CH 335

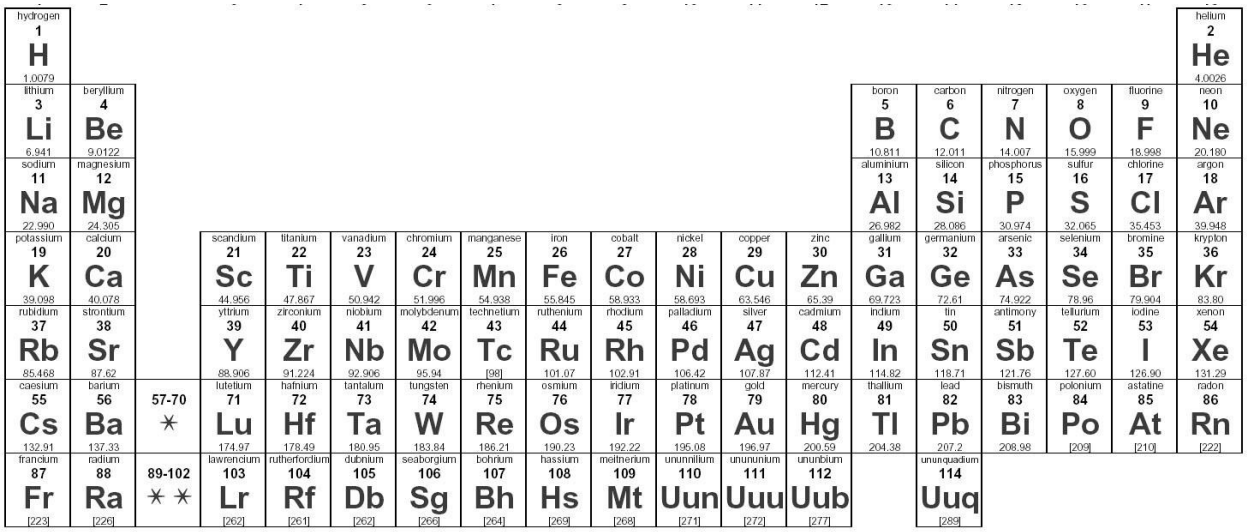
First Midterm Exam Monday, January 24, 2022

Form A

Name_____

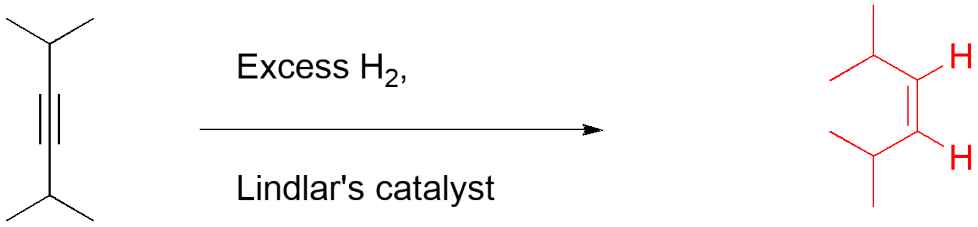
You may use model kits but no other material with chemical information without instructor approval.

Please do not use any electronic gadgets.

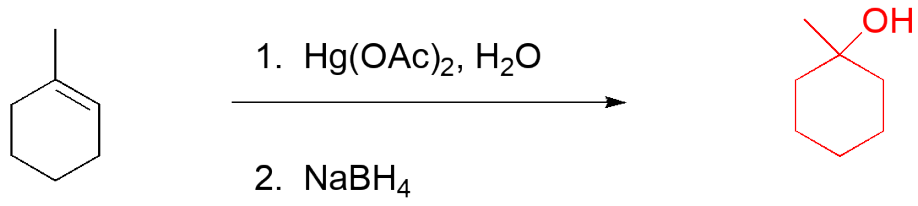


1. (30 points) Write the expected products for each of the following reactions. Specify stereochemistry where appropriate (you may write “racemic” in place of drawing a second enantiomer).

