CHEM 3331 **Exam #2** **Name** Key
Dr. Minger **July 27, 2015**

Please read and sign the Honor Code statement below:

I pledge that on my honor, as a University of Colorado at Boulder student, I have neither given nor received unauthorized assistance on this exam.

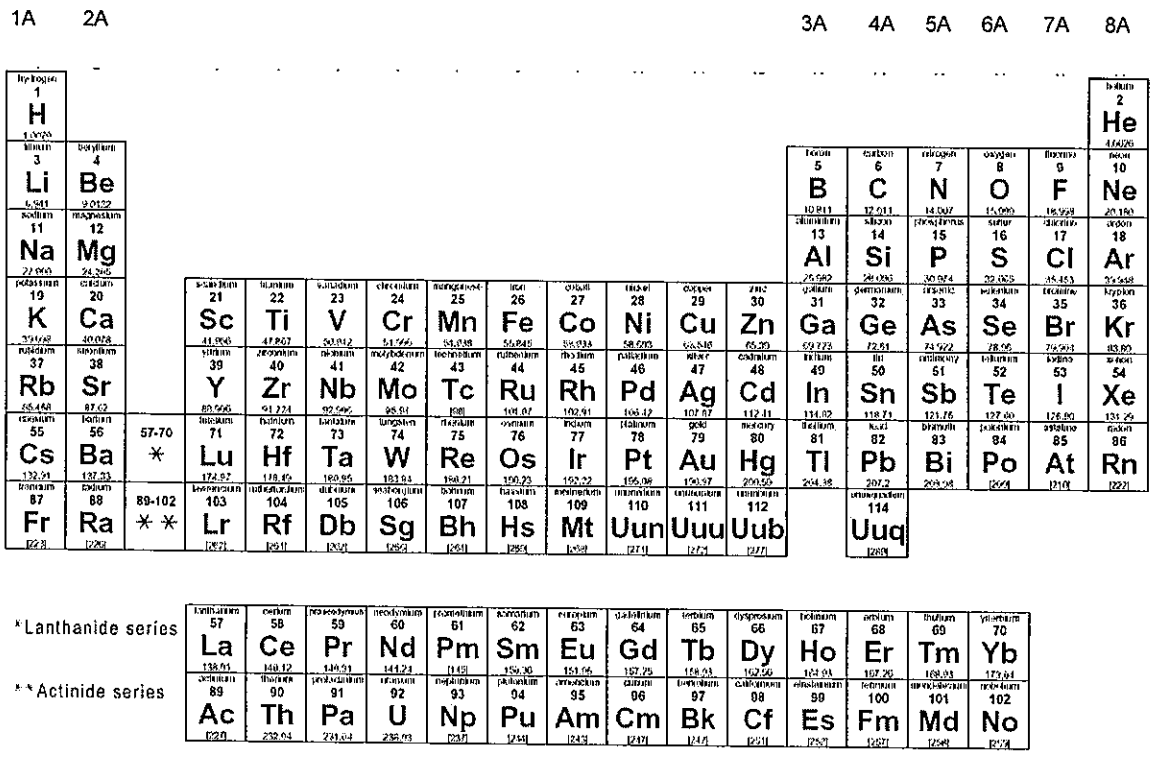
_____
Signature

General Instructions: There are 25 questions. Be sure you have them all. Read each question carefully so that you know exactly what is being asked.

Each multiple choice question (1-25) is worth **4 points and has only one correct answer.** Bubble in your answers to these questions on the Scantron provided. **Only the Scantron will be graded, not anything that you write on the exam.**

At the end of the exam, turn in your Scantron and this signed cover sheet. You may keep the rest of the exam to check your answers against the key later. Grades will be uploaded to D2L.

Good luck!

