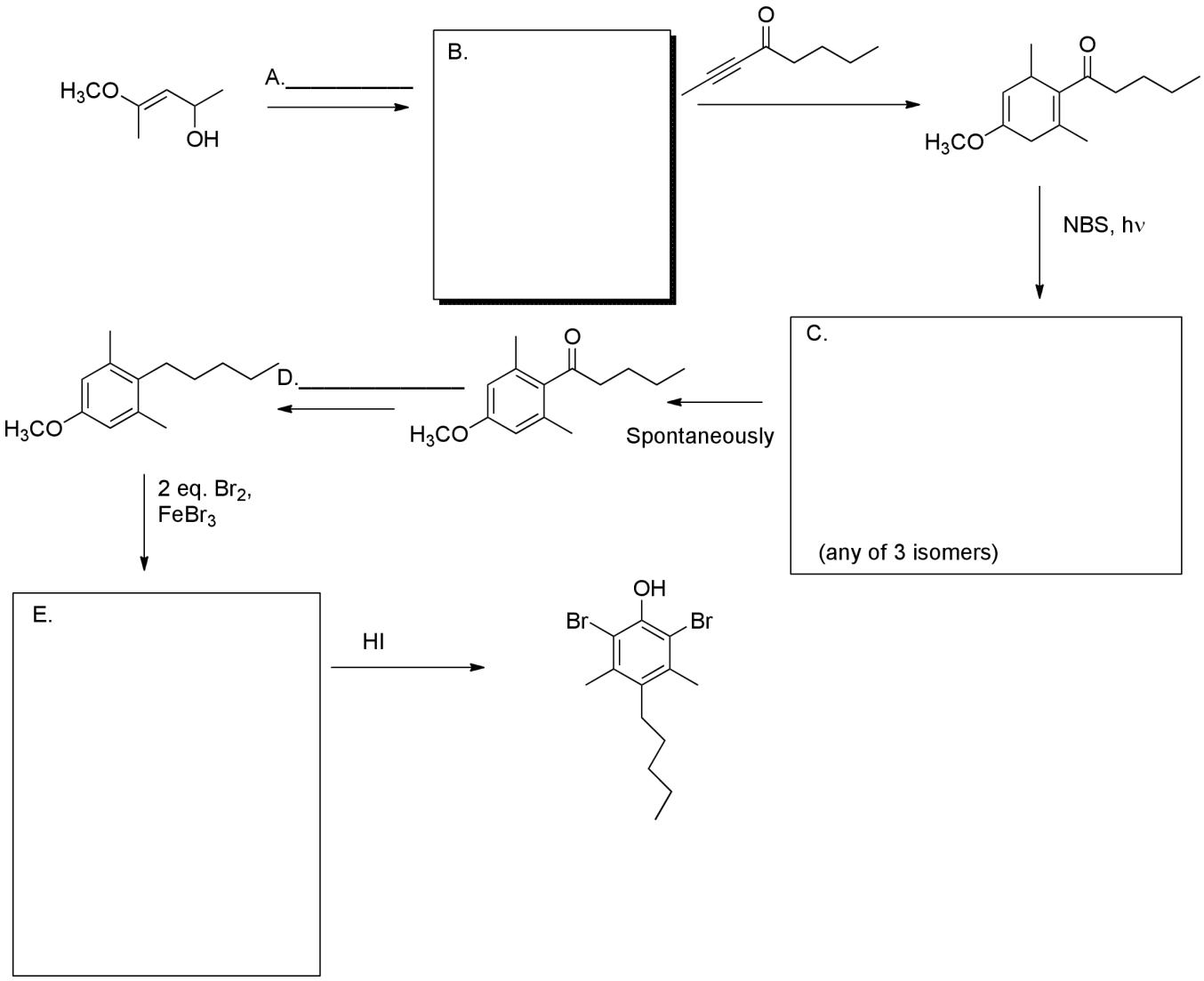
Optically active

Both racemic

B.



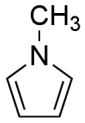
4. (15 points) Fill in the reagents or the boxed structures for A-E in the synthesis of the hexasubstituted benzene shown below.



5. (10 points) As we know, nitration of anisole is directed to the ortho and para sites. The usual conditions (HNO_3/H_2SO_4) gives a 31:2:67 mixture of ortho:meta:para nitroanisole.

A. Using the very reactive salt $NO_2^+BF4^-$ by itself in a polar solvent gives a 72:0:27 ortho:meta:para mixture at the same temperature. Explain why. (Hint: look at the intermediate(s) formed; think about reversibility in different parts of the mechanism.)

B. The nitrogen-containing 5-member ring N-methylpyrrole (shown) can be selectively nitrated with $NO_2^+BF_4^-$ to give predominantly one of two possible products. Which one would you expect to predominate and why?



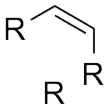
N-methylpyrrole

Bond strengths (kcal/mol):

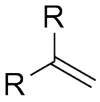
F-F	38
Cl-Cl	58
Br-Br	46
I-I	36
H-F	136
H-Cl	103
H-Br	87
H-I	71
CH_3-H	105
CH_3CH_2-H	101
$(CH_3)_2CH$-H	98.5
$(CH_3)_3C$-H	96.5
CH_3-F	110
CH_3-Cl	85
CH_3-Br	70
CH_3-I	57
CH_3CH_2-F	111
CH_3CH_2-Cl	84
CH_3CH_2-Br	70
CH_3CH_2-I	56
$(CH_3)_2CH$-F	111
$(CH_3)_2CH$-Cl	84
$(CH_3)_2CH$-Br	71
$(CH_3)_2CH$-I	56
$(CH_3)_3C$-F	110
$(CH_3)_3C$-Cl	85
$(CH_3)_3C$-Br	71
$(CH_3)_3C$-I	55

Typical Heats of Hydrogenation

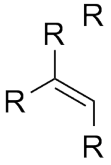
-30 kcal/mol



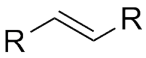
-28.2 kcal/mol



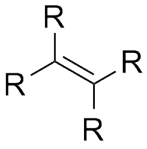
-27.9 kcal/mol



-26.5 kcal/mol



-27.4 kcal/mol



-26.3 kcal/mol