

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!

1A 2A 3A 4A 5A 6A 7A 8A

hydrogen 1 H 1.0079																	helium 2 He 4.0026			
lithium 3 Li 6.941	beryllium 4 Be 9.0122											boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180			
sodium 11 Na 22.990	magnesium 12 Mg 24.305											aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948			
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80			
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	paladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29			
cesium 55 Cs 132.91	barium 56 Ba 137.33	lanthanum 57-70 * Lu 174.97	hafnium 71 Hf 178.49	tantalum 72 Ta 180.95	tungsten 73 W 183.84	rhenium 74 Re 186.21	osmium 75 Os 190.23	iridium 76 Ir 192.22	platinum 77 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]			
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * * Lr [262]	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]	unnilium 110 Uu [271]	ununium 111 Uu [272]	ununilium 112 Uu [277]	ununquadium 114 Uu [285]

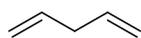
\* Lanthanide series

lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

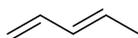
\*\* Actinide series



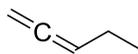
1. The description "1,3" refers to
- Conjugate addition
  - Direct addition
  - Electrophilic addition of HBr to a diene
  - A minor or unobserved product of a Diels Alder reaction
  - All of the above
2. Place the three dienes in order of *decreasing*  $\Delta H_{\text{hydrogenation}}$  (largest  $\Delta H$  to smallest  $\Delta H$ ).



W

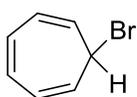


X

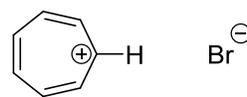
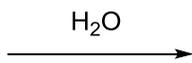


Y

- $W > X > Y$
  - $Y > X > W$
  - $Y > W > X$
  - $X > W > Y$
  - $W > Y > X$
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



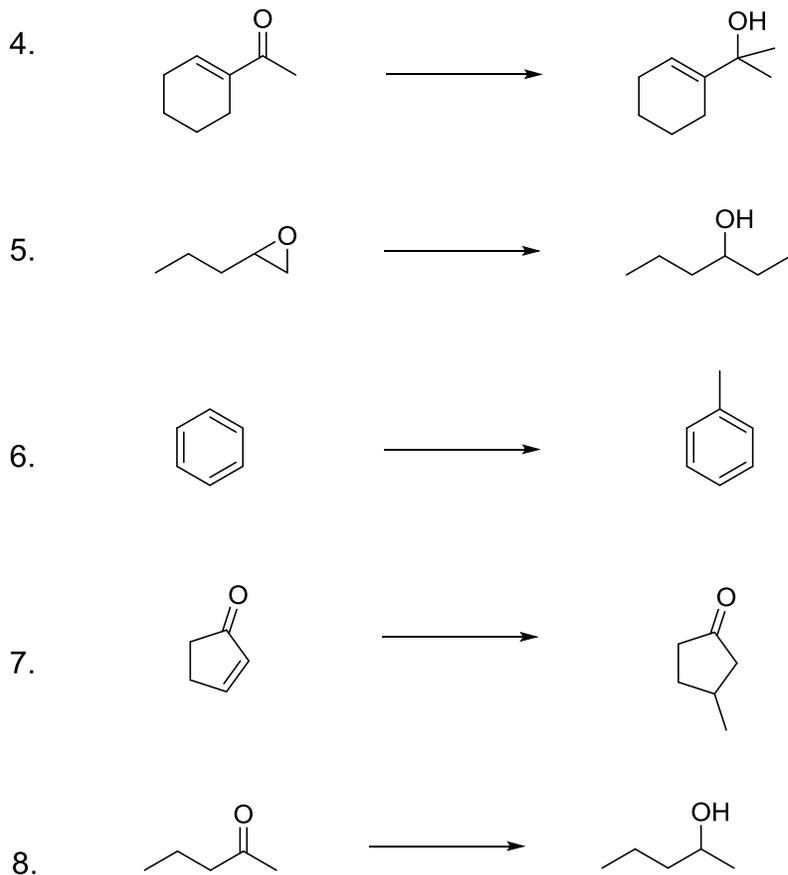
Tropylium ion

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 best explanation for the stability of the tropylium ion?

