CHEM-4430/6430
Advanced Synthesis
Exam 1 – 105 points
February 1, 2024

Name:_____ _____
last **first**

1. 45 pts _____

2. 20 pts _____

3. 5 pts _____

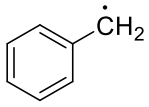
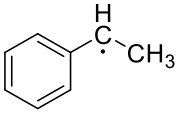
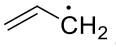
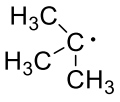
4. 15 pts _____

5. 20 pts _____

TOTAL: _____

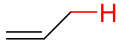
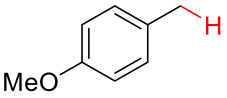
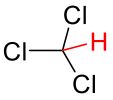
1. For each of the following questions only one answer is correct. Write the number corresponding to the correct answer in the space provided. (3 points each)

(a) Which radical is the most stable?

(1)  , (2)  , (3)  , (4)  , (5) 

(a) 2

(b) Which one of the following compounds has the highest C-H bond dissociation energy?

(1)  , (2)  , (3)  , (4)  , (5) 

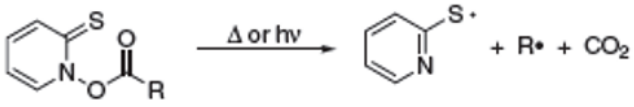
(b) 3

(c) Which one of the following radicals **X** will be formed from **HX** at the slowest rate?

(1) •SH, (2) •SiH_3, (3) •CH_3, (4) •NH_2, (4) HO•, (5) F•

(c) 5

(d) Which pathway of radical formation is not favorable?

(1) 

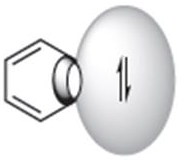
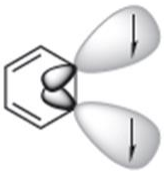
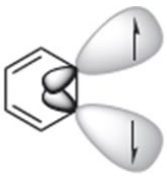
(2) $RO{-}N{=}O \xrightarrow{\Delta \text{ or } h\nu} RO\bullet + \bullet NO$

(3) $RO{-}OR \xrightarrow{\Delta \text{ or } h\nu} 2\,R\bullet + O_2$

(4) $RN{=}NR \xrightarrow{\Delta \text{ or } h\nu} 2\,R\bullet + N_2$

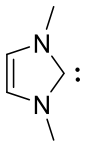
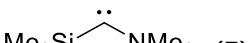
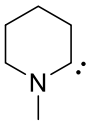
(d) 3

(e) What is the most likely electronic structure for benzyne (has lowest energy)?

(1)  , (2)  , (3) 

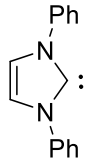
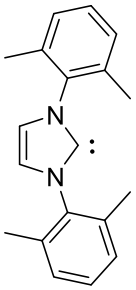
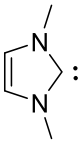
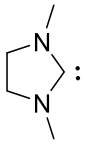
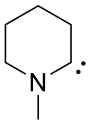
(e) 1

(f) Which one of the following carbenes is most nucleophilic?

(1)  , (2)  , (3)  , (4)  , (5) 

(f) 3

(g) Which one of the following N-heterocyclic carbenes is most stable?

(1)  , (2)  , (3)  , (4)  , (5)  (g) 2

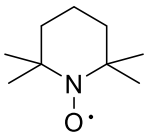
(h) Which one of the above-mentioned (problem **g**) N-heterocyclic carbenes is least stable?

(1), (2), (3), (4), (5) (h) 5

(i) How many hybrid orbitals with lone pairs of electrons are on the N atom in singlet nitrenes?

(1) one, (2) two, (3) three, (4) four (i) 2

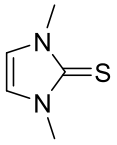
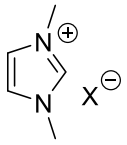
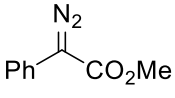
(j) Which one of the following oxygen containing radicals is persistent?

(1) $^{\cdot}OH$, (2) $^{\cdot}OCH_3$, (3) $^{\cdot}ON{=}O$, (4) $^{\cdot}ONO_2$, (5)  (j) 5

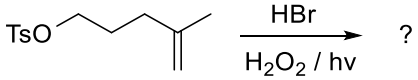
(k) Aromatic diradicals can be generated from:

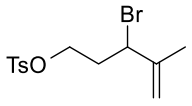
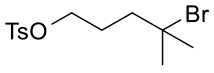
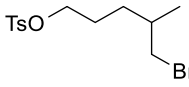
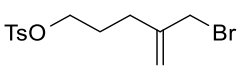
(1) enediynes, (2) enynes, (3) allenes, (4) dienes, (5) diynes (k) 1

(l) Which one of the following compounds <u>is not</u> a carbenoid?

