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**NAME**

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**Student Number**

**University of Toronto ~ Faculty of Arts & Sciences**

**CHEMISTRY 310S**

**•Final Examination, Spring, 2009•**

**DO NOT OPEN UNTIL INSTRUCTED TO BEGIN!!!!**

Answer all questions in **ink**; simply cross out mistakes; **Yes you can use your calculator**. Your work should be your own-absolutely no talking during the test. If you have questions please raise your hand. **Thank you**.

**The Test is 11 pages; 18 questions; 193 Points; 3 Hours in Length.**  
**[there is a 'work sheet' at the back if you need extra space for calculations]**

"We see only what we know.

~ *Goethe*

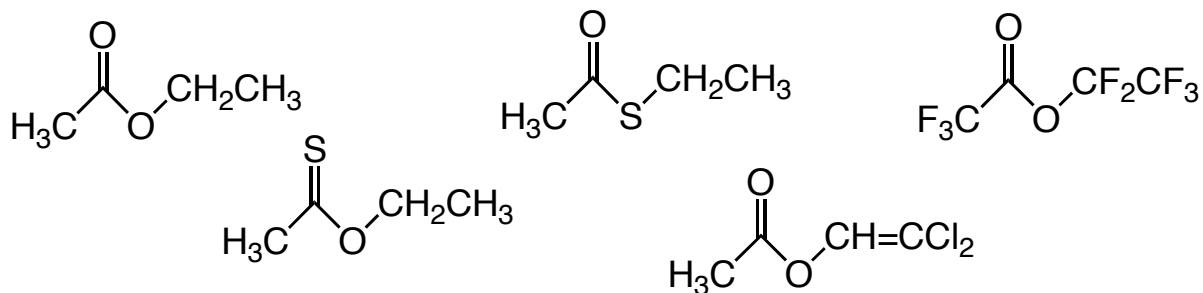
"Science is organized knowledge. "

~ Herbert Spencer

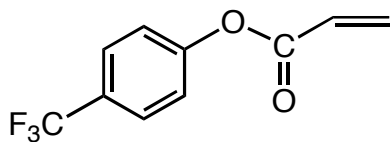
FINAL TEST GRADE \_\_\_\_\_

**1/11**

1. (10 Points). Please rank the following compounds with respect to their relative hydrolysis rates with 1 is the fastest and 5 as the slowest:



2. (10 Points). For the chemical shown, what three physical properties would you need to 'measure' in order to predict what matrix it would most likely be found in if released to the environment? Briefly describe the basic setup for making these measurements:



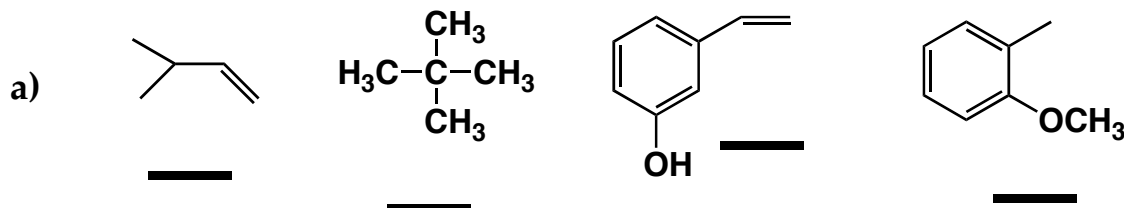
3. (4 Points). Provide a brief explanation for the following with respect to the Kow calculation method:

a) the correction factor of 1.0 (Log Kow) for an intramolecular H-bond involving OH:

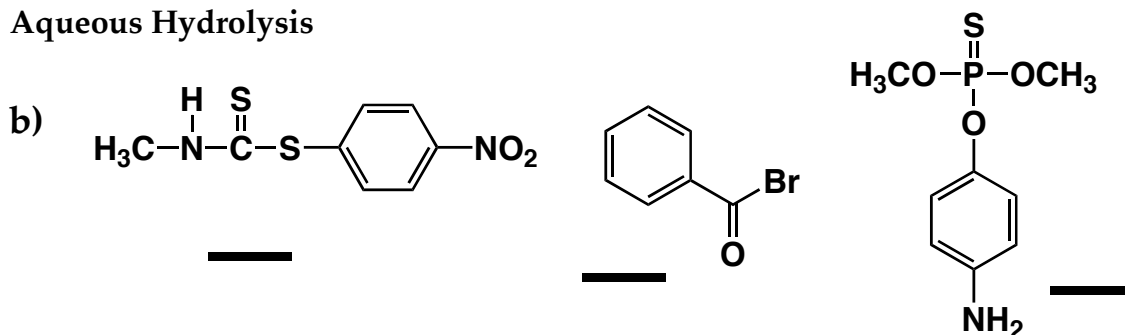
b) the correction factor of  $-0.13$  for a non-polar chain branch in aliphatic compounds:

4. (26 Points). For the following four sets of chemicals, please arrange their order of reactivity with respect to the indicated reaction/sphere where '1' is the fastest reaction.

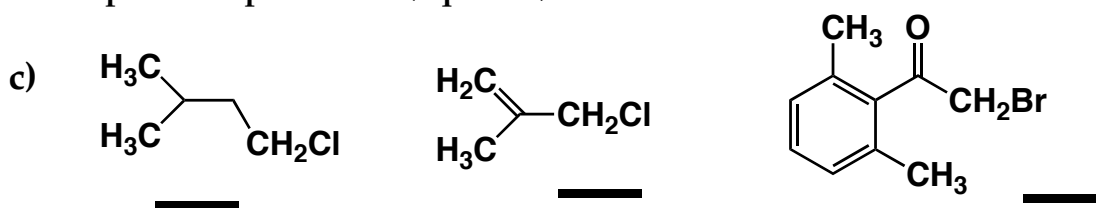
Atmospheric Oxidation



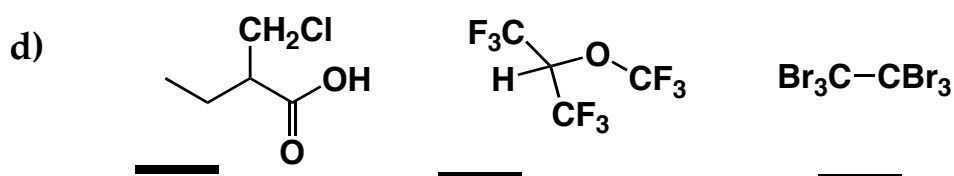
Aqueous Hydrolysis



