

Answer Key
Name _____

CHEMISTRY 310S

• Environmental Chemistry •

MidTerm Examination

March 3, 2011

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 the weather 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.

"Colonialism is a terrible bane for a people upon whom it is imposed, but a blessing for a language. English's drive to exploit the new and the alien, its zeal in robbing words from other languages, its incapacity to feel qualms over the matter, its museum-size overabundance of vocabulary, its shoulder-shrug approach to spelling, its don't-worry-be-happy concern for grammar-the result was a language whose colour and wealth Henry loved."

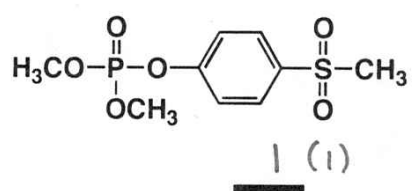
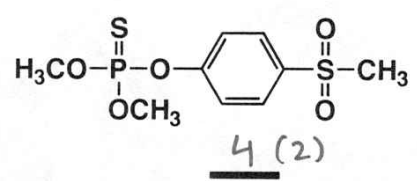
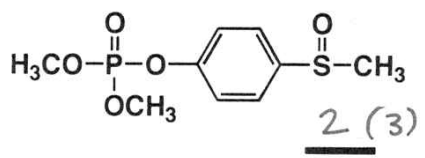
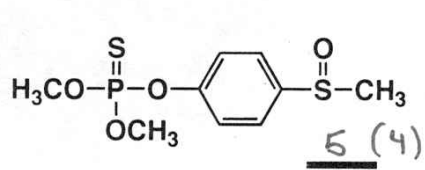
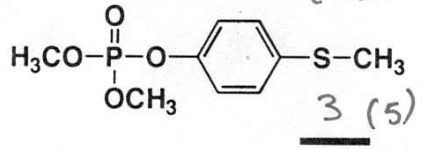
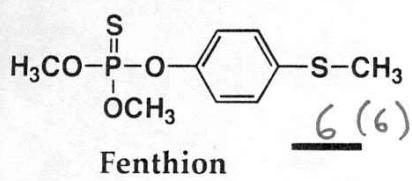
~ Yann Martel (*Beatrice & Virgil*)

Hammett Substituent Constants

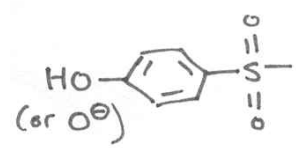
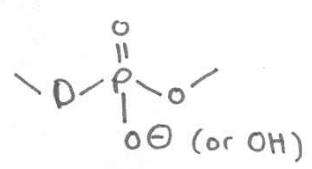
Group	σ_{para}	σ_{meta}
NH ₂	-0.57	-0.16
OH	-0.38	0.13
OCH ₃	-0.28	0.11
CH ₃	-0.14	-0.16
H	0	0
Phenyl	0.05	0.05
F	0.15	0.34
Cl	0.24	0.37
Br	0.26	0.39
I	0.28	0.35
COOH	0.44	0.35
CF ₃	0.53	0.43
CN	0.70	0.61
NO ₂	0.81	0.71

Total: 76 Pts; 9 Questions; *only* 5 pages

1. (8 Points). On the line please put a number 1 to 6 to relate the relative hydrolysis rate you would expect for the compounds below under conditions expected of Lake Ontario (pH of ~8); 1 is the **fastest** and 6 the slowest. When you have completed that please draw the structures of the hydrolysis products for the one you have labeled as the fastest (ie #1). (also acceptable)

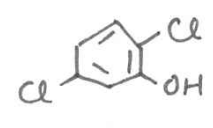
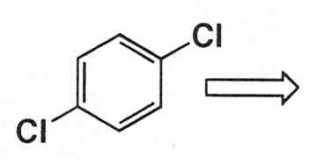


Two Products:



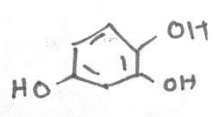
2. (18 Points). Dichlorobenzene (DCB) is used widely as a disinfectant in toilet bowls. Please provide the structures you expect for the following conditions:

a)

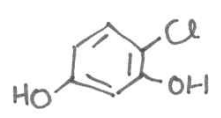


1st stable product of OH rxn in the atmosphere

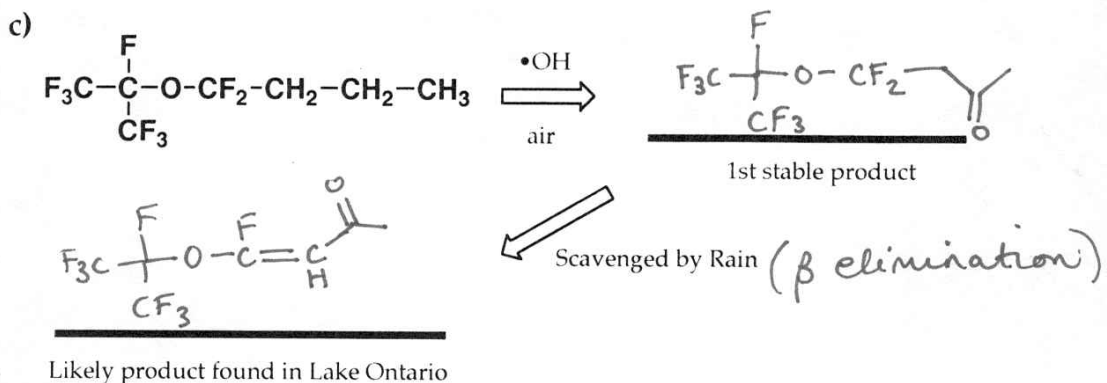
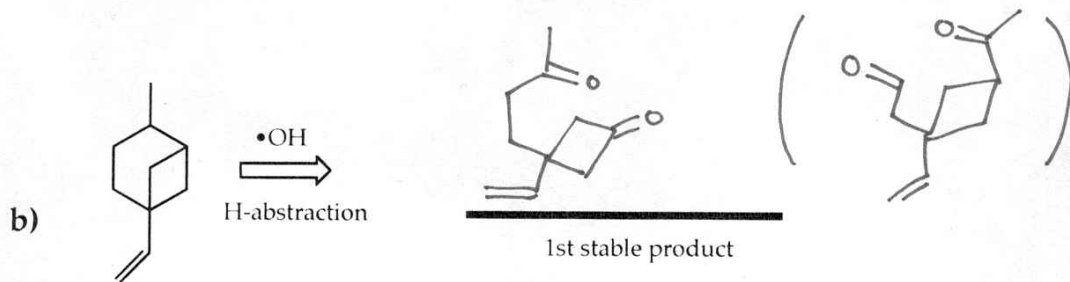
photonucleophilic displacement
 (photonucleophilic substitution)



...and the product of one more cycle of that rxn



Scavenged by rain and deposited in Lake Ontario name the rxn would you expect it would undergo and a possible product please:



3. (16 Points). Please provide persuasive short, two to three sentence answers to the queries below. Wherever appropriate illustrate with a figure, scheme, or structures:

a) What is quantum yield, for a given photochemical process, and how would it be determined?

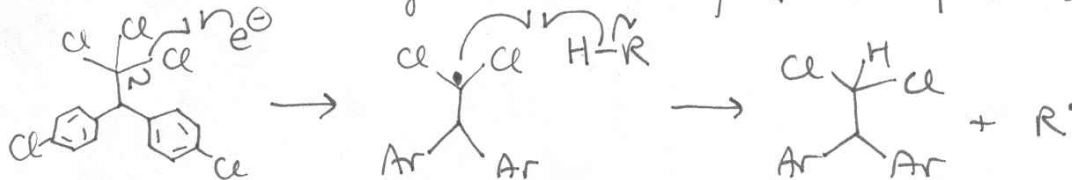
* efficiency of a particular fate for an excited molecules

$$\Phi = \frac{\# \text{ photons leading to process/rxn}}{\# \text{ photons absorbed}}$$

* quantify by (e.g.) chemical actinometry, comparing to a reaction with a known quantum yield

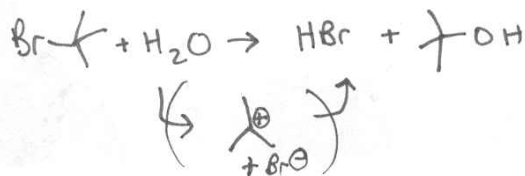
b) What is hydrogenolysis and give an example showing the reaction steps?

reductive dehalogenation whereby $\text{X}\cdot$ is replaced with $\text{H}\cdot$

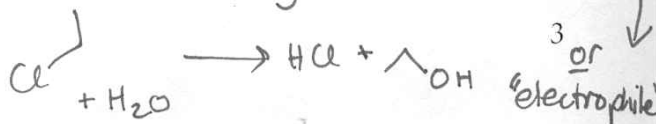


c) What drives the rate of reaction for $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ and please provide an example of each showing reagents and products.

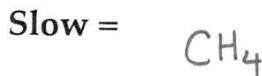
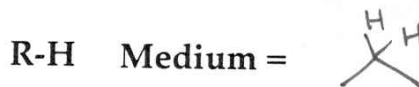
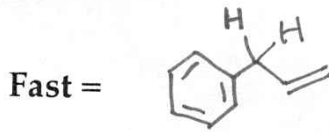
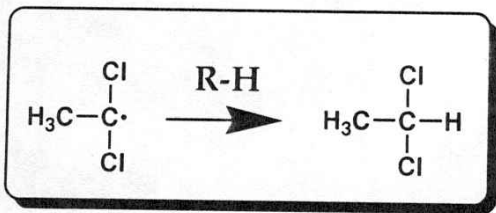
$\text{S}_{\text{N}}1$ • leaving group ability/stability
• stability of carbocation



$\text{S}_{\text{N}}2$ • nucleophilicity of Nucleophile
• leaving group ability/stability
• electrophilicity of (C-centre)
• crowding/sterics of (C-centre)

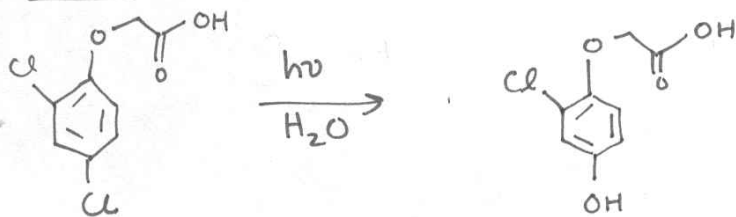


d) Perhaps a followup to your example in 'b' above: please provide three structures for R-H that would yield fast, medium, and slow abstraction of H•: (examples)



6. (10 Points). Provide a plausible structure of an pesticide of your choice (identify the general class) that you feel confident will have the potential to undergo direct photolysis. Then please list the four possible 'fates' of the excited state (ie removal of excess energy) for your herbicide after it absorbs a photon of actinic radiation; one of these will be direct photodegradation so please provide a possible photoproduct for your compound.

example

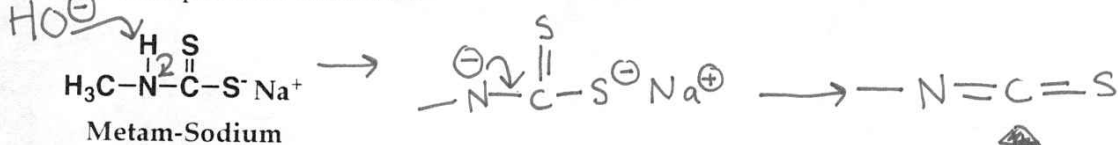


2,4-D

broadleaf
herbicide

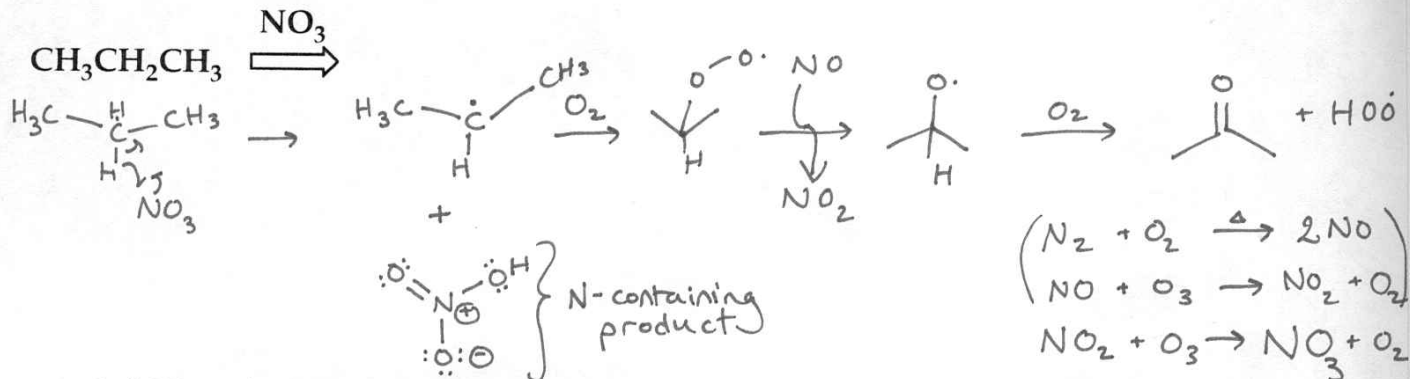
- 1) direct photodegradation
- 2) fluorescence
- 3) quenching
- 4) vibrational relaxation (heat)

7. (6 Points). In the late 1980s a train carrying Metam-Sodium spilled into the upper Sacramento River in Northern California and quickly killing all 'life' in this trophy trout stream. Please provide a chemically appropriate mechanistic explanation for what transpired in that river.



Very electrophilic C.
is toxic via reaction
with endogenous
nucleophiles

8. (8 Points). While BBQing late at night you notice a gas leak from your propane tank. What would the fate of propane be if it reacted with NO_3 ? Please draw all rxns & products, list the appropriate reagents, and draw the full structure (showing all bonds/electrons) for the 'nitrogen' containing product of the reaction shown. Finally, please indicate how the NO_3 is formed.



9. (10 Points). Please fill in the provided spaces to show the probable biodegradation pathway of 4-chlorobenzotrifluoride, a commonly used paint solvent. The initial reaction to remove it from the atmosphere is an abiotic OH addition reaction. For the final three products of the meta pathway, please circle the compound that will not degrade further under any environmental conditions. You can assume that no intermediates in the biotic pathway will inhibit the process.

