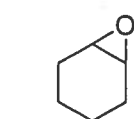
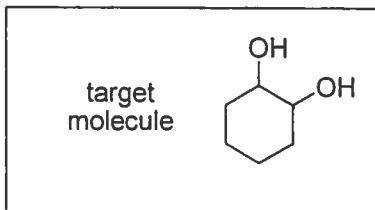


Key - Summer 2012
Exam 1

1. Which of the following compounds could be used to make this target in one step (including any necessary workup)?

D



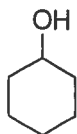
+ H_3O^+ or OH^-

A



+
 OsO_4
TBHP
 H_2O

B



can't do
in one step

C

Either
A or B

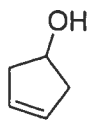
A, B or C

D

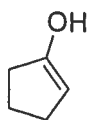
E

2. Select the enol from the structures shown.

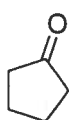
B



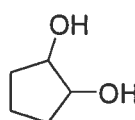
A



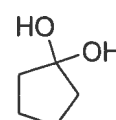
B



C



D



E

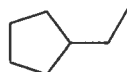
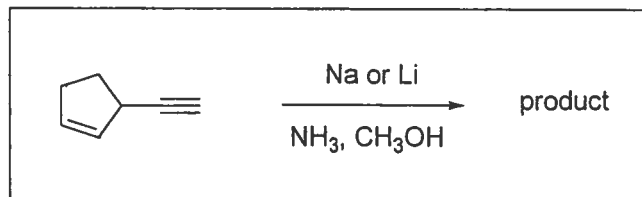
3. Which of these hydride sources is non-nucleophilic?

C

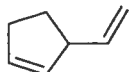
- a. NaBH_4
- b. LAH
- c.** NaH
- d. All are nucleophilic
- e. All are non-nucleophilic

4. Which of these structures is the product of the reaction?

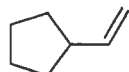
B



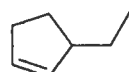
A



B



C



D

None of these is the product

E

5. You wish to make an epoxide from an alkene, but you have no mCPBA. However, you do have access to all the reagents listed below, plus all the materials necessary for appropriate aqueous workups. Can you make the epoxide?

B

Reagents available:

NaOCH₃/CH₃OH

LDA

NaH

NaOH(aq)

H₂O

Hg(OAc)₂

OsO₄

TBHP

HIO₄

NaNH₂

O₃

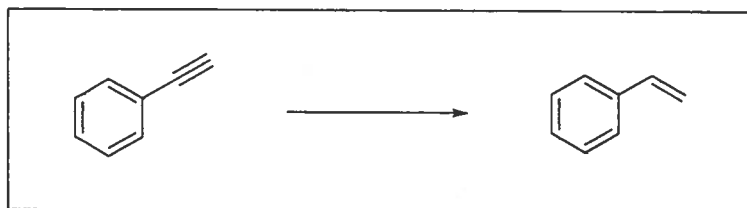
H₂O₂

a. Yes! I can make the epoxide using some or all of the reagents above.

b. No! An epoxide cannot be made from an alkene with the reagents shown above. *you would need Br₂/H₂O, then NaH*

6. What are the best conditions to use to accomplish this transformation?

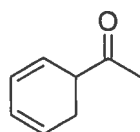
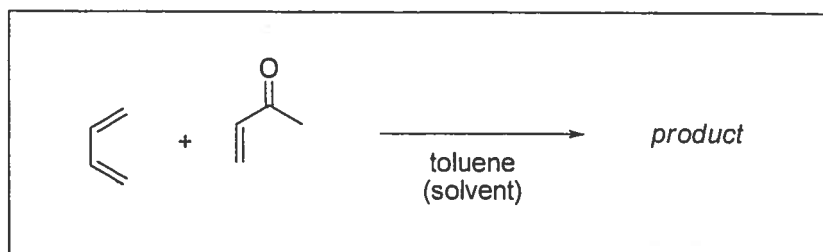
A



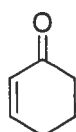
- a. H₂ and Lindlar's catalyst
b. Na, NH₃ → *will react with benzene too*
c. H₂ and Pd/C
d. Either a or b
e. a, b or c would all work

