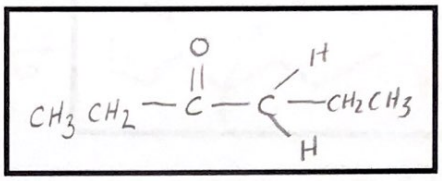
Anna Makridis

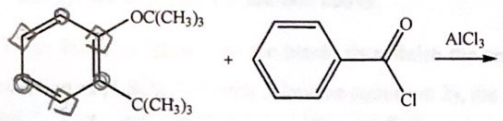
Chemistry 14D Lecture 2 Fall 2016 Exam 2 Page 1

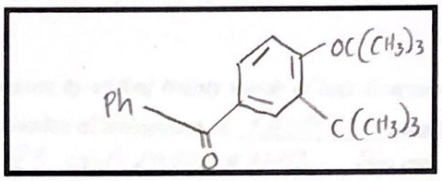
OK to use "Ph" anywhere on this exam where appropriate.
Exceeding the specified word limit on an answer will result in a point deduction for that answer.

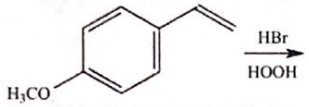
1. (15) For the reactions shown below, write ***the*** (i.e., ***one***) major organic product in the corresponding box. Do not include any mechanism details. If no reaction occurs, write "NR" in the product box. *Hint: Organic products contain carbon.*

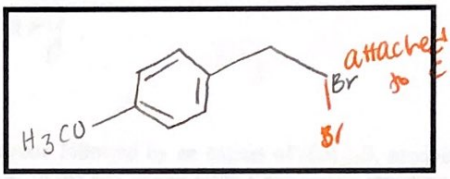
(a) $CH_3CH_2-C\equiv C-CH_2CH_3$ $\xrightarrow[H_2O]{H_2SO_4}$

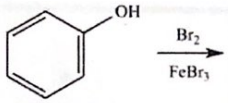


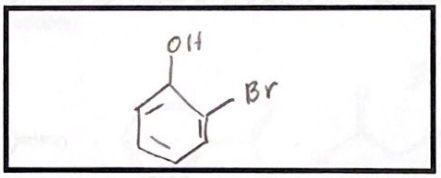
(b) 

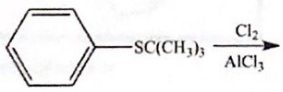


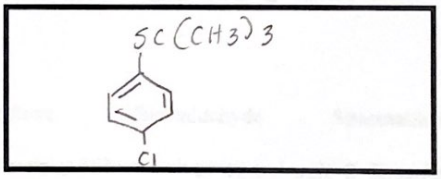
(c) 



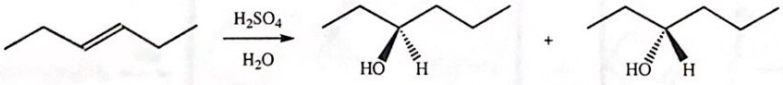
(d) 



(e) 

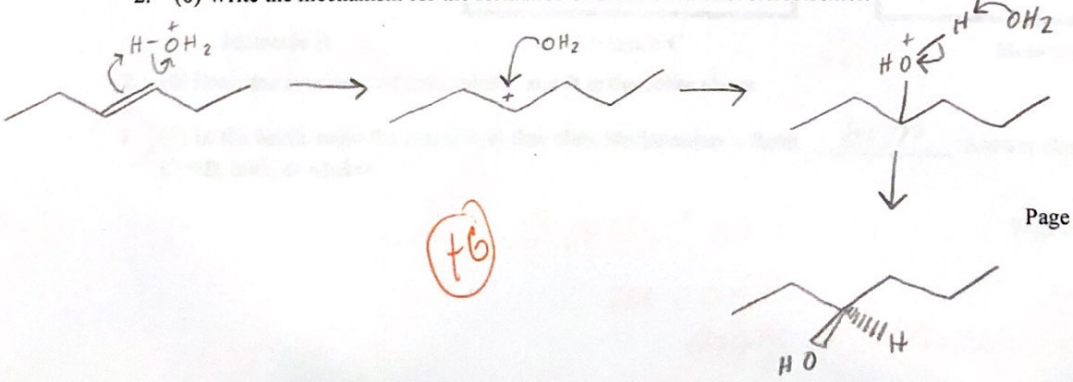


Questions 2 and 3 refer to this reaction:



3-Hexene (*S*)-3-Hexanol (*R*)-3-Hexanol

2. (6) Write the mechanism for the formation of either 3-hexanol stereoisomer.