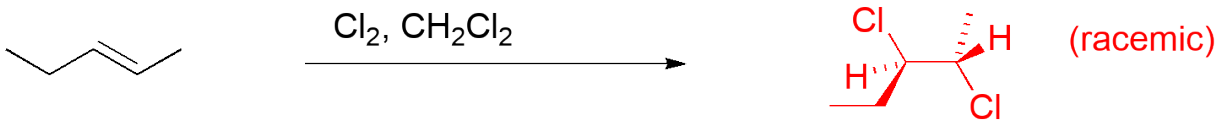
A.



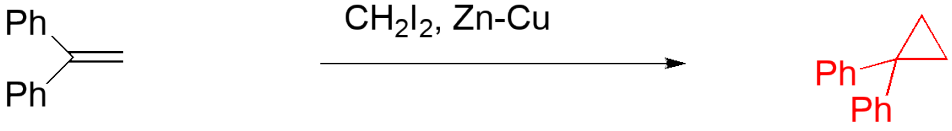
B.



C.

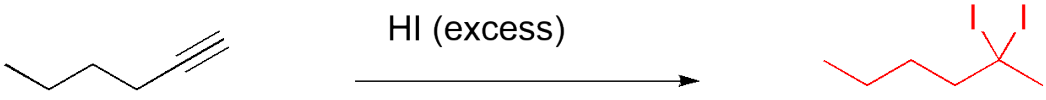


D.



E.

F.

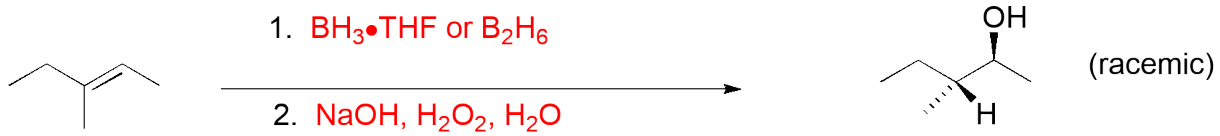


2. (25 points) Write (over the arrow) the reagents needed to accomplish the following transformations.

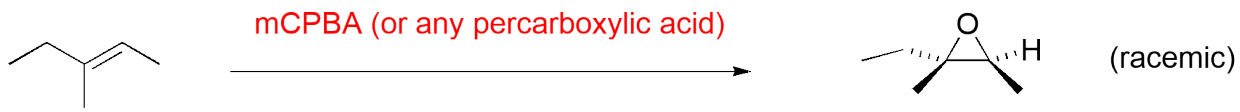
A. 

B. 

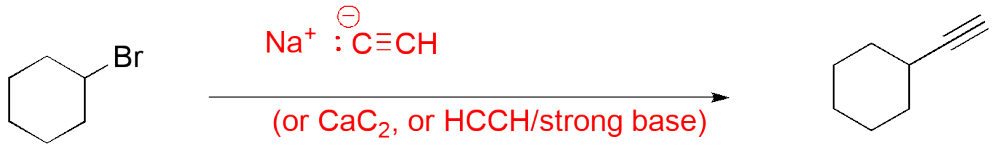
(racemic)

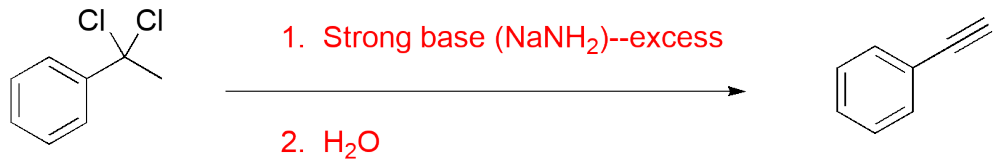
C. 

(racemic)

D. 