7. Which is the correct product of this reaction?

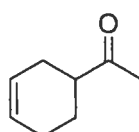
C



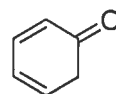
A



B



C



D

None of these is the product

E

8. Select the reagent you would use to accomplish the following transformation.

A



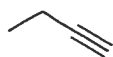
- a. LAH, then H_3O^+ workup
- b. $\text{NaOH}(\text{aq})$
- c. H_3O^+
- d. NaH , then H_3O^+ workup
- e. This transformation cannot be accomplished in one step.

9. Which of these is the *most* acidic hydrocarbon?

B



A



B



C



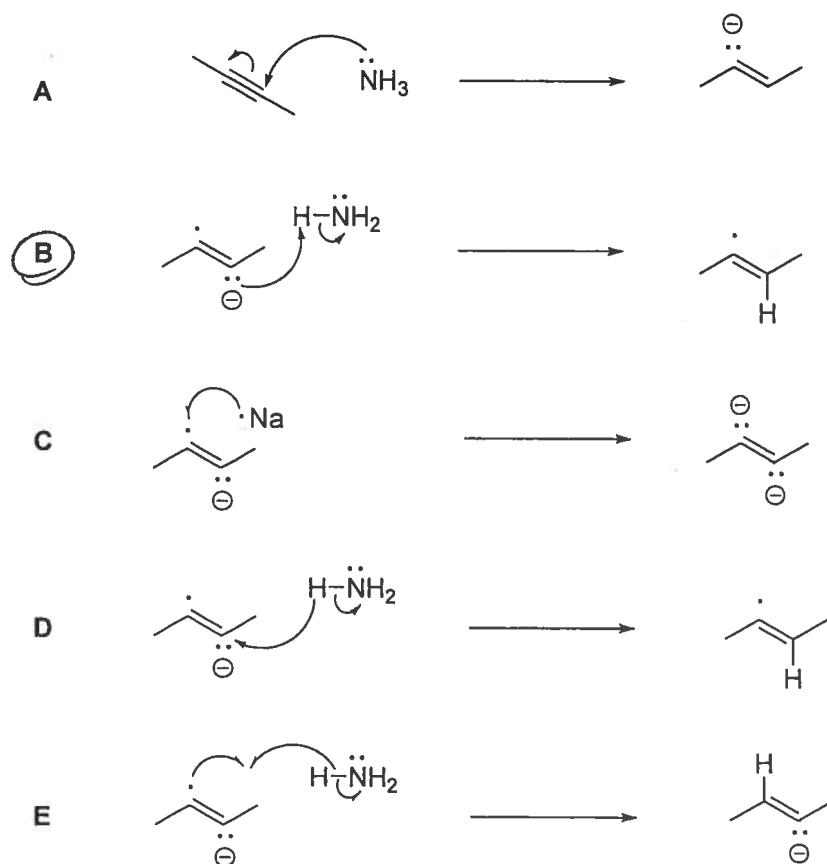
D

All are equally acidic

E

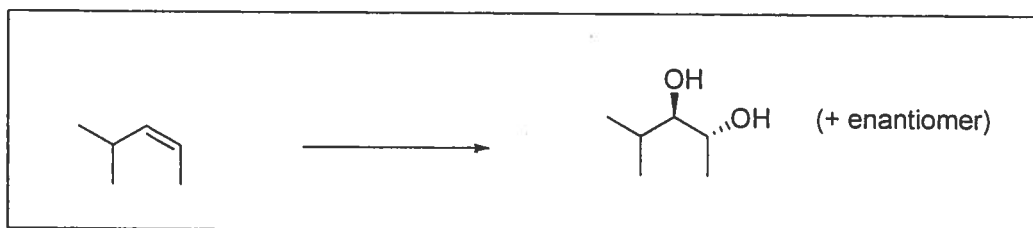
10. Which of the following is a mechanistic step in the dissolving metal reduction of an alkyne with sodium metal in liquid ammonia as the solvent?