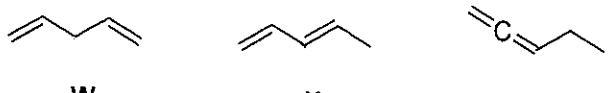


1. The description "1,3" refers to

D

~~a.~~ Conjugate addition 1,4
~~b.~~ Direct addition 1,2
~~c.~~ Electrophilic addition of HBr to a diene 1,2 or 1,4
✓d. A minor or unobserved product of a Diels Alder reaction
~~e.~~ All of the above

2. Place the three dienes in order of *decreasing* $\Delta H_{hydrogenation}$ (largest ΔH to smallest ΔH).



W X Y

C

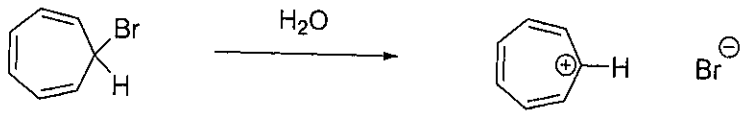
Most Stable - Smallest ΔH_{hydrog}

Least stable - largest ΔH_{hydrog}

Y > W > X

a. W > X > Y
b. Y > X > W
(c.) Y > W > X
d. X > W > Y
e. W > Y > X

3. 7-Bromo-1,3,5-cycloheptatriene dissolves rapidly in water, ionizing to form an ion pair: the tropylium ion and a bromide ion:



7-bromo-1,3,5-cycloheptatriene Tropylium ion

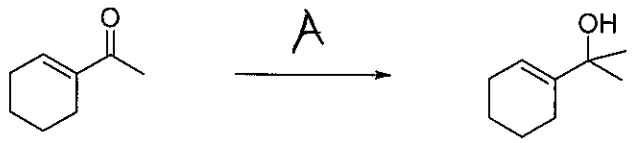
E

The tropylium ion forms much more rapidly than most carbocations. According to the Hammond postulate, the transition state for the tropylium ion is stabilized by the same factors that stabilize the ion itself. What is the <u>best</u> explanation for the stability of the tropylium ion?

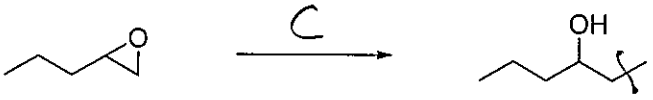
a. The tropylium ion contains conjugation. True but not best explanation
b. The tropylium ion is an allylic carbocation. " "
c. The tropylium ion is antiaromatic. False
d. The tropylium ion is benzylic. False
(e.) The tropylium ion is aromatic.

For questions 4 through 8, select the best reagent from the list to accomplish the transformation. Assume that there is an aqueous acid workup (H_3O^+) following the use of each reagent. Choices may be used once, more than once, or not at all.

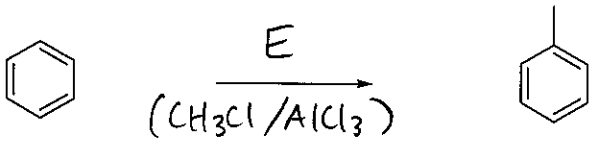
a. MeLi
b. MeMgBr
c. Me_2CuLi
d. Any of these reagents could accomplish the transformation
e. None of these reagents could accomplish the transformation

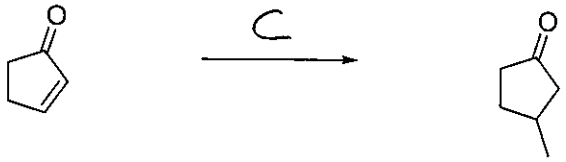
4. 

MeMgBr gives mixtures of products when reacted with enones

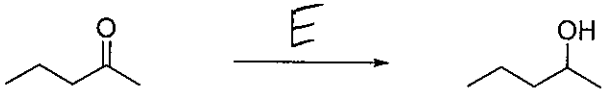
5. 

Epoxide opening

6. 

7. 

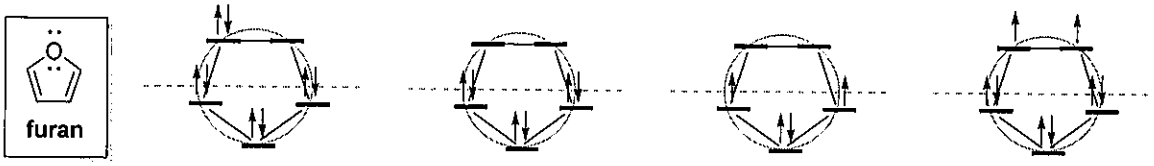
Conjugate addition

8. 

reduction - would need LAH or $NaBH_4$

9. Which of these drawings is the correct Frost circle for furan?

B

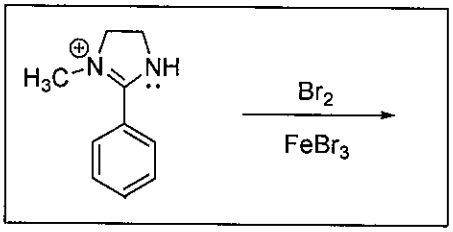


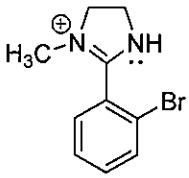
A (B) C D

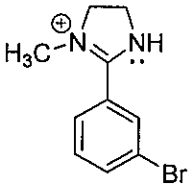
10. Select the major product of this reaction.