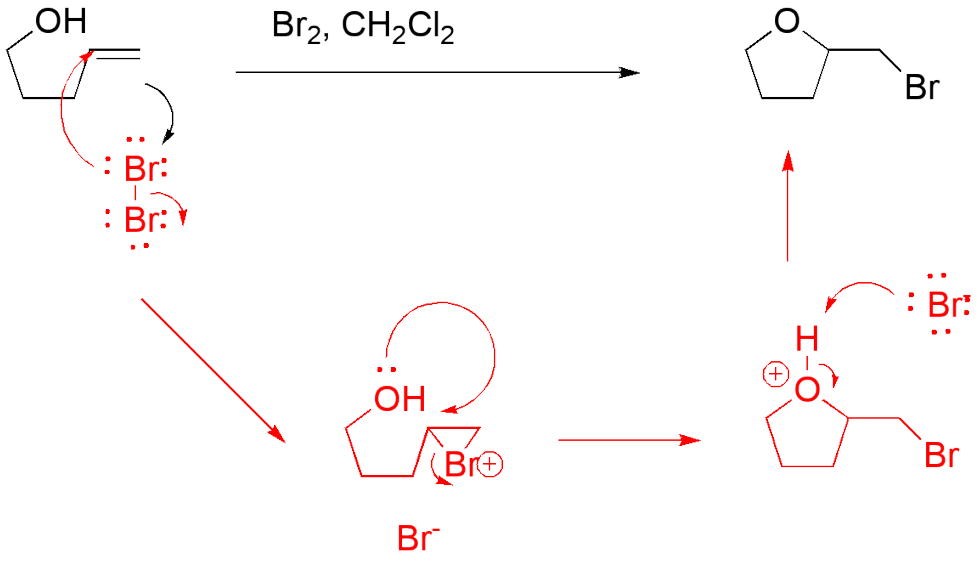
(racemic)

E. 

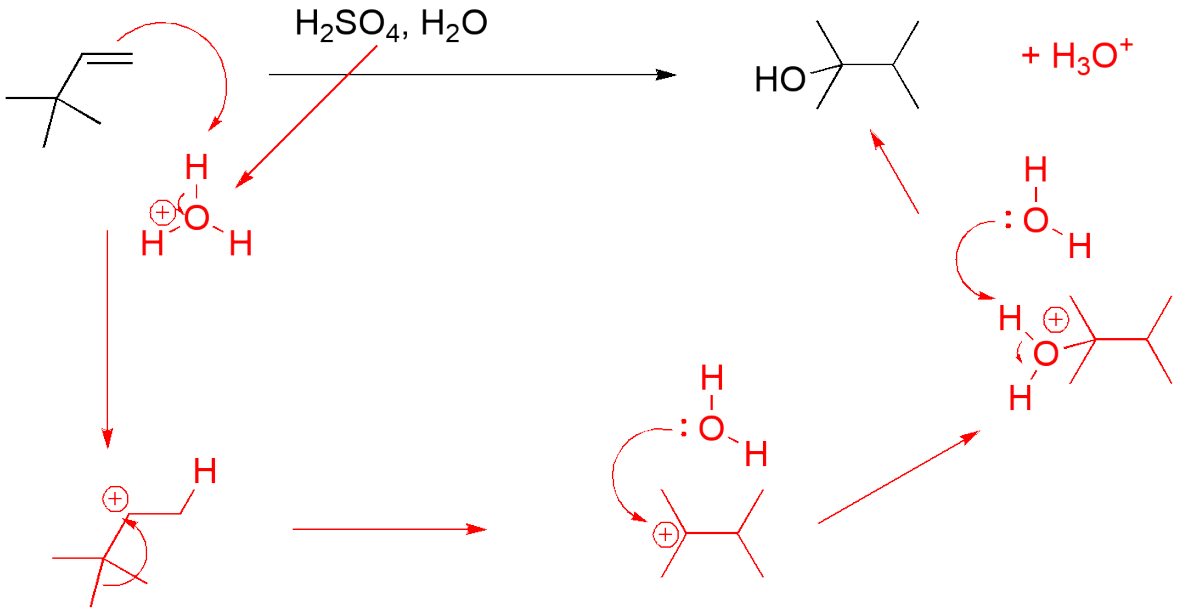
F. 

3. (20 points) Write mechanisms (using the correct electron-pushing formalism, and as many steps as needed) for each of the following transformations.

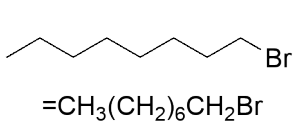
A.



B.



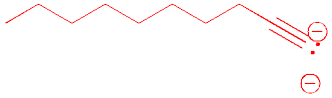
4. (16 points) Long-chain fatty alcohols are often observed to be chemical signaling agents in insect biochemistry. Fill in the boxes for intermediate structures or reagents in the following synthesis of (9S, 10R)-1,9,10-octadecanetriol. (You may abbreviate using the $(CH_2)_n$ terminology).