B



11. What conditions could be used to accomplish this transformation?

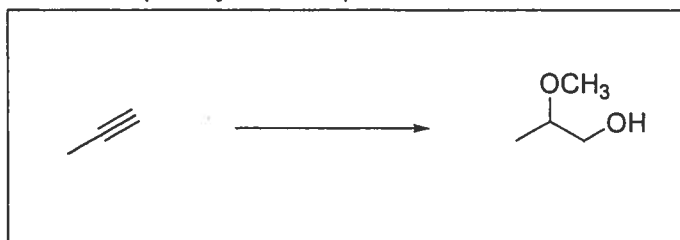
A



- a. mCPBA, then H_3O^+ - cleaves diol
 b. HIO_4 (periodic acid) - cleaves diol
 c. OsO_4 , TBHP, and H_2O - syn diol
 d. $\text{Hg}(\text{OAc})_2$, H_2O ; then NaBH_4 - Markovnikov alcohol
 e. None of these conditions would work

12. Which of the following synthetic sequences produces the target molecule from the starting material? (Assume appropriate aqueous workups for all steps even if not explicitly written.)

D



- a. 1. H_2, Pd — reduces alkyne to alkane
 2. mCPBA
 3. CH_3OH, H_2SO_4

- b. 1. Na, NH_3
 2. mCPBA
 3. $NaOCH_3, CH_3OH$, then H_3O^+

this would make

- c. 1. $H_2/Lindlar$ catalyst
 2. mCPBA
 3. $NaOH, H_2O$, then H_3O^+

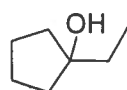
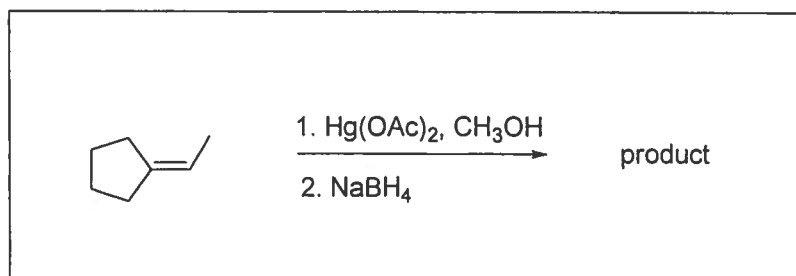
this would make

- ✓ (d). 1. $H_2/Lindlar$ catalyst
 2. mCPBA
 3. CH_3OH, H_2SO_4

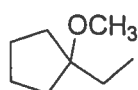
- e. None of these syntheses will produce the target molecule

13. What is the major product of this reaction?

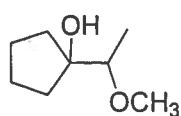
B



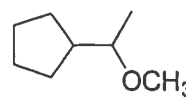
A



(B)



C



D

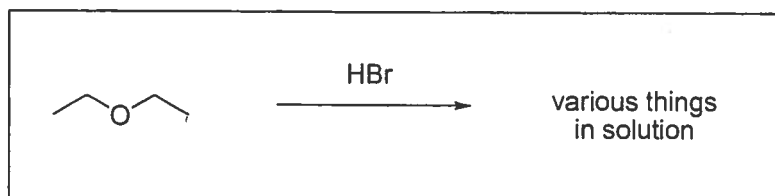
None of these is the major product

E

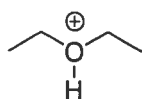
alkoxymercuration-reduction

14. When a small amount of HBr is added to diethyl ether, there are various species present in solution. Which of the structures shown would you NOT expect to find in this solution?