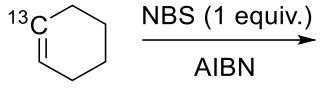
(1)  , (2)  , (3)  , (4) CH_2Cl_2, (5) $CHCl_3$ (l) 4

(m) What would be the product of the following reaction?



(1)  , (2)  , (3)  , (4)  (m) 3

(n) How many major products are formed in the following reaction?

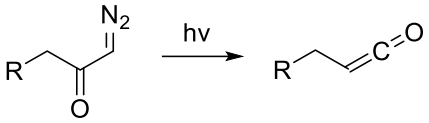


(1) one, (2) two, (3) three, (4) four, (5) five (n) 3

(o) What molecule is released after fragmentation in the Kolbe electrolysis?

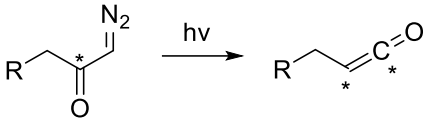
(1) NO, (2) CO_2, (3) a ketone, (4) CO, (5) N_2 (o) 2

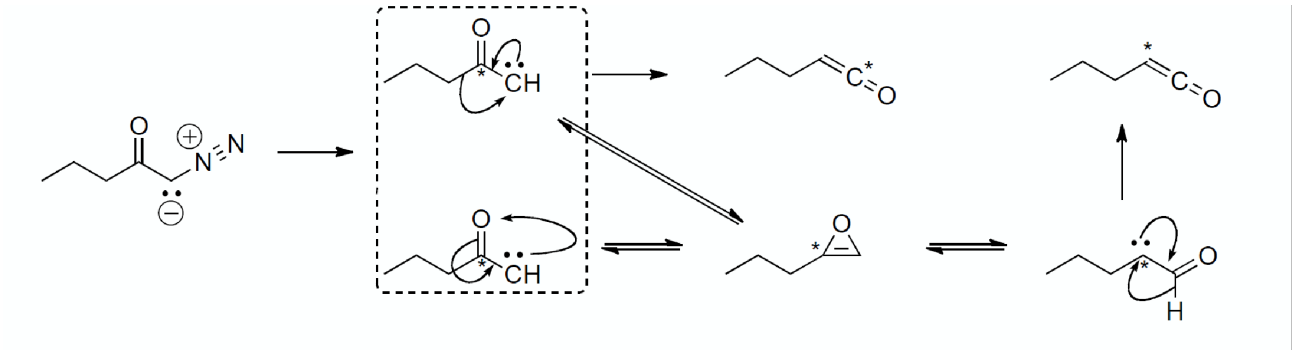
2. The Wolff rearrangement is a reaction of α-diazoketones that leads to the formation of a ketene.



Write a reasonable mechanism for this reaction (10 points).

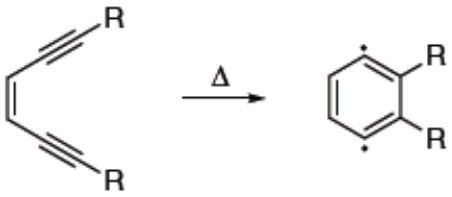
Does your mechanism change if the reaction of the diazoketone labeled in the carbonyl carbon leads to a product where the label is distributed through two positions, as indicated below? If so, how? (10 points)





3. Suggest a reason why the Myers-Saito cyclization should be so much more facile than the Bergman cyclization (5 points).

