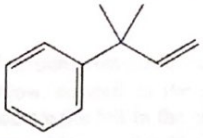
80

Anna Makridis

Chemistry 14D Fall 2017 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.
Transition states are not necessary unless the question specifically requires them.

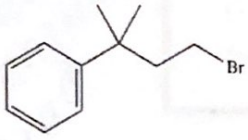
Questions 1–5 refer to the reaction of molecule **A** with HBr.



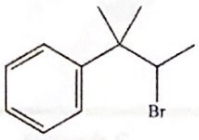
Molecule **A**

+2

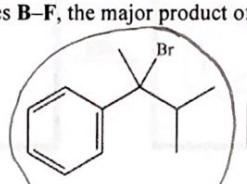
1. (2) Write a letter in the blank. Among molecules **B–F**, the major product of this reaction is molecule D.



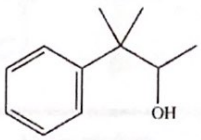
Molecule **B**



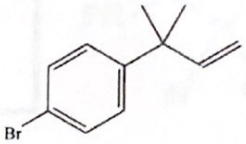
Molecule **C**



Molecule **D**

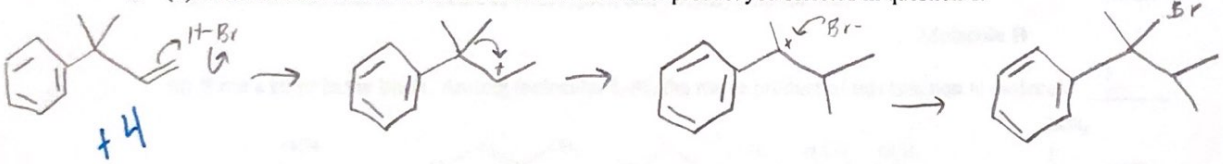


Molecule **E**



Molecule **F**

2. (4) Write a rational mechanism for the formation of the product you selected in question 1.



+4

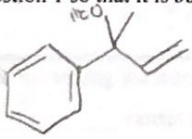
3. (8) Some of the products shown in question 1 just aren't possible from the reaction of molecule **A** with HBr. For each part below write the letter of one of these irrational products in the blank then complete the statement by adding ***no more than fifteen words*** in each case.

+8

(a) Molecule F is not a rational product because...
its formation requires breaking ring aromaticity
not most energetically favorable

(b) Molecule E is not a rational product because...
There is no water present for a
hydration reaction

4. (3) By adding, subtracting, or changing into another element ***no more than four atoms anywhere in the reaction***, rewrite the reaction of question 1 so that it is ***obviously faster***. Include all reactants and the major product, but do not include a mechanism.



+4

5. (3) Complete this statement by adding ***no more than fifteen words***: My new reaction of question 4 is faster than the reaction of question 1 because...
I increased the resonance stabilization
of the carbocation through
O lone pairs

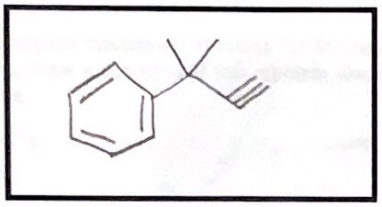
Page 1 score = 18

6. (2) Complete this statement by adding ***no more than ten words***: Once we know the product and mechanism of an alkene reaction, we have a good idea of the product and mechanism of the same reaction with an alkyne because these functional groups both have...

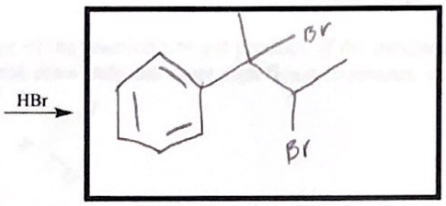
+2 π bonds

7. (3) Imagine we change the alkene of molecule **A** into an alkyne (the number of carbons remains unchanged). We'll call this alkyne molecule **G**. Write the structure of molecule **G** in the box below, as well as the major product formed when molecule **G** is reacted with a large excess of HBr. If no reaction occurs write NR in the product box.

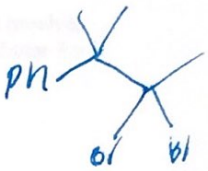
vinyl carbocation arrangement are rare



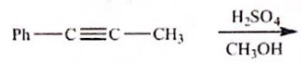
Molecule **G**



Major product



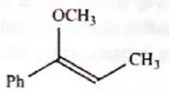
8. (12) Consider reaction of molecule **H** with H_2SO_4 and CH_3OH (the solvent):



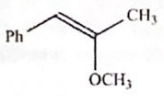
Molecule **H**

(a) Write a letter in the blank. Among molecules **I–M**, the major product of this reaction is molecule L.

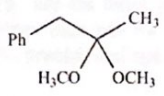
+6



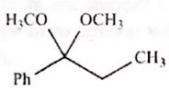
Molecule **I**



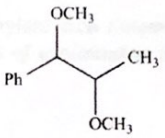
Molecule **J**



Molecule **K**

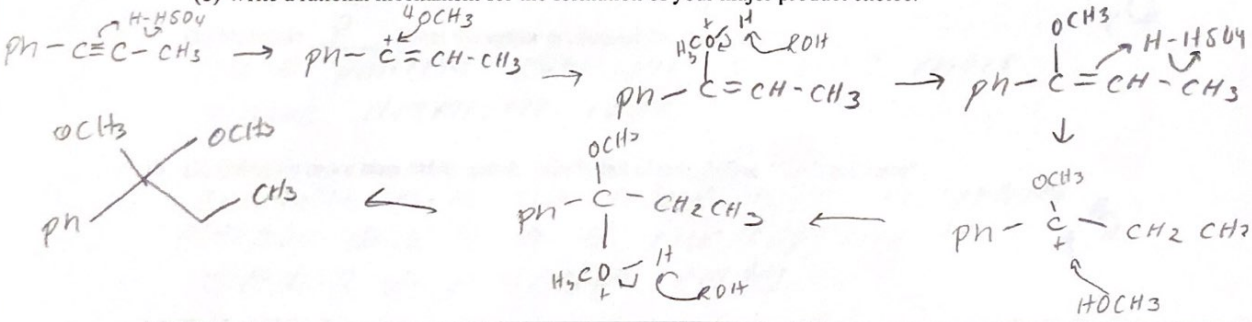


Molecule **L**



Molecule **M**

(b) Write a rational mechanism for the formation of your major product choice.



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9. (2) Complete this sentence by writing the name of a molecule in the blank: Reaction of pulmonary surfactant with atmospheric ozone causes degradation and reduced function of the pulmonary surfactant.

+2

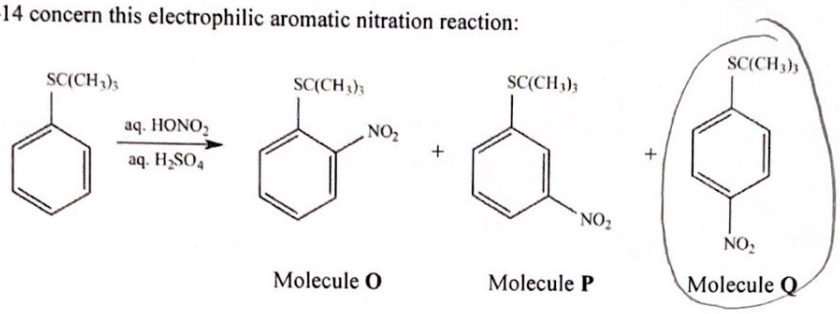
10. (3) Biological conversion of squalene oxide into lanosterol involves at least one of the common carbocation fates. Write all of the carbocation fates involved in this reaction sequence.

+3

Deprotonate form a π bond
capture a nucleophile
rearrangement

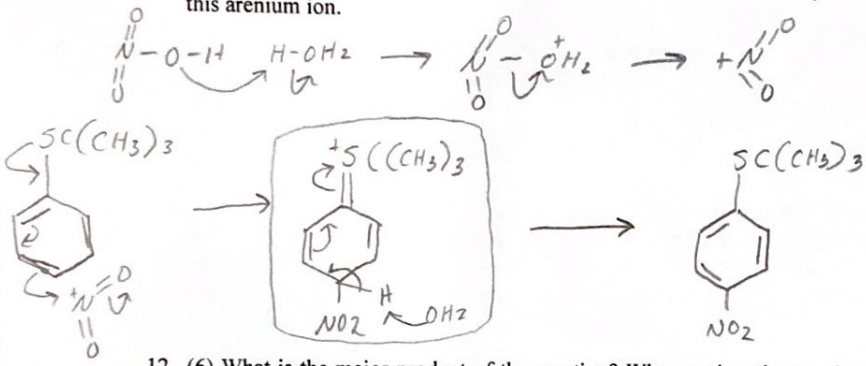
Page 2 score = 13

Questions 11–14 concern this electrophilic aromatic nitration reaction:



Molecule **O** Molecule **P** Molecule **Q**

11. (10) Write a complete mechanism showing the formation of the reaction's major product. If the mechanism involves an arenium ion, draw a box around this arenium ion, and draw only the most significant resonance contributor for this arenium ion.



+10

12. (6) What is the major product of the reaction? Why are the other products not major? Complete each statement by writing the molecule letter (**O**, **P**, or **Q**) in each blank then add ***no more than fifteen words of explanation*** in each case. Make your reasons as different as possible. Be precise and specific.

(a) Molecule O is not the major product of the reaction because...
steric hindrance from tert butyl group make ortho attack less likely.

(b) Molecule P is not the major product of the reaction because...
meta position does not produce most stable arenium ions.

+6

13. (3) Using ***no more then thirty words***, briefly but clearly define: "EAS activator".
aromatic ring substituent that increases electron density and nucleophilicity speeding up reaction rates.

+3

14. (2) Complete this statement by writing 'faster than', 'slower than', or 'equal to' in the blank: The reaction of $PhSC(CH_3)_3$ with aq. $HONO_2$/aq.H_2SO_4 is faster than the reaction of benzene with aq. $HONO_2$/aq.H_2SO_4.

+2

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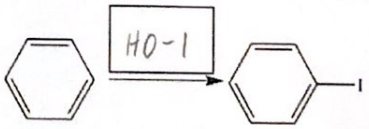
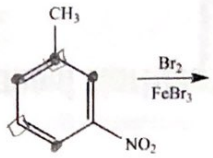
15. (2) Write in the box the molecular structure of the ***electrophile*** that attacks the benzene ring to produce iodobenzene (Ph–I):

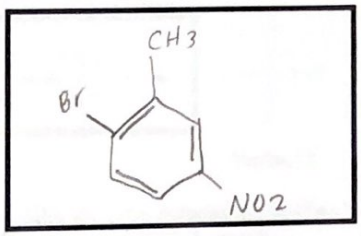


1+

Page 3 score = 21

16. (3) Draw in the box the major product of this reaction:

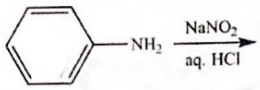


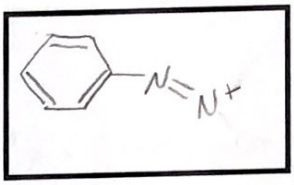


+3

17. (4) Diazo coupling is employed to produce thousands of useful molecules on an industrial scale.

(a) Complete this diazotization reaction example by writing the structure of molecule **R** in the box.





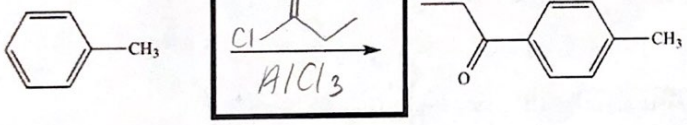
Molecule **R**

(b) Molecule **R** (or molecules like it) can be reacted with a wide range of aromatic molecules to produce diazo compounds (also called azo compounds). Complete the following statement by adding ***no more than five words***: An important, widespread use of azo compounds is as...

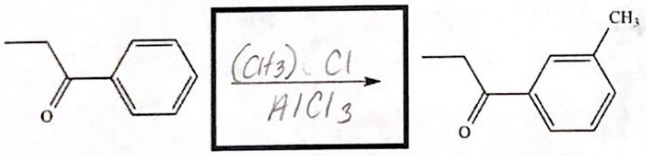
used as dyes

18. (4) Complete these reactions by writing the missing reactant(s) (not just the electrophile intermediate) above and/or below the arrows:

(a)



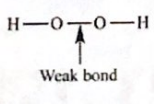
(b)

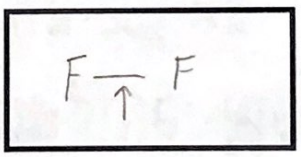


+4

The remaining exam questions are all related to chlorofluorocarbon-caused depletion of the Earth's ozone layer.

19. (2) The Br–Br bond of Br_2, the Cl–Cl bond of Cl_2, and the O–O bond of HOOH are all weaker than other typical single bonds such as the C–C bond of $H_3C–CH_3$. Using any number of any atoms of any element(s) except Br, Cl, or O, draw in the box the structure of a molecule having one or more bonds that are weak for the same reason as Br_2, Cl_2, and HOOH. Draw a clear arrow pointing to the weak bond.

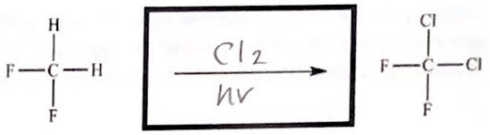




+2

Page 4 score = 9

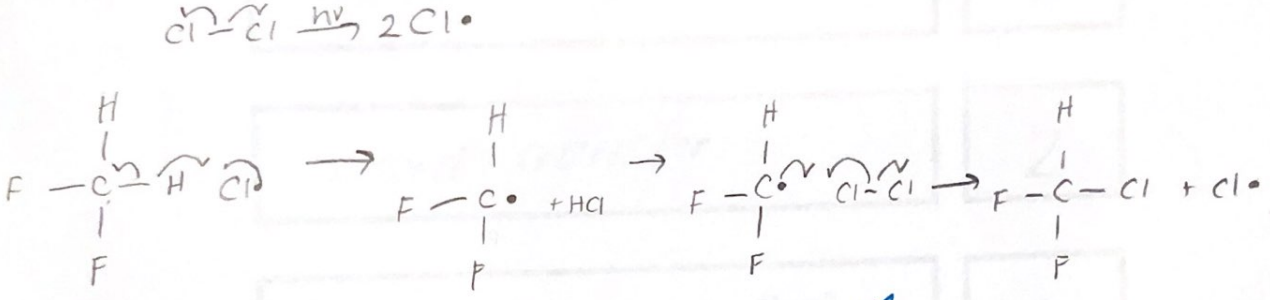
20. (2) In the box write the missing reactant(s) and other necessities that might be used to produce Freon-12 from difluoromethane by this free radical halogenation reaction:



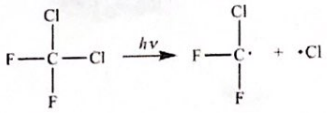
Difluoromethane Freon-12

+2

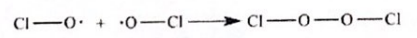
21. (7) Write a rational mechanism showing how your reaction of question 20 installs the first chlorine atom (i.e., concerts difluoromethane into chlorodifluoromethane).



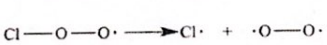
Now consider this simplified mechanism showing how Freon-12 might convert ozone into dioxygen (O_2):

Step 1: 

Step 2: 

Step 3: 

Step 4: 

Step 5: 

22. (3) Using ***no more then thirty words***, briefly but precisely define: Chain reaction.

A reaction in which mechanism steps are repeated indefinitely creating products that can be used again. +3

23. (1) Is the ozone depletion mechanism a chain reaction? In the blank write 'Y' is yes, 'N' if no, or 'X' if it cannot be determined: Y +1

24. (3) In each blank write the step number(s) of the ozone depletion mechanism steps(s) which are the following. If none of the mechanism steps meet the requirement write "0" in the blank.

Initiation step(s): 1 Propagation step(s): 2, 3, 4, 5 Termination step(s): 0

+3

Page 5 score = 16

25. (6) In the Name of Fate boxes write the three common radical fates (one different fate per box). (Hint: 'termination' is not a correct fate.) In the Example Step box write the number of one ozone depletion mechanism step that fits this fate category. If the fate is not represented in the ozone depletion mechanism, write '0' in the corresponding Example Step box.

Name of Fate	Example Step
Addition to a π bond	0
atom transfer	2
radical combination	3

x6

Page 6 score = 6