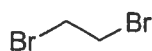
B



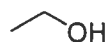
see last page



A



B



C



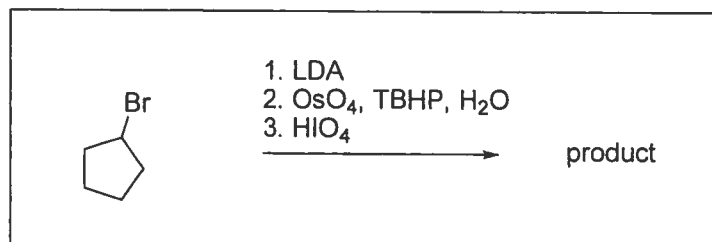
D



E

15. Which statement about the final product of the sequence of reactions shown is *true*?

C



see below

- The product contains at least one ketone
- The product contains at least one OH group
- C** The product contains at least one aldehyde
- The product contains an epoxide
- The product contains an alkene

16. Which of these C₅H₈ dienes is least stable?

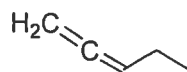
C



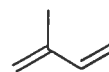
A



B



C

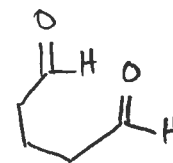
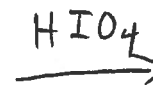
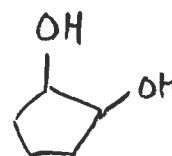
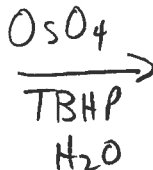
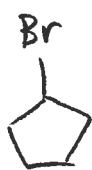


D

All are equally stable

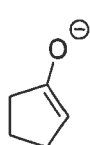
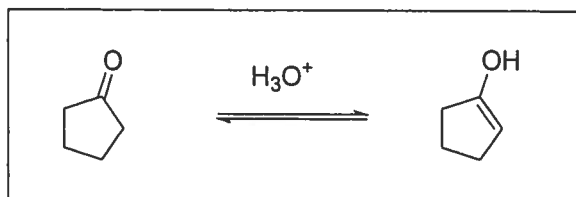
E

15

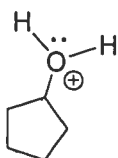


17. In aqueous acid, carbonyls are in equilibrium with their enol forms through a process called keto-enol tautomerization. In the example below, a ketone is placed in aqueous acid and allowed to come to equilibrium with its enol form. Which of these intermediates is observed in the tautomerization mechanism shown in class?

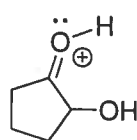
E



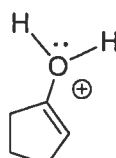
A



B



C



D

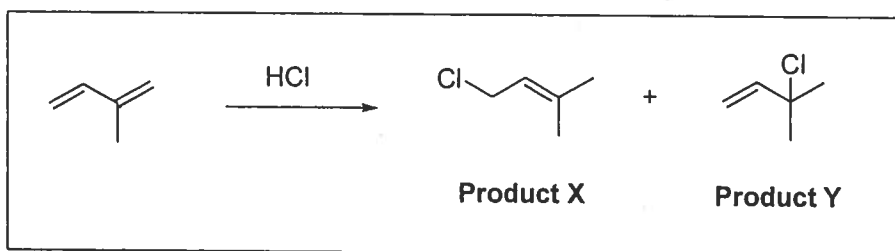
None of these intermediates is observed in the mechanism

E

See below

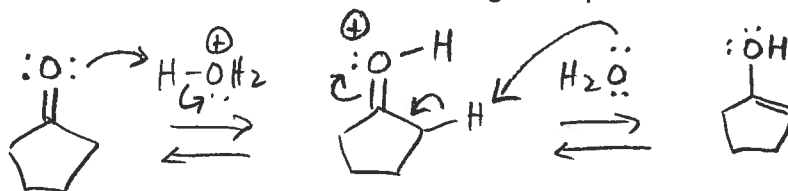
18. Which of the following statements is true about this reaction? (Note that if any part of a statement is not true, then you should reject the entire statement.)

B

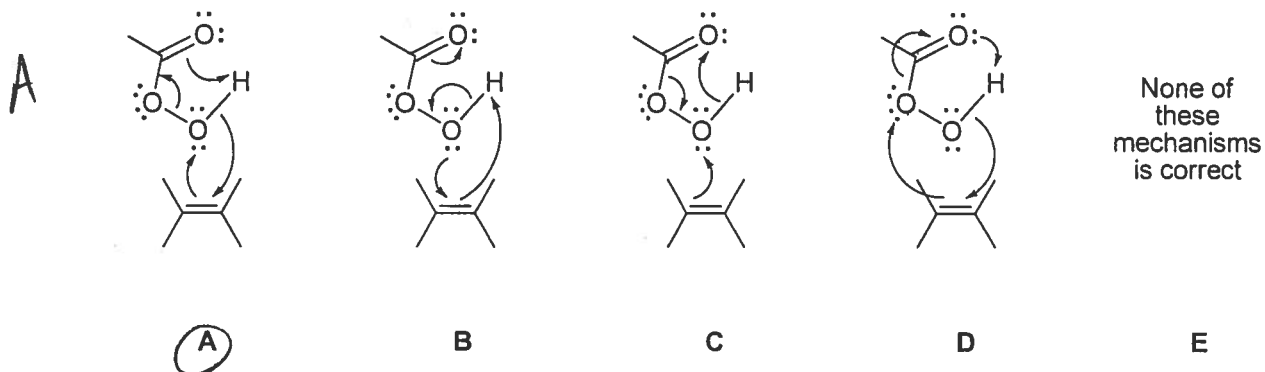


- a. Product X is the thermodynamic product and could be formed using short reaction times and low temperatures.
- b.** Product X is the thermodynamic product and could be formed using long reaction times and high temperatures.
- c. Product Y is the thermodynamic product and could be formed using short reaction times and low temperatures.
- d. Product Y is the thermodynamic product and could be formed using long reaction times and high temperatures.

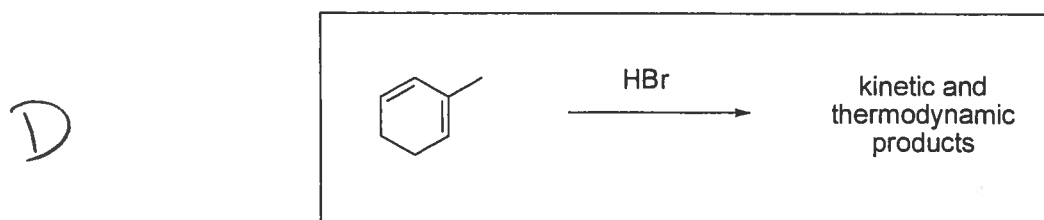
17



19. Which of these mechanisms is the correct depiction of the reaction of a peroxydicarboxylic acid (such as mCPBA or peracetic acid) with an alkene?



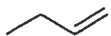

20. Consider this reaction:



Both kinetic and thermodynamic products can be formed in this reaction, depending on the conditions used. Which of these statements about this reaction is incorrect?

- T a. The kinetic product forms fastest because the nucleophile is close to the new carbocation that forms when the diene is protonated.
- T b. To form the thermodynamic product, the reaction mixture needs time to equilibrate.
- T c. The thermodynamic product is more stable than the kinetic product.
- F d. The path leading to the thermodynamic product has a lower activation energy than the path leading to the kinetic product.
- T e. Both the kinetic product and the thermodynamic product share a common intermediate, which is a carbocation.

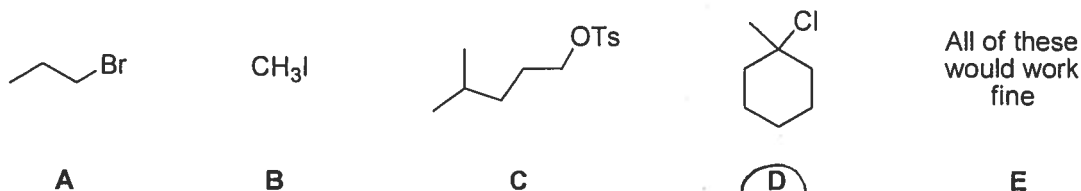
21. Given the following information, what is the resonance energy for 1,3-butadiene? (The heats of hydrogenation in this table are experimentally determined.)

Compound	$ \Delta H_{\text{hydrogenation}} $ (kcal/mol)
1-butene 	30
1,3-butadiene 	56.6

C

- a. $56.6 - 30$
 b. $56.6 + 30$
 c. $60 - 56.6$
 d. $60 - (30 + 56.6)$
 e. $56.6 + 60$
22. Acetylide ions can be alkylated by treating them with a variety of electrophiles. One of these compounds would not be appropriate for an alkylation reaction with an acetylide ion. Which is it?

D



too hindered - E2 would predominate

23. One version of the Lindlar catalyst includes Pd, CaCO₃ or BaSO₄, a lead(II) (Pb²⁺) salt such as Pb(OAc)₂, and a compound called quinoline. The Lindlar catalyst is called a "poisoned" catalyst. What is a poisoned catalyst?

B

- a. It is a catalyst that has no effect on the reaction it is supposed to catalyze
 b. It is a catalyst that is less effective than a catalyst that is not poisoned
 c. It is a catalyst that accelerates the rate of the forward reaction, but slows the rate of the reverse reaction so that you get more product
 d. It is a deadly, evil catalyst that goes around poisoning people

24. Which of the following reagents would you use to make a quantitative yield of an alkoxide ion from an alcohol?

B

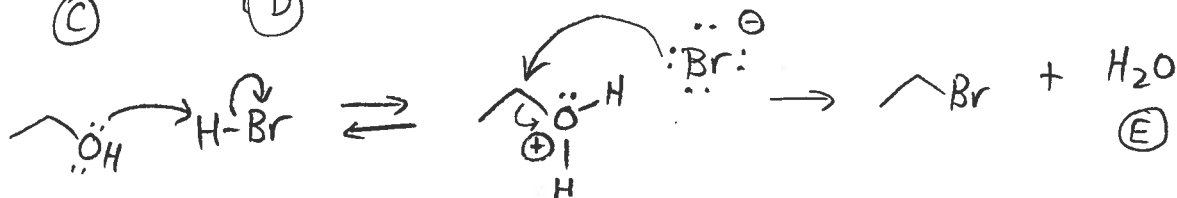
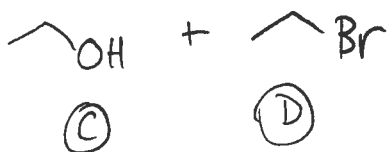
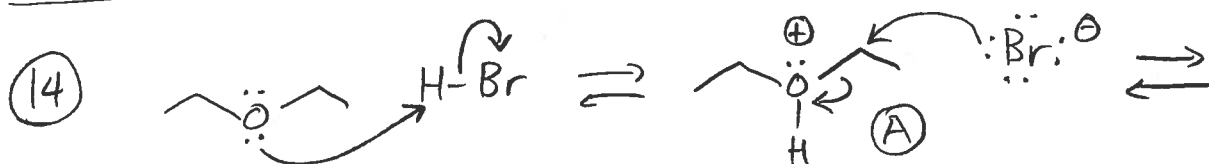
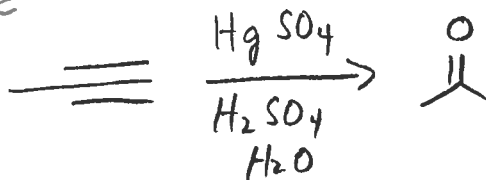
- a. H_2 (with or without a metal catalyst)
- b. NaH**
- c. NaOH
- d. Any alkoxide ion
- e. None of the above

25. It's official -- Kim Kardashian and Kanye West are a couple! Even better, they're going to open a new business called "Kim 'n' Kanye's Ketone Korner". They want to produce ketones using alkynes as the starting material. Which of the following reagents should they order to make their ketones?

C

- a. Catechol borane, hydrogen peroxide, and aqueous NaOH
- b. Disiamylborane, hydrogen peroxide, and aqueous NaOH
- c. Mercury (II) sulfate, sulfuric acid, water**
- d. Periodic acid, hydrogen peroxide, and water
- e. The business will fail. Ketones cannot be produced from alkynes.

A and B also acceptable since the alkyne wasn't specified as terminal.



can't make $\text{Br}-\text{C}_2\text{H}_5-\text{Br}$ - there is only one carbon that is electrophilic (i.e. has something attached that can function as a leaving group under the conditions)