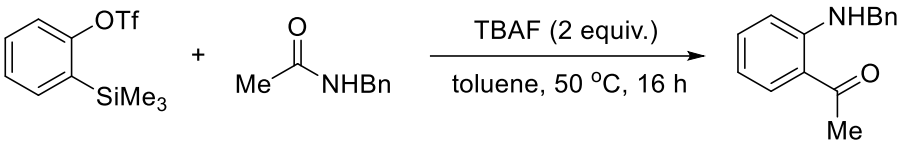
Myers-Saito cyclization

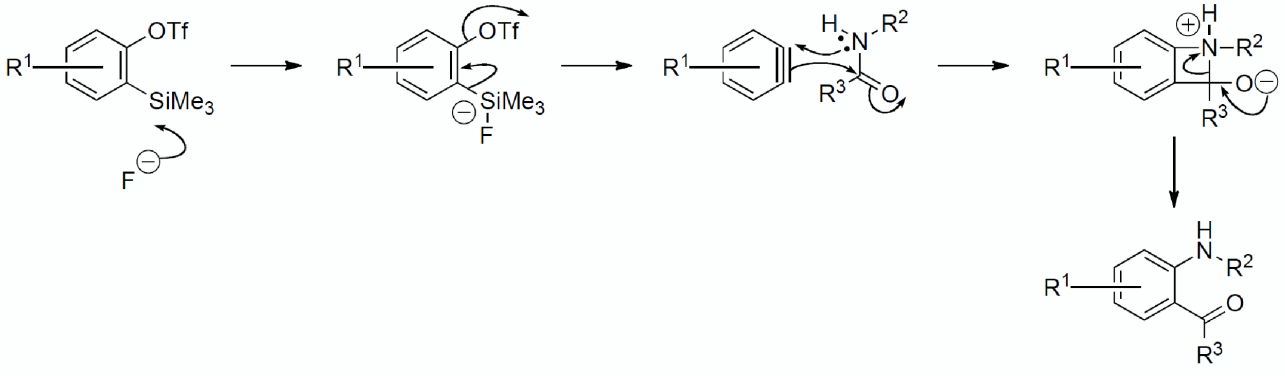


Bergman cyclization

The two cyclizations differ in the structure of the initial diradical product, as shown below. In the Myers-Saito cyclization, the diradical has one aryl radical center, and one benzylic radical center. The Bergman cyclization, however, gives a diradical where both unpaired electrons are aryl radicals, and therefore not stabilized by resonance. The benzylic radical is stabilized by resonance, so the Myers-Saito diradical is expected to be of lower energy, and the Myers-Saito cyclization to be less endothermic.

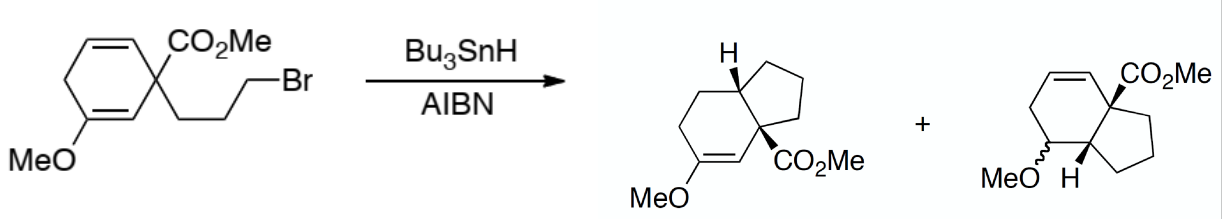
4. Suggest a reasonable mechanism for the reaction below (15 points).



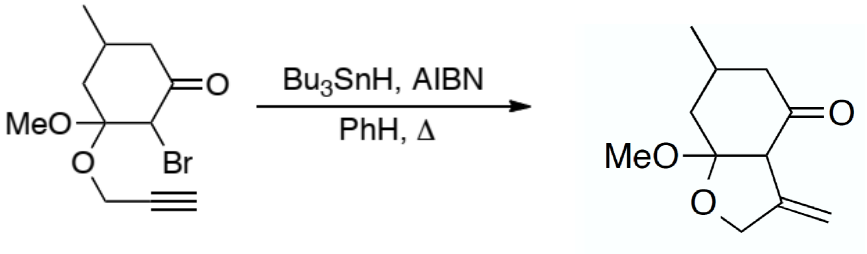


5. Draw the structure of the major organic product that will be formed in each reaction (20 points).

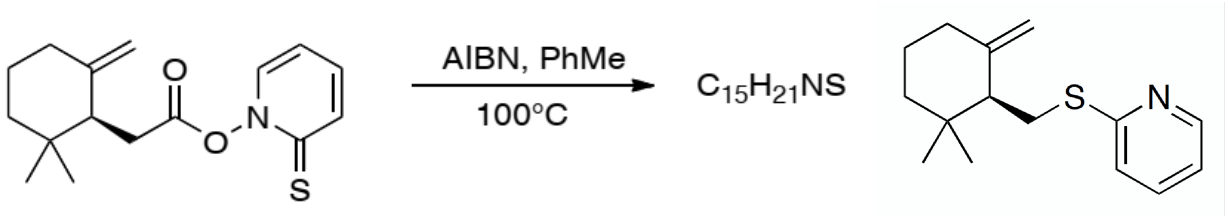
(a)



(b)



(c)



(d)