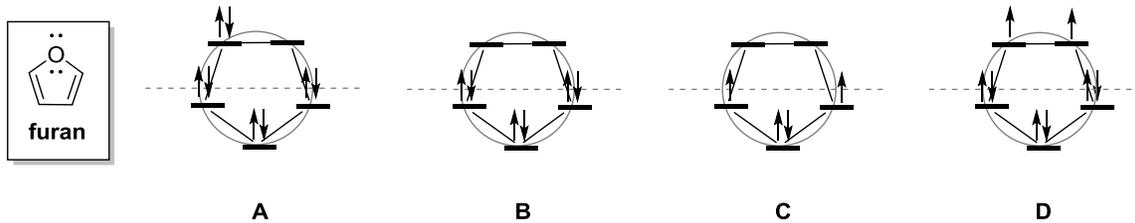
- The tropylium ion contains conjugation.
- The tropylium ion is an allylic carbocation.
- The tropylium ion is antiaromatic.
- The tropylium ion is benzylic.
- The tropylium ion is aromatic.

For questions 4 through 8, select the best reagent from the list to accomplish the transformation. Assume that there is an aqueous acid workup ( $\text{H}_3\text{O}^+$ ) following the use of each reagent. Choices may be used once, more than once, or not at all.

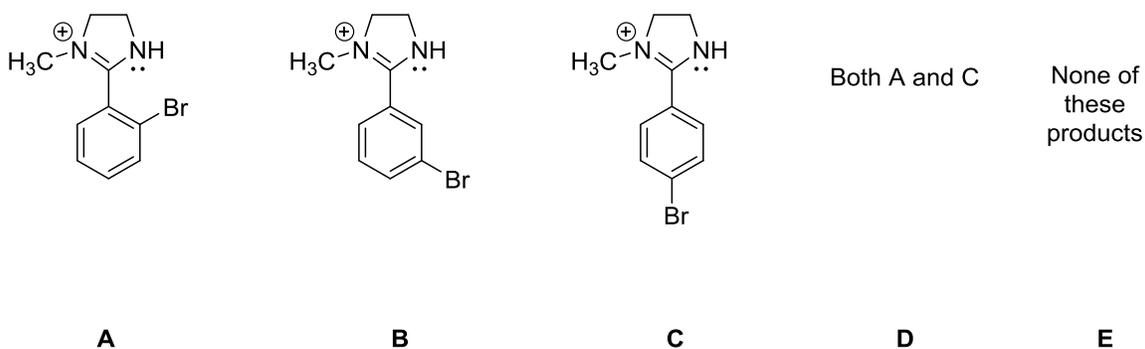
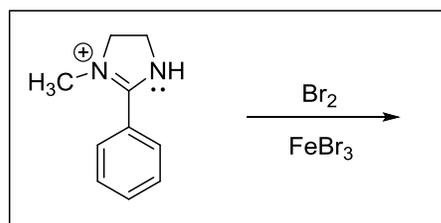
- a. MeLi
- b. MeMgBr
- c.  $\text{Me}_2\text{CuLi}$
- d. Any of these reagents could accomplish the transformation
- e. None of these reagents could accomplish the transformation



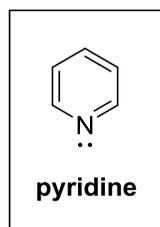
9. Which of these drawings is the correct Frost circle for furan?



10. Select the major product of this reaction.

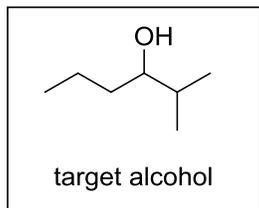


11. How many electrons are in the  $\pi$  system in pyridine?

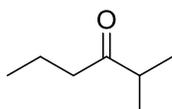


- a. 2
- b. 4
- c. 6
- d. 8
- e. None of these

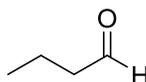
12. From which of the following structures can the target alcohol *not* be made in one synthetic operation, including aqueous workup?