$=CH_3(CH_2)_6CH_2Br$

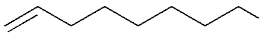
1 eq. CaC_2

A.



Without protonation by water!

$=CH_3(CH_2)_6CH_2—C\equiv C:^{\ominus}$



$= CH_2=CH-(CH_2)_5CH_2Br$

B.

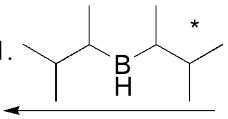
$=CH_3(CH_2)_6CH_2—C\equiv C—(CH_2)_6CH=CH_2$

C.

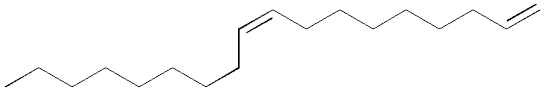
H_2, Lindlar's Catalyst
(Pd, $BaCO_3$, C)

D.

1.

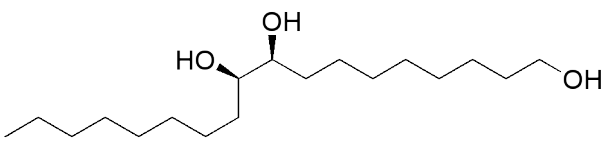


2. $NaOH$, H_2O_2, H_2O



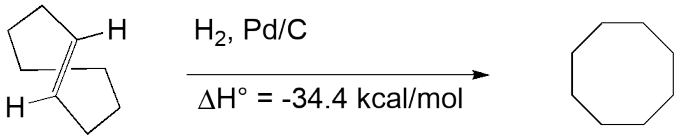
* This reagent reacts selectively with monosubstituted alkenes in the presence of more highly substututed alkenes

1. OsO_4
2. $NaHSO_3$

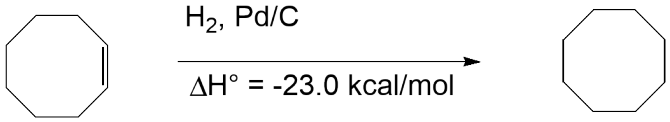


5. (9 points) The heat of hydrogenation for *trans*-cyclooctene, shown at the right) is -34.4 kcal/mol.

Explain why this is different from that for *cis*-cyclooctene (-23.0 kcal/mol).



Trans cyclooctene is a strained alkene. Placing the trans double bond in a ring imposes a force that slightly twists the C=C bond, decreasing the overlap between p orbitals and weakening the pi bond. Numerically, this effect is worth 11.4 kcal/mol.



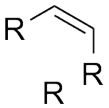
(A secondary observation, not necessary to answer what was asked, is that cis cyclooctene gives a much lower than expected heat of hydrogenation. This is due to ring strain arising mostly from torsional eclipsing interactions in cyclooctane.)

Bond strengths (kcal/mol):

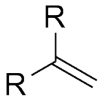
F-F	38
Cl-Cl	58
Br-Br	46
I-I	36
H-F	136
H-Cl	103
H-Br	87
H-I	71
CH_3-H	105
CH_3CH_2-H	101
$(CH_3)_2CH$-H	98.5
$(CH_3)_3C$-H	96.5
CH_3-F	110
CH_3-Cl	85
CH_3-Br	70
CH_3-I	57
CH_3CH_2-F	111
CH_3CH_2-Cl	84
CH_3CH_2-Br	70
CH_3CH_2-I	56
$(CH_3)_2CH$-F	111
$(CH_3)_2CH$-Cl	84
$(CH_3)_2CH$-Br	71
$(CH_3)_2CH$-I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

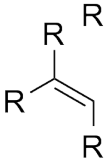
-30 kcal/mol



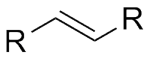
-28.2 kcal/mol



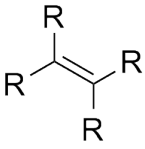
-27.9 kcal/mol



-26.5 kcal/mol



-27.4 kcal/mol



-26.3 kcal/mol