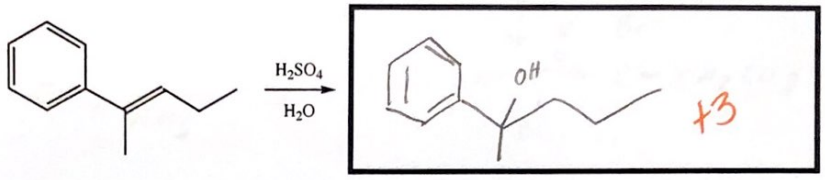


Page 1 score = 21

3. (2) The most accurate statement is (write ***one letter*** from below): C
   (a) The major product of this reaction is (*S*)-3-hexanol.
   (b) The major product of this reaction is (*R*)-3-hexanol.
   (c) The *S* and *R* stereoisomers are produced in equal (or very nearly equal) amounts.
   (d) The *S* and *R* stereoisomers are both produced, but in significantly unequal amounts.

+2

Questions 4 and 5 refer to this reaction:



+3

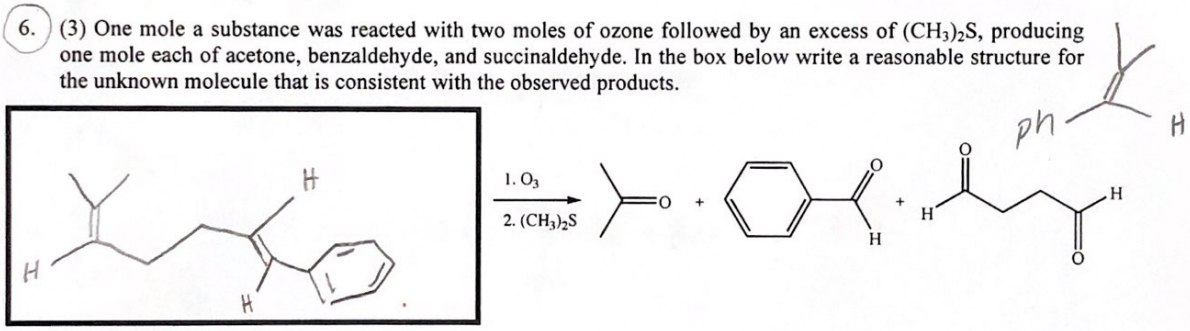
Molecule **A**

4. (3) Write the major product in the box above.

5. (4) Write 'faster' or 'slower' in the blank, then finish the sentence ***by adding twenty words or less***: Compared to the reaction of H_2SO_4/H_2O with 3-hexene (question 2), the reaction of molecule **A** is faster because...
   The carbocation formed is 3° w/ resonance from ring as opposed to secondary.

+4

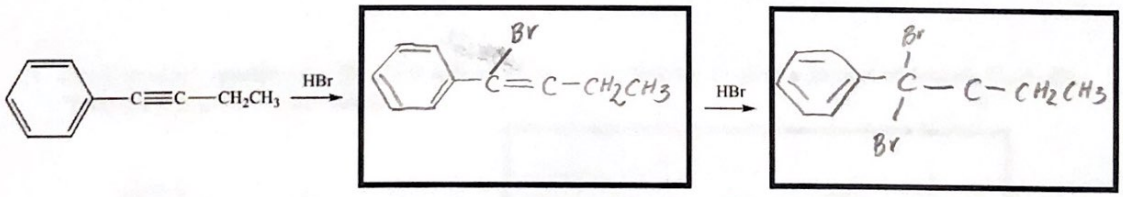
6. (3) One mole a substance was reacted with two moles of ozone followed by an excess of $(CH_3)_2S$, producing one mole each of acetone, benzaldehyde, and succinaldehyde. In the box below write a reasonable structure for the unknown molecule that is consistent with the observed products.



+3

Unknown substance Acetone Benzaldehyde Succinaldehyde

Questions 7–9 concern the reaction of molecule **B** with one molecule of HBr, which gives molecule **C**. Reaction of molecule **C** with one molecule of HBr gives molecule **D**:



Molecule **B** Molecule **C** Molecule **D**

+6

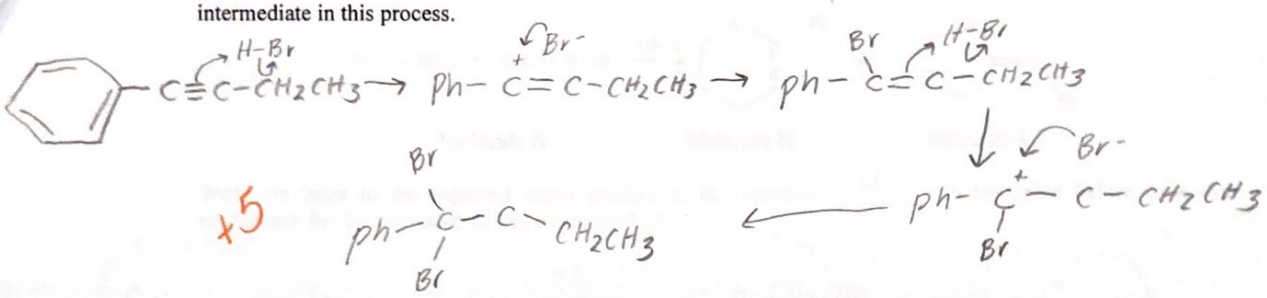
7. (6) Draw the structures of molecules **C** and **D** in the boxes above.

8. (2) In the blank write the reaction(s) that obey Markovnikov's Rule: both Answer choices: **B→C**, **C→D**, both, or neither.

B lacks H so can't apply markovnikov

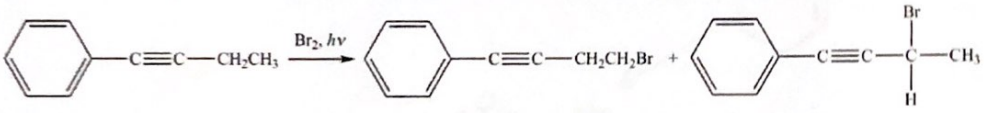
Page 2 score = 15

9. (5) Write the mechanism for the conversion of molecule **B** into molecule **D**. Note that molecule **C** is an intermediate in this process.



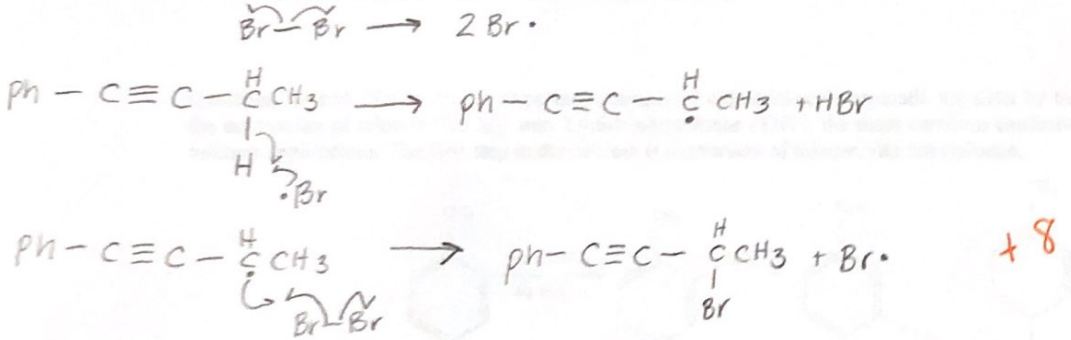
+5

10. (8) Consider the hypothetical reaction of molecule **B** with Br_2 and $h\nu$ to give molecule **E** and molecule **F**:



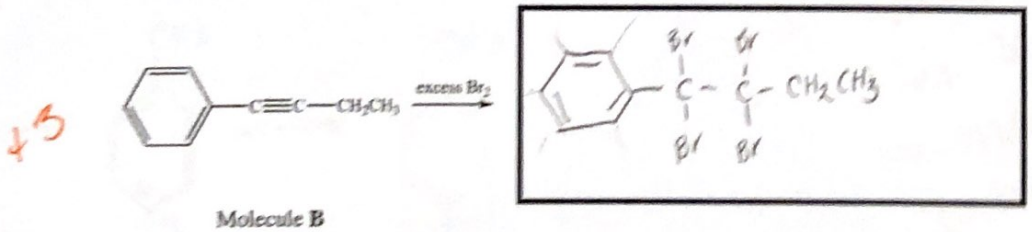
Molecule **B** Molecule **E** Molecule **F**

Write the letter of the expected major product of this reaction: F. In the space below write the mechanism for the formation of this major product.



+8

11. (3) In actuality, reaction of molecule **B** with an excess of Br_2 without $h\nu$ gives a product of formula $C_{10}H_{10}Br_4$. Write this product in the box below.

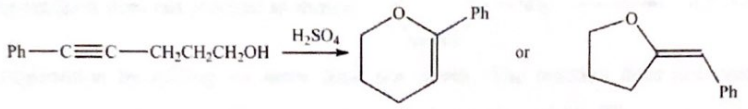


+3

Molecule **B**

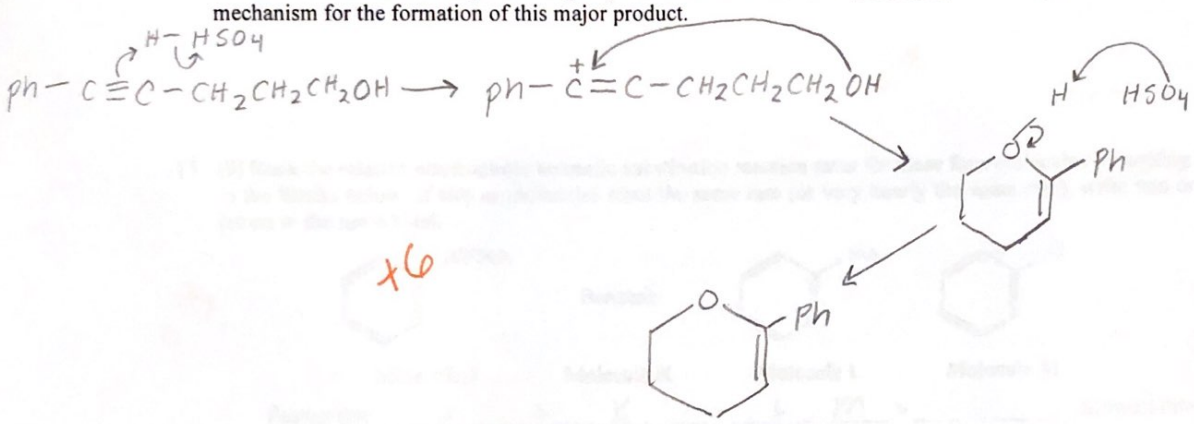
Page 3 score = 16

12. (7) Examine the reaction of molecule **G** with sulfuric acid:



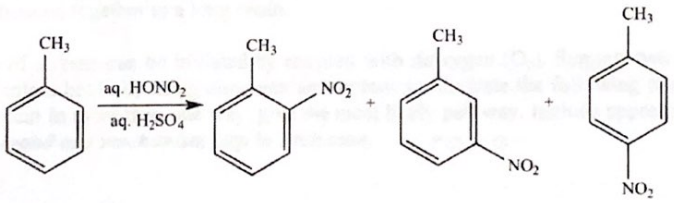
Molecule **G** Molecule **H** Molecule **I**

Write the letter of the expected major product of this reaction: H. In the space below write the mechanism for the formation of this major product.

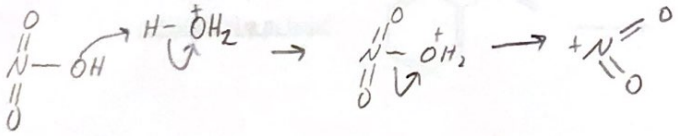


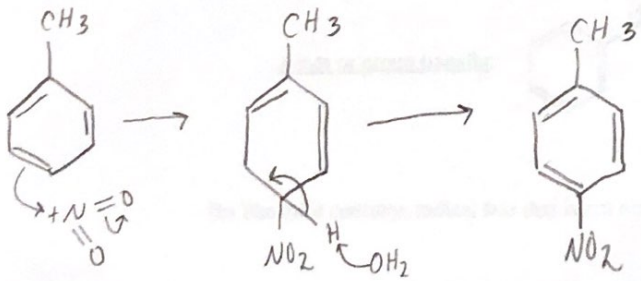
+6

Questions 13 and 14 concern an important example of industrial-scale aromatic nitration by the EAS mechanism: the conversion of toluene ($PhCH_3$) into 2,4,6-trinitrotoluene (TNT), the most common explosive for industrial and military applications. The first step in the process is conversion of toluene into nitrotoluene:



13. (12) Write the mechanism for the conversion of toluene into *para*-nitrotoluene. Label the rate-determining step as "rds." ***For any intermediates having resonance, draw only the most significant resonance contributors.***

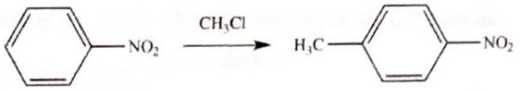




+10 Draw most important resonance contributor

Page 4 score = 16

14. (3) The following reaction does not proceed as shown:

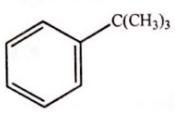


Complete this explanation by adding ***no more than ten words***: The reaction does not proceed as written because...

No $AlCl_3$ to polarize CH_3Cl.
Too unstable for Friedel Crafts

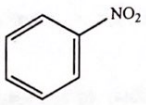
+3

15. (3) Rank the relative electrophilic aromatic substitution reaction rates for these four molecules by writing letters in the blanks below. If two or molecules react the same rate (or very nearly the same rate), write two or more letters in the same blank.

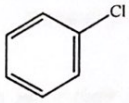


Molecule **J**

Benzene



Molecule **K**



Molecule **L**

Molecule **M**

+3

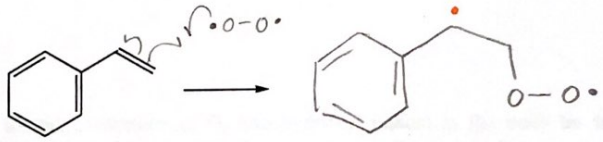
Fastest rate J > K > L, M > _____ Slowest rate

16. (5) Styrene ($PhCH{=}CH_2$, also called vinylbenzene) was first isolated as a pure substance in 1839 by distillation from storax (a tree resin). After a few days, the purified styrene formed a solid mass, which was later found to be a crude form of polystyrene, similar to the plastic in CD cases, etc. Polystyrene consists of millions of styrene molecules bonded together in a long chain.

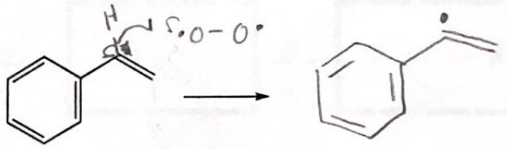
(a) Polymerization of styrene can be initiated by reaction with dioxygen (O_2). Suggest two ways in which this polymerization might begin by using dioxygen and styrene to illustrate the following common radical fates. If the fate can occur in more than one way, give the most likely pathway. Include appropriate curved arrows, but ***do not go beyond one mechanism step in each case.*** •O–O•

+4

Addition to a pi bond:



Atom or group transfer:



H–O–O•

(b) The third common radical fate that is not mentioned in part (a) is radical combination

Page 5 score = 10

17. (2) Complete this statement by writing one or more letters in the blank: Chlorofluorocarbons (CFCs) such as Freon-12 pose a threat to the ozone layer because... _____. Answer choices:

(a) ...CFCs are chemically unreactive. → reacts w/ light

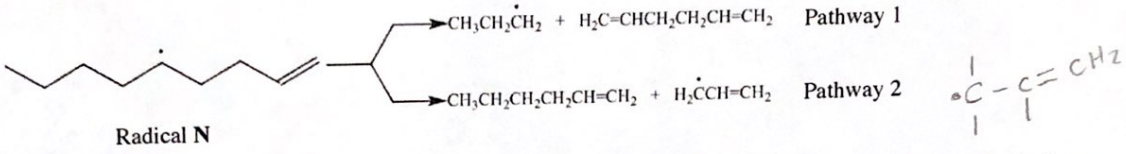
(b) ...CFCs can initiate a chain reaction.

(c) ...many thousands of tons of CFCs were released into the stratosphere prior to the Montreal Protocol.

(d) ...CFCs are radicals.

↳ not radicals all e⁻ are paired

Questions 18 and 19 concern radical fragmentation, another (albeit uncommon) radical fate. For example, radical **N** might fragment by pathway 1 or by pathway 2:



Radical **N**

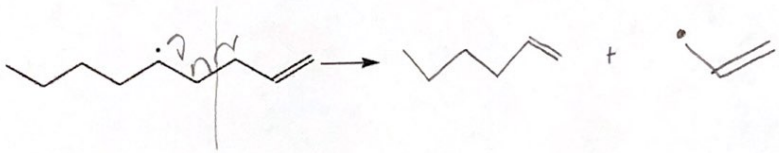
18. (5) Write '1' or '2' in the blank, then complete the statement by adding ***no more than 25 words***: Pathway

2 is the most likely radical **N** fragmentation pathway because...

It produces a primary radical stabilized by π bond resonance whereas pathway 1 makes a primary radical.

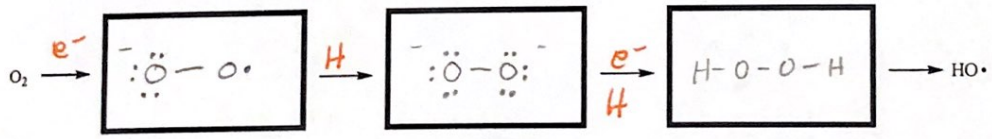
+5

19. (2) Draw the curved arrows for the fragmentation pathway you selected in question 18.



+2

20. (4) Complete this series of steps for the conversion of O_2 into hydroxyl radical in the body by writing the correct structures in the boxes. Write "superoxide" below the structure(s) that are superoxide.



superoxide

HO-O•

Page 6 score = 8