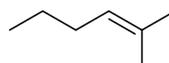
**A**



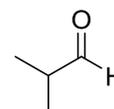
**B**



**C**

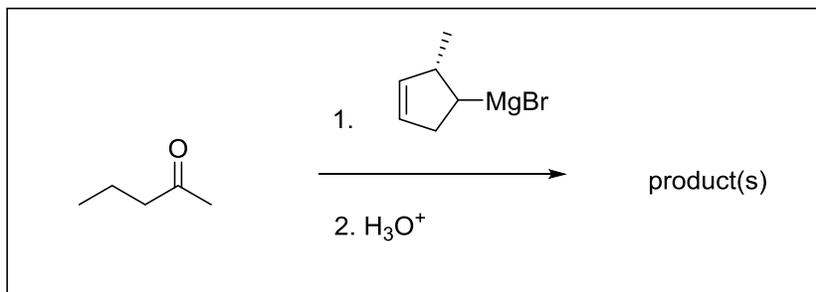


**D**



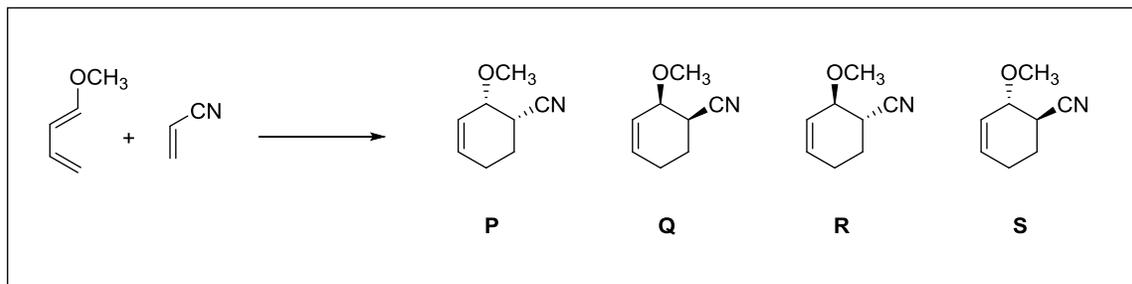
**E**

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.



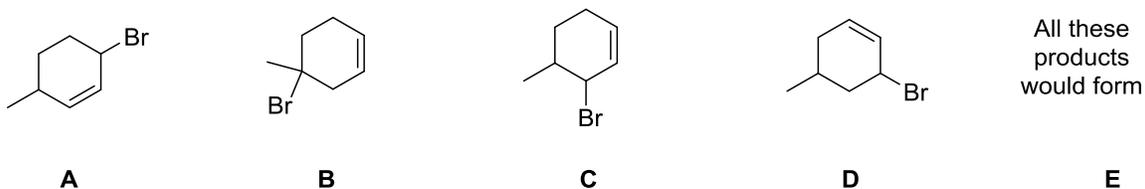
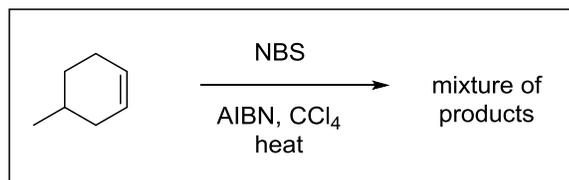
- a. A single achiral molecule
- b. A single chiral molecule
- c. Racemic mixture (enantiomers in equal amounts)
- d. Diastereomers in unequal amounts
- e. Diastereomers in equal amounts

14. A Diels Alder reaction yields the products shown:

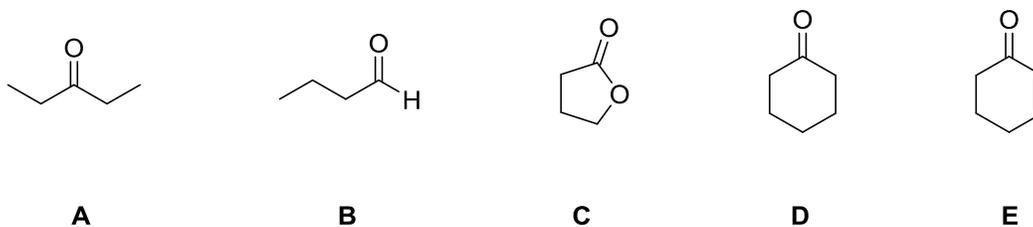


Which of these are endo products?

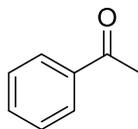
- P and Q
  - P and R
  - Q and S
  - Q and R
  - R and S
15. Which of the compounds shown would not be expected to form under the reaction conditions?



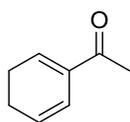
16. Which of these compounds will react fastest with methyllithium in diethyl ether solvent?



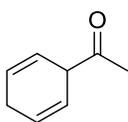
17. In the 1959 horror classic *House on Haunted Hill*, a skeleton pushes a woman into a vat of aqueous acid consisting of water and sulfuric acid. In her right hand, the woman is clutching a vial that contains the product of the Birch reduction of this compound:



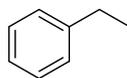
After several minutes of evil cackling, the skeleton takes a sample of the solution in the vat and returns to its laboratory, where it extracts the aqueous solution and isolates an organic compound. Which of the following compounds does the skeleton isolate?



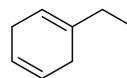
A



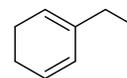
B



C



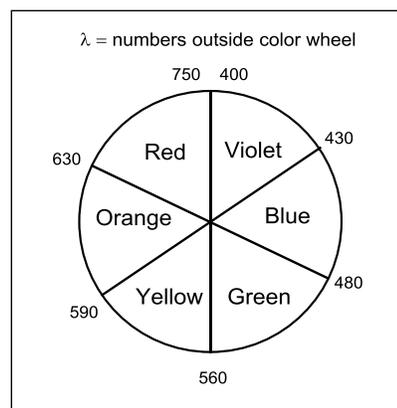
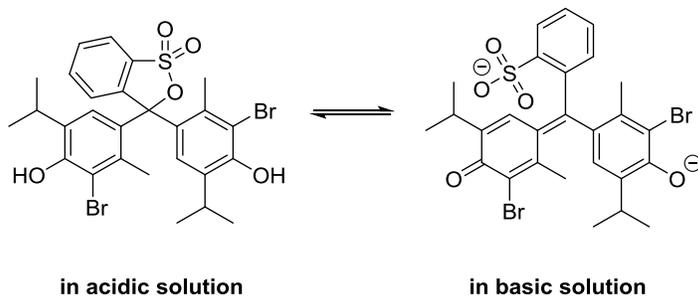
D



E

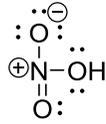
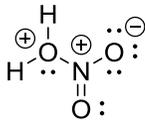
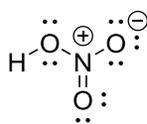
18. Bromothymol sulfone phthalein (also known as “BTB”) is an acid-base indicator that is commonly used to test the pH of swimming pools and fish tanks. In acidic solution, its maximum absorbance ( $\lambda_{\max}$ ) is around 427 nm, and in basic solution its  $\lambda_{\max}$  is 602 nm. The skeleton 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?

- Red
- Yellow
- Green
- Violet
- Blue



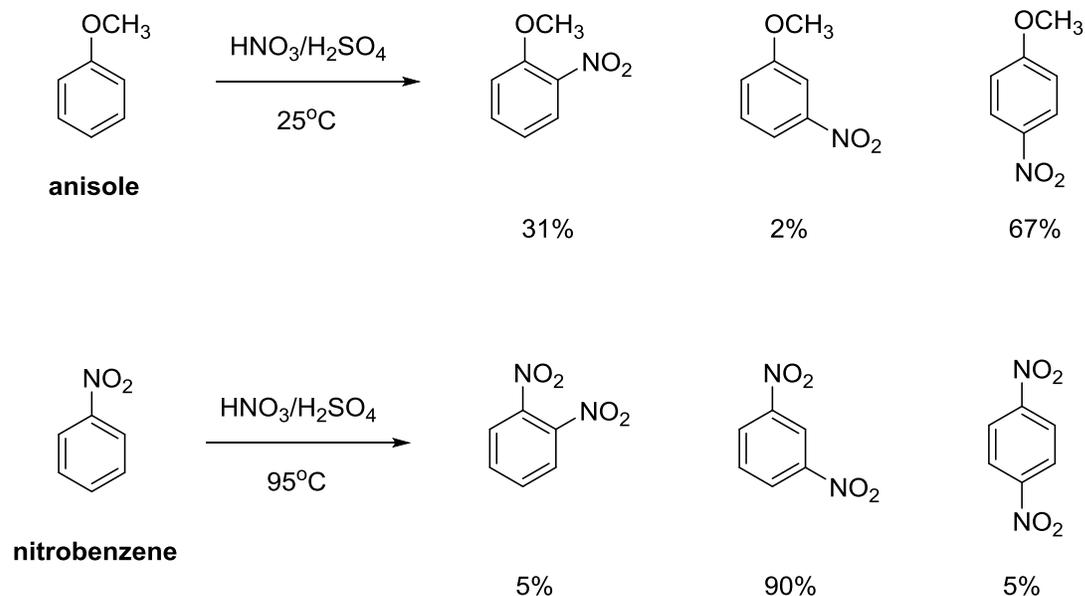
19. Which of the following events is responsible for causing the transmission of a visual signal to the brain?
- Retinol is transformed enzymatically into 11-cis-retinal.
  - Carrots are eaten and  $\beta$ -carotene is absorbed by the body.
  - 11-Cis-retinal binds to opsin via a Schiff base linkage.
  - Rhodopsin absorbs a photon and 11-cis-retinal isomerizes to 11-trans-retinal.
  - A lysine residue detaches from the protein opsin.

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



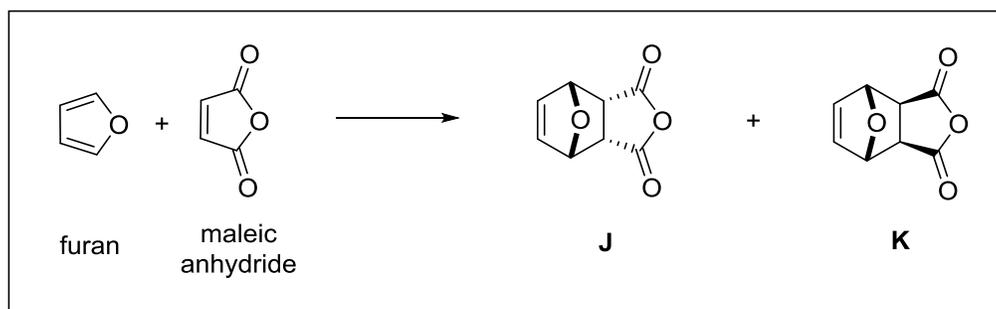
**E** None of these structures is the electrophile

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.



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:
- The  $\text{OCH}_3$  group on anisole is an ortho, para director.
  - The ring in anisole is deactivated
  - The  $\text{OCH}_3$  group withdraws electron density from the ring by an inductive effect
  - The ring in nitrobenzene is deactivated
  - The nitro group donates electron density to the ring by resonance
22. What is the best explanation for the formation of the *major* product in the nitration of nitrobenzene?
- The nitro group deactivates the ring toward electrophilic aromatic substitution.
  - 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
  - The formation of the electrophile is slowed by the presence of the nitro group already on the ring in nitrobenzene
  - Resonance structures of nitrobenzene place negative charge on the ring carbons at the meta positions

23. Which of the following statements about the nitration of anisole is true?
- Both ortho and para products form preferentially, but the para product is favored because of steric hindrance at the ortho position.
  - The meta product forms preferentially because the pathway for meta attack has the most stable carbocation intermediate in the rate-limiting step.
  - The meta product is favored because the nitro group is electron-withdrawing and a meta director.
  - The meta product is disfavored because the nitro group is electron-withdrawing and a meta director.
24. The Diels Alder reaction of furan and maleic anhydride can provide two products, J and K, as shown here:

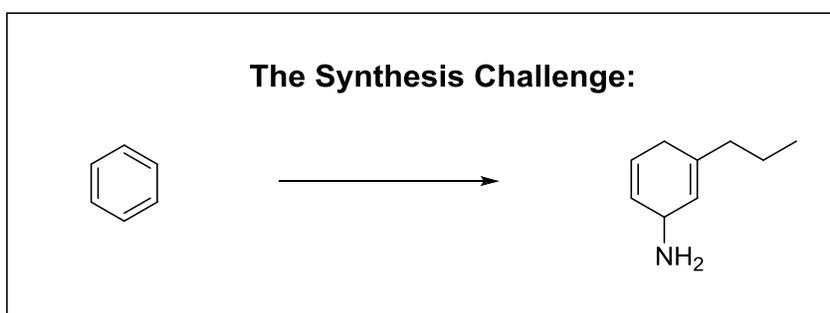
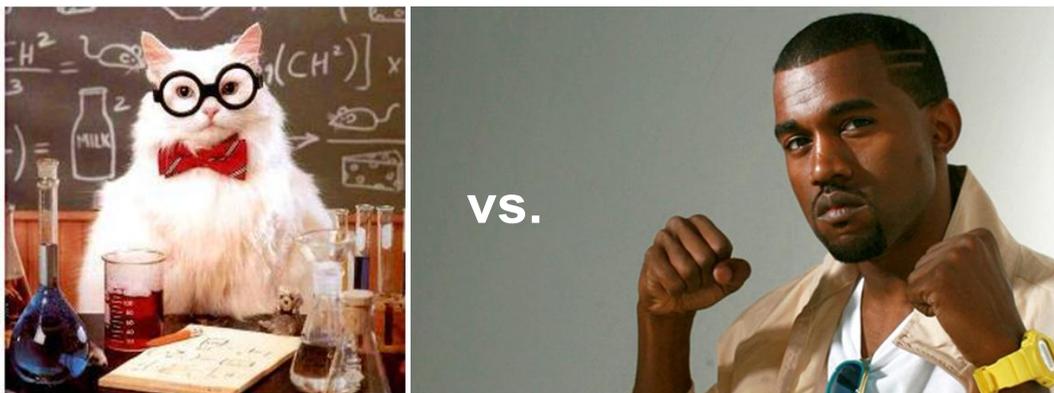


The reactants are combined in acetonitrile solution at 40°C. Initially, a small amount of product J forms and no K is observed. After about 20 minutes, the concentrations of J and K are the same. After that, the concentration of K increases and the concentration of J decreases. After 48 hours, the only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

Select the true statement(s) about this reaction.

- J is the kinetic product.
  - J is the thermodynamic product.
  - K is more stable than J.
- I
  - I and III
  - II
  - II and III
  - None of the statements are true

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



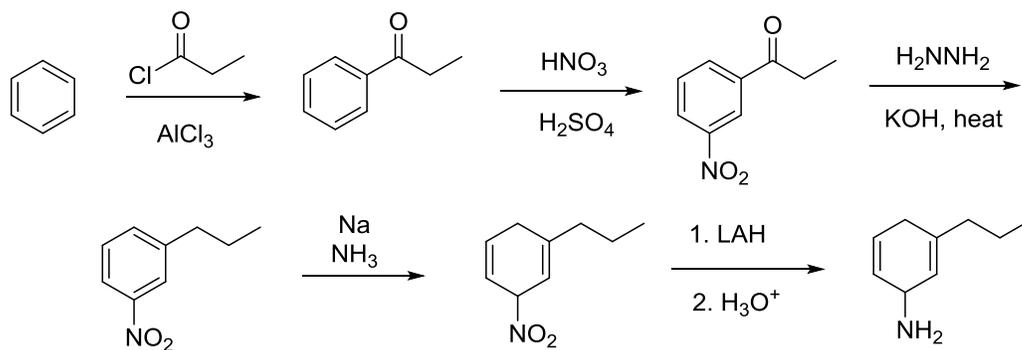
Contest rules state that each step in the synthesis must provide the desired/proposed product of that step as the major product. The winner is the one who has more correct steps. *The contestants' proposed syntheses are shown on the next page.*

Who wins the contest?

- Kanye wins. The Chemistry Cat's synthesis has between 1 and 3 steps that would not work as proposed.
- The Chemistry Cat wins. Kanye's synthesis has between 1 and 3 steps that would not work as proposed.
- Kanye wins. The Chemistry Cat's synthesis has 4 to 5 steps that would not work as proposed.
- The Chemistry Cat wins. Kanye's synthesis has 4 to 5 steps that would not work as proposed.
- 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:



### Kanye's Synthesis:

