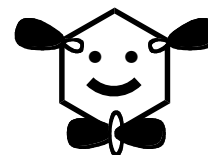


Name _____



CHEMISTRY 310S

• Environmental Chemistry •

MidTerm Examination

February 26, 2009

DO NOT OPEN UNTIL INSTRUCTED TO BEGIN!!!

Answer all questions in **ink**; simply cross out mistakes. There should be **NO** talking or conversing or discussions of politics during the test. If you have questions please raise your hand. Please leave as quietly as possible so that others may continue to take their tests without interruption. Thank you and have a good time.

"I'm not really interested in persuading people...what I'd like to do is help people persuade themselves."

~ Noam Chomsky

"If you torture data sufficiently, it will confess to almost anything."

~Fred Menger

Hammett Substituent Constants

Group	σ_{para}	σ_{meta}
NH ₂	-0.57	-0.16
OH	-0.38	0.13
OCH ₃	-0.28	0.11
CH ₃	-0.14	-0.16
H	0	0
Phenyl	0.05	0.05
F	0.15	0.34
Cl	0.24	0.37
Br	0.26	0.39
I	0.28	0.35
COOH	0.44	0.35
CF ₃	0.53	0.43
CN	0.70	0.61
NO ₂	0.81	0.71

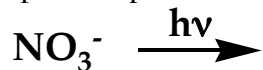
Total: 66 Pts; 10 Questions; *only* 5.5 pages

1. (10 Points). Please provide lewis structures for the following:

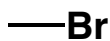
a) Hydroxide ion:

b) Carbonate radical:

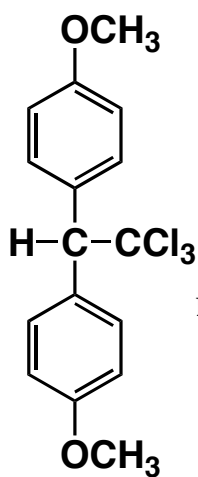
c) Nitrate plus the products of the photolysis rxn (3 lewis structures in all):



2. (5 Points). Please arrange the following five "substituents" in order of their $F(x)$ value used for $\bullet\text{OH}$ abstraction values. Place a "1" in the box to represent the highest value and a "5" the lowest value for $F(x)$.

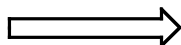


3. (4 Points). Please fill in the two blanks with the appropriate structures:

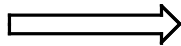


Methoxychlor

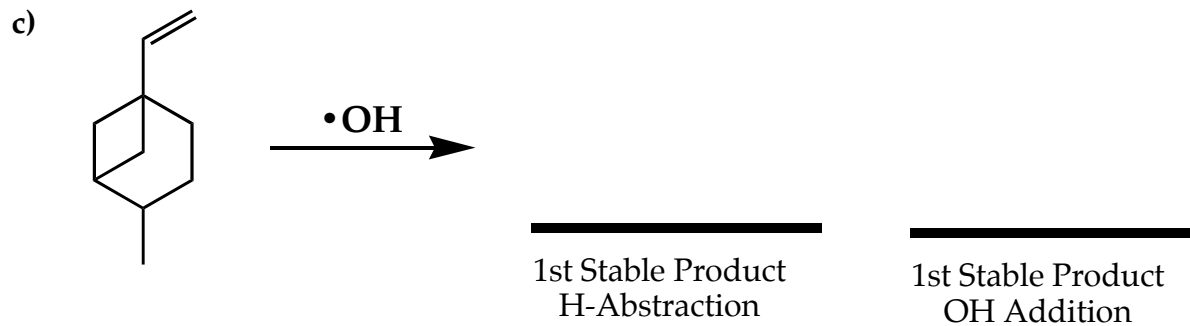
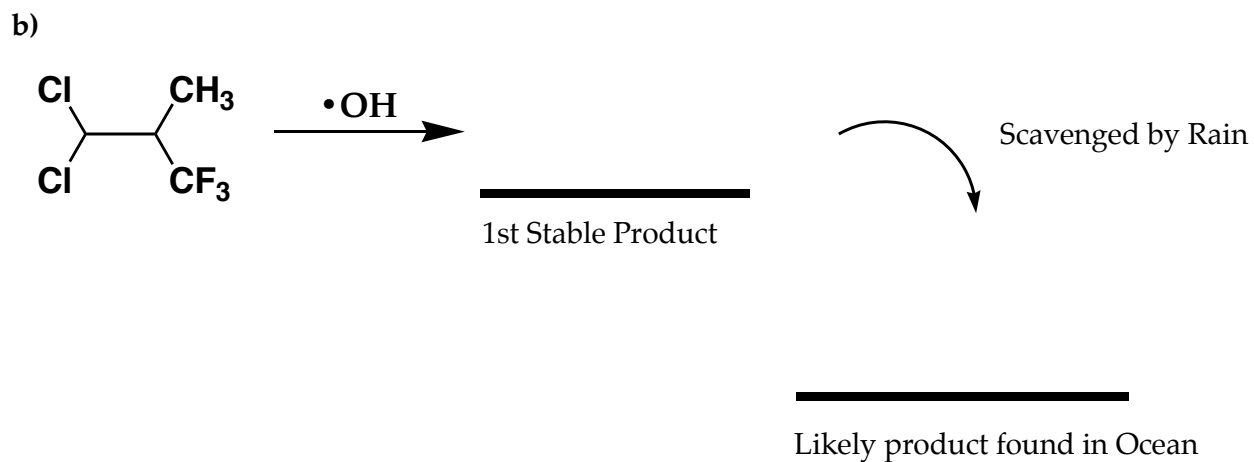
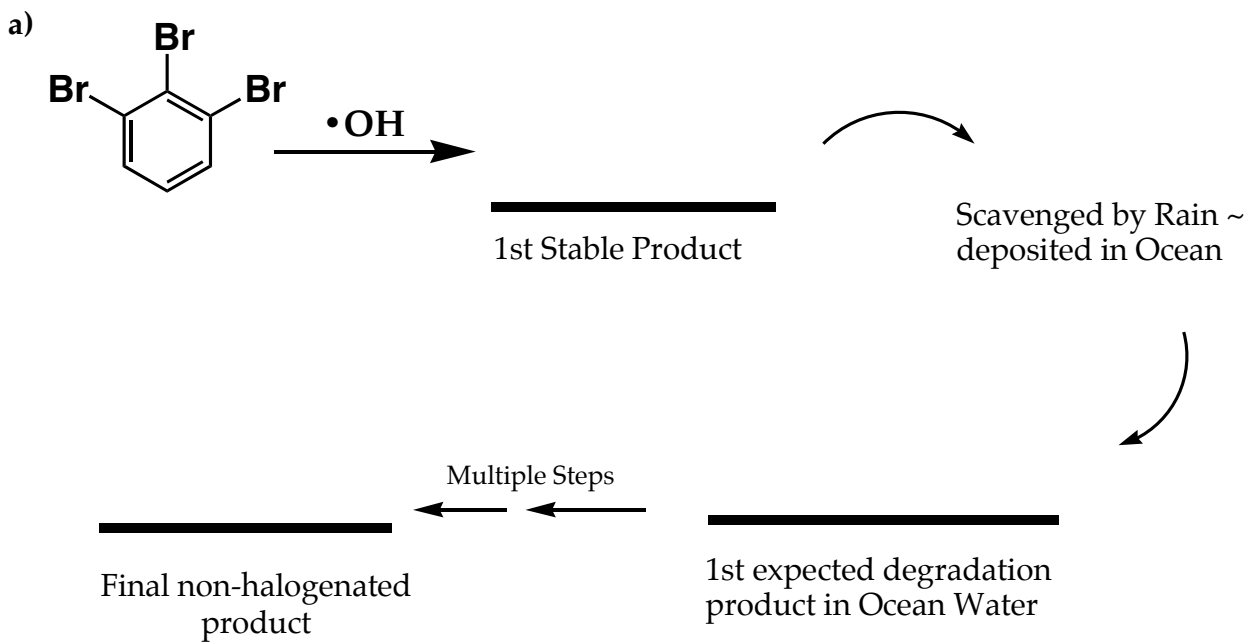
Hydrogenolysis



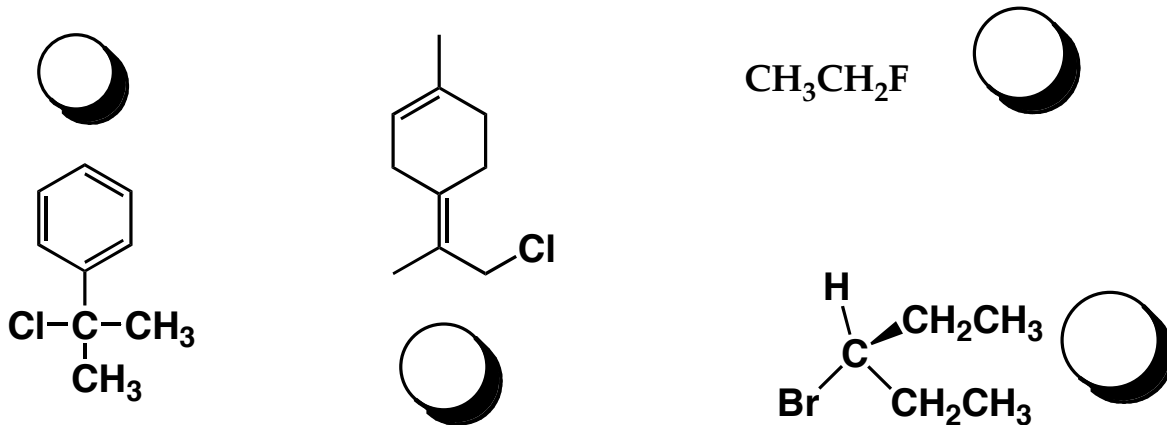
Dehydrodehalogenation



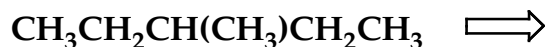
4. (14 Points). Please provide the structures you expect for the following conditions starting in the atmosphere:



5. (6 Points). Please consider elimination reactions in regards to the fate of the following chemicals in water. You are to arrange them in order of lifetime with "1" being the chemical with the smallest half-life while "4" would be allocated to the one with the longest half-life. Put your numbers in the available circles please.

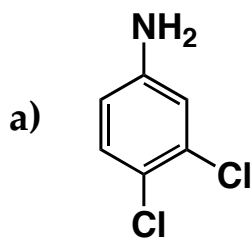


6. (6 Points). The following hydrocarbon is emitted from a paint factory and ultimately finds its way to the local sewage treatment plant. Please indicate the most likely biodegradation reaction steps and indicate a plausible end degradation product that would be released from the treatment plant into Lake Ontario.

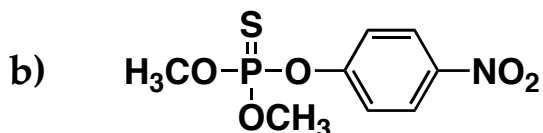


7. (5 Points). Your chance to choose: Please provide a reasonable chemical structure for a compound that would be considered highly persistent under atmospheric conditions and yet would be rapidly degraded in the sediment at the bottom of Lake Ontario. Do also indicate the reaction and first product expected for your 'fast' reaction:

8. (6 Points). Please answer each of the parts with an appropriate structure and text if needed:



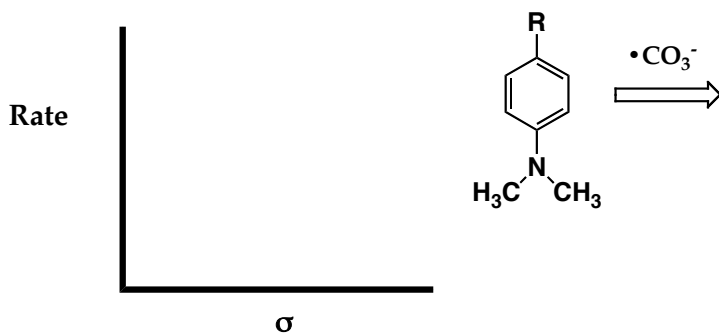
Please draw a resonance structure to predict which chlorine is most likely to be replaced via a hydrogenolysis reduction:



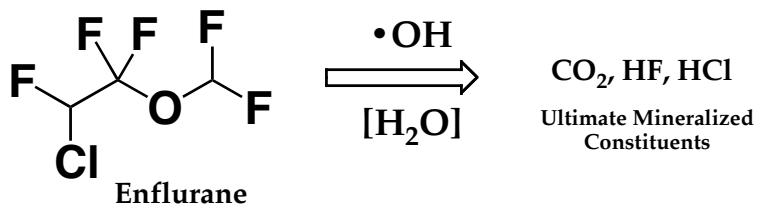
Explain, using whatever persuasive tools you have, how reduction might influence the hydrolytic stability of this organophosphate pesticide:

c) When actually doing an anaerobic sediment experiment to measure the rate of reduction of "MP" above, the mass balance of product (ie the MP reduction product) is much less than the amount of MP shown to dissipate. One theory is that the product itself has become chemically 'bound' to organic matter in the sediment through a covalent bond. Based on what you know of the structural features of humic acids, please suggest a plausible reaction of how this could occur....and do give provide a structure to illustrate your answer:

9. (4 Points). Please put in a line, with positive or negative slope, to relate the rate of this rxn between the compound shown and carbonate radical. Please also provide the structure for the "N containing" product of the reaction.



10. (6 Points). Enflurane is a widely utilized anesthetic in surgery. Interestingly, one can draw plausible reaction pathways that lead to the ultimate mineralization of this compound using only **one** equivalent of $\bullet\text{OH}$ to initiate the reaction. The literature is silent on the atmospheric fate of this compoundbut I'd like you to please draw the salient reactions showing how this could happen. You are to end up with the mineralized products shown and yes their aqueous analogues are fine.



You're Done!