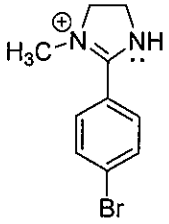
B

meta director, deactivating









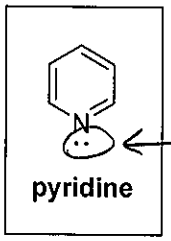
Both A and C

None of these products

A (B) C D E

11. How many electrons are in the π system in pyridine?

C

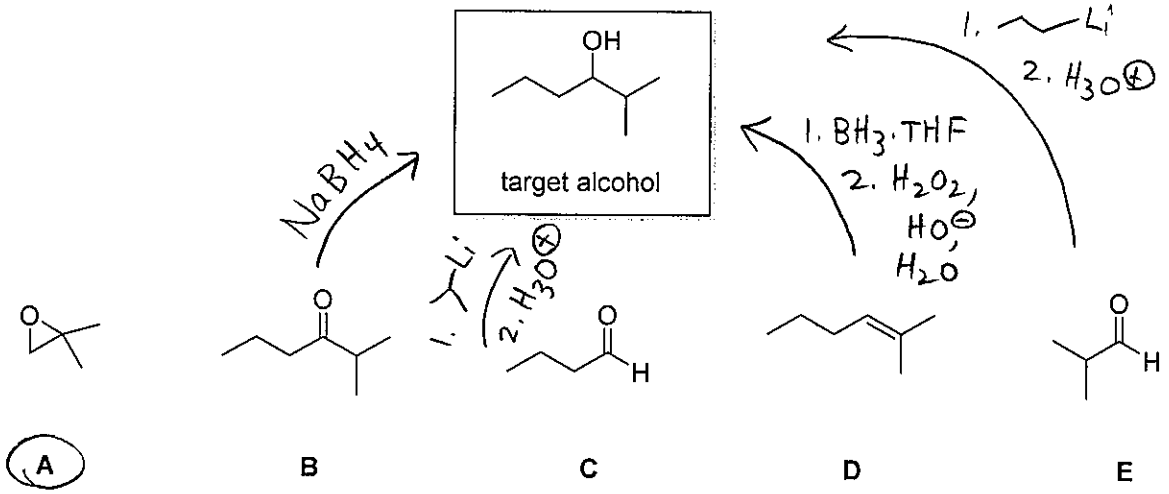


in an sp^2

a. 2
b. 4
(c.) 6
d. 8
e. None of these

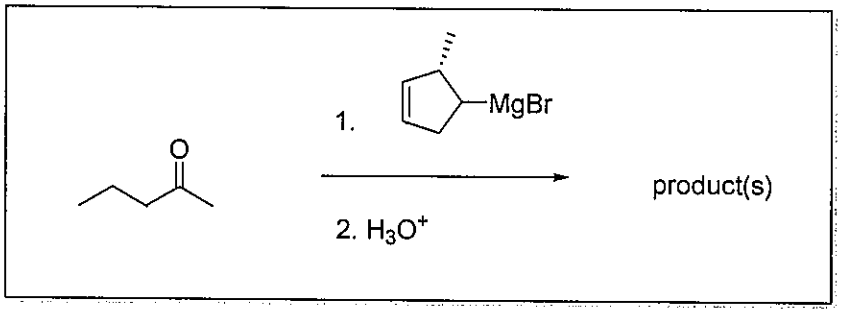
12. From which of the following structures can the target alcohol *not* be made in one synthetic operation, including aqueous workup?

A



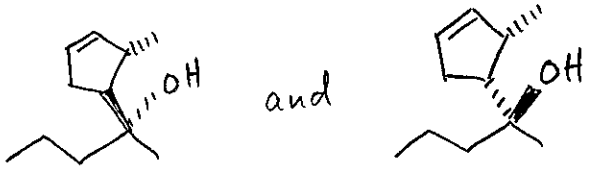
13. A ketone is treated with a chiral Grignard reagent as shown in the reaction in the box. Select the phrase that best describes the product(s) of the reaction.

D



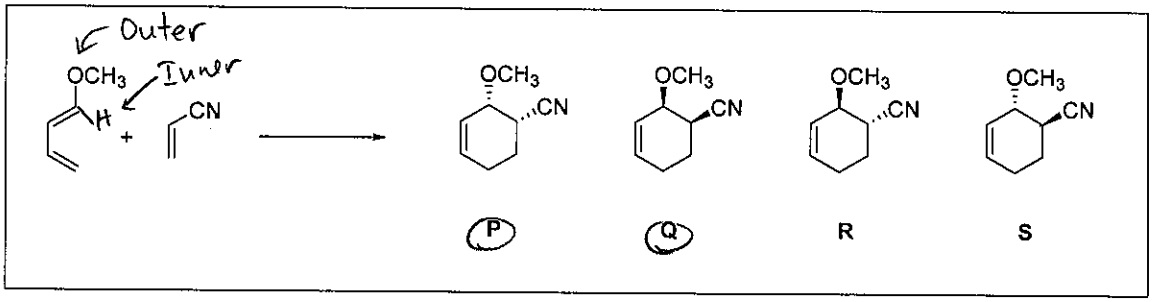
Since there is optical activity in the starting materials, we expect optical activity in the product(s).

a. A single achiral molecule
b. A single chiral molecule
c. Racemic mixture (enantiomers in equal amounts)
(d.) Diastereomers in unequal amounts
e. Diastereomers in equal amounts



14. A Diels Alder reaction yields the products shown:

A

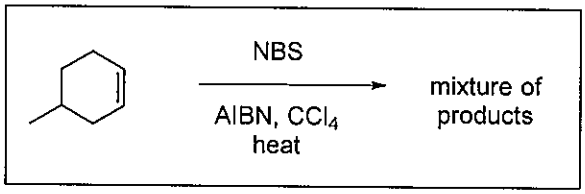


Which of these are endo products? Endo = Dienophile group is cis to outer substituent of diene

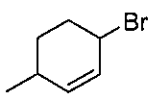
a. P and Q
b. P and R
c. Q and S
d. Q and R
e. R and S

15. Which of the compounds shown would not be expected to form under the reaction conditions?

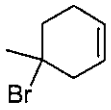
B



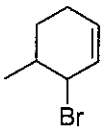
See over →



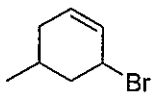
A



B



C



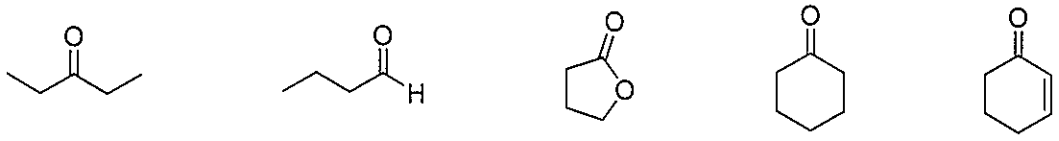
D

All these products would form

E

16. Which of these compounds will react fastest with methyllithium in diethyl ether solvent?

B

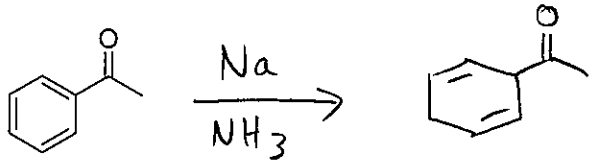


A B C D E

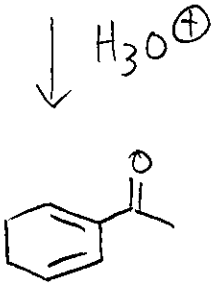
Aldehydes are more electrophilic than ketones or esters

17. In the 1959 horror classic *House on Haunted Hill*, a skeleton pushes a woman into a vat of aqueous acid consisting of water and sulfuric acid. In her right hand, the woman is clutching a vial that contains the product of the Birch reduction of this compound:

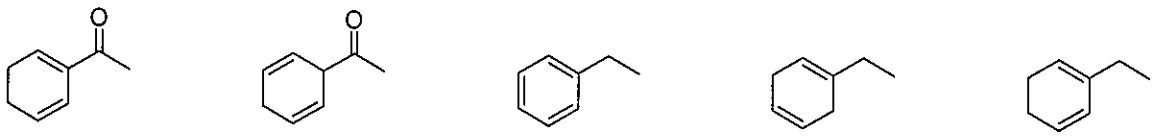
A



Contents of vial



After several minutes of evil cackling, the skeleton takes a sample of the solution in the vat and returns to its laboratory, where it extracts the aqueous solution and isolates an organic compound. Which of the following compounds does the skeleton isolate?



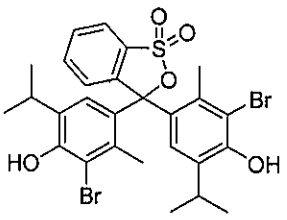
(A) B C D E

18. Bromothymol sulfone phthalein (also known as "BTB") is an acid-base indicator that is commonly used to test the pH of swimming pools and fish tanks. In acidic solution, its maximum absorbance (λ_{max}) is around 427 nm, and in basic solution its λ_{max} is 602 nm. The skeleton in question 17 puts on its goggles and adds some BTB to the vat of aqueous acid (sulfuric acid and water). What color is the aqueous solution in the vat?

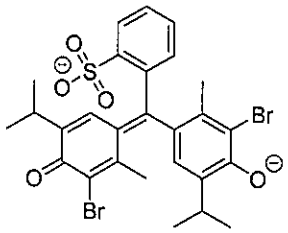
B

a. Red
(b.) Yellow
c. Green
d. Violet
e. Blue

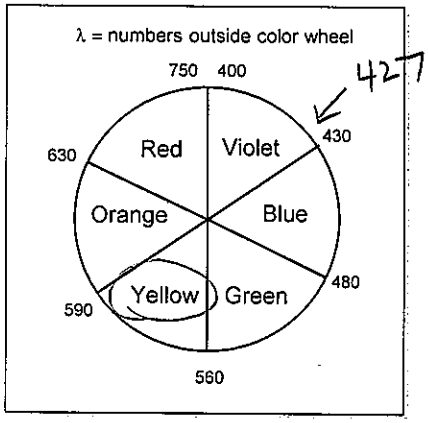
We see the color opposite the absorbed λ_{max}.



in acidic solution



in basic solution



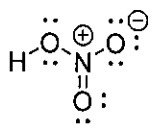
19. Which of the following events is responsible for causing the transmission of a visual signal to the brain?

D

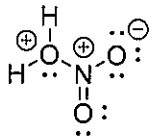
a. Retinol is transformed enzymatically into 11-cis-retinal.
b. Carrots are eaten and β-carotene is absorbed by the body.
c. 11-Cis-retinal binds to opsin via a Schiff base linkage.
(d.) Rhodopsin absorbs a photon and 11-cis-retinal isomerizes to 11-trans-retinal.
e. A lysine residue detaches from the protein opsin.

20. Which of these structures is the electrophile in the nitration of benzene?

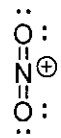
C



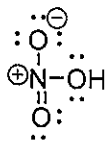
A



B



(C)

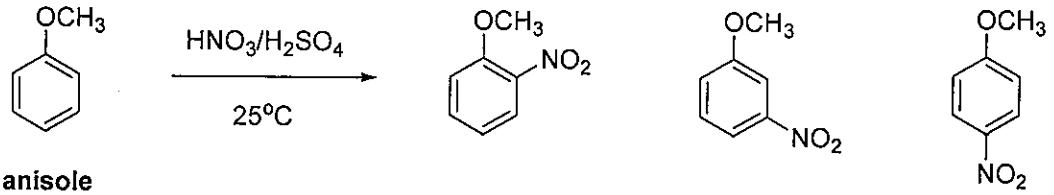


D

None of these structures is the electrophile

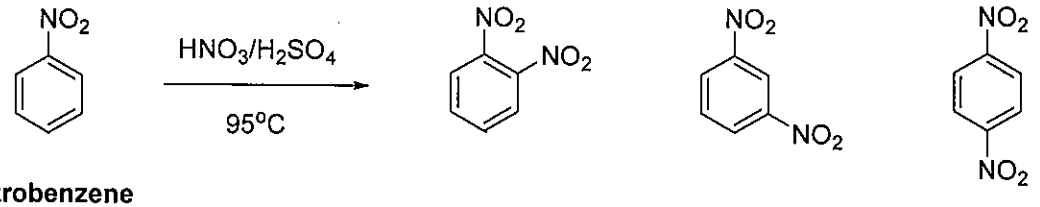
E

Questions 21, 22, and 23 refer to the following data from the nitration of anisole and nitrobenzene. Percentages under each product refer to the relative amounts of each product recovered at the end of the reaction.



anisole

31% 2% 67%



nitrobenzene

5% 90% 5%

21. The nitration of anisole proceeds at about room temperature, yet the nitration of nitrobenzene requires harsher conditions (much higher temperature). The most likely reason for this result is:

D

a. The OCH_3 group on anisole is an ortho, para director. True, but not the reason
b. The ring in anisole is deactivated False
c. The OCH_3 group withdraws electron density from the ring by an inductive effect True, but not the reason
(d.) The ring in nitrobenzene is deactivated
e. The nitro group donates electron density to the ring by resonance False

22. What is the best explanation for the formation of the *major* product in the nitration of nitrobenzene?

B

a. The nitro group deactivates the ring toward electrophilic aromatic substitution. True, but not the correct explanation
(b.) In the rate limiting step, the carbocation intermediate in the ortho and para pathways is destabilized, but in the meta pathway it is not; thus, the meta product forms faster True
c. The formation of the electrophile is slowed by the presence of the nitro group already on the ring in nitrobenzene False
d. Resonance structures of nitrobenzene place negative charge on the ring carbons at the meta positions False

23. Which of the following statements about the nitration of anisole is true?

A

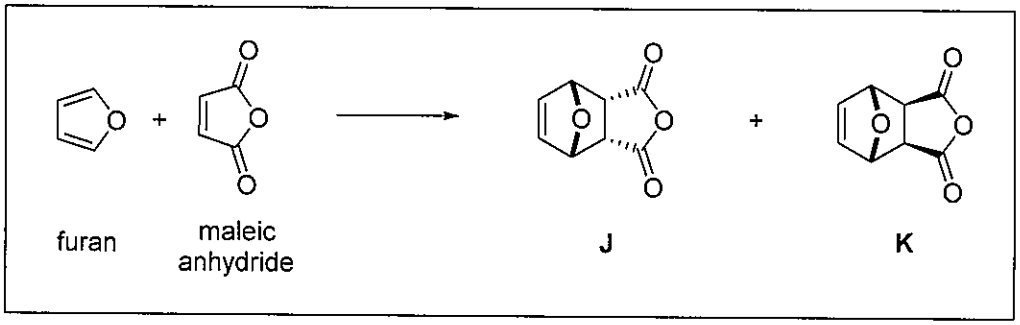
(a.) Both ortho and para products form preferentially, but the para product is favored because of steric hindrance at the ortho position. True

b. The meta product forms preferentially because the pathway for meta attack has the most stable carbocation intermediate in the rate-limiting step. False

c. The meta product is favored because the nitro group is electron-withdrawing and a meta director. NO_2 group isn't on the ring yet!

d. The meta product is disfavored because the nitro group is electron-withdrawing and a meta director. Same reasoning as "c"

24. The Diels Alder reaction of furan and maleic anhydride can provide two products, J and K, as shown here:



B

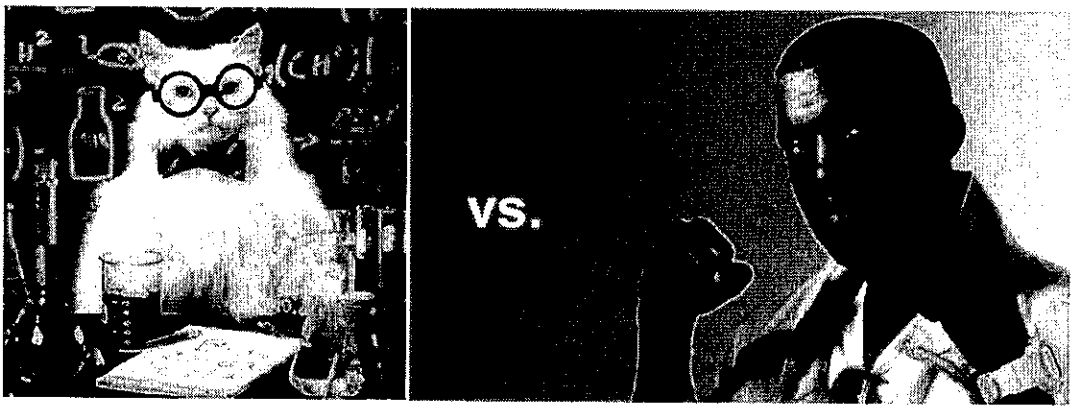
The reactants are combined in acetonitrile solution at 40°C. Initially, a small amount of product J forms and no K is observed. After about 20 minutes, the concentrations of J and K are the same. After that, the concentration of K increases and the concentration of J decreases. After 48 hours, the only product in solution is K.

Select the true statement(s) about this reaction.

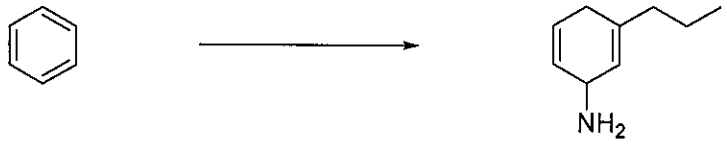
✓I. J is the kinetic product.
✗II. J is the thermodynamic product.
✓III. K is more stable than J.

a. I
(b.) I and III
c. II
d. II and III
e. None of the statements are true

25. Kanye West has challenged the Chemistry Cat to a Synthesis Showdown!



The Synthesis Challenge:



D

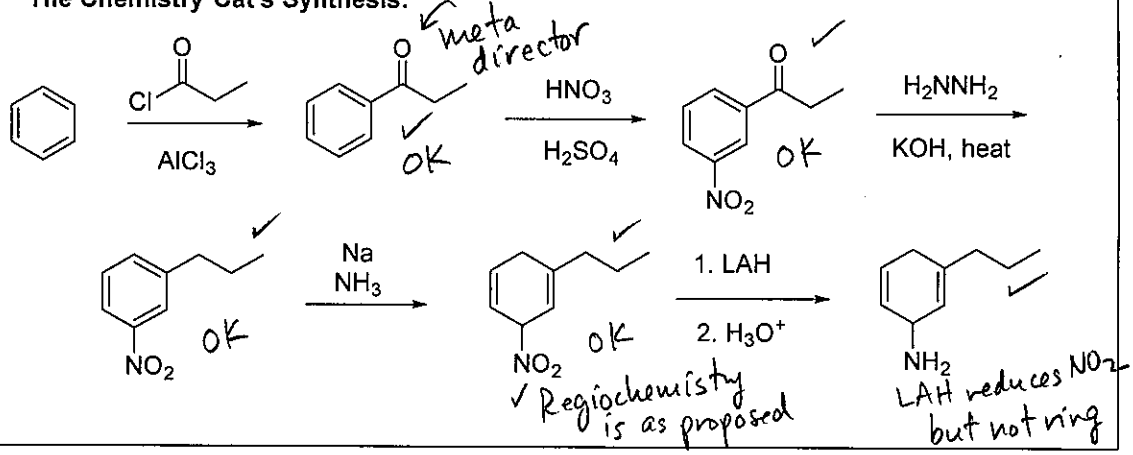
Contest rules state that each step in the synthesis must provide the desired/proposed product of that step as the major product. The winner is the one who has more correct steps. *The contestants' proposed syntheses are shown on the next page.*

Who wins the contest?

a. Kanye wins. The Chemistry Cat's synthesis has between 1 and 3 steps that would not work as proposed.
b. The Chemistry Cat wins. Kanye's synthesis has between 1 and 3 steps that would not work as proposed.
c. Kanye wins. The Chemistry Cat's synthesis has 4 to 5 steps that would not work as proposed.
(d.) The Chemistry Cat wins. Kanye's synthesis has 4 to 5 steps that would not work as proposed.
e. Neither the Chemistry Cat nor Kanye wins. They have an equal number of incorrect steps in their proposed syntheses.

Syntheses for Question 25:

The Chemistry Cat's Synthesis:



(Good job, Chemistry Cat)

Kanye's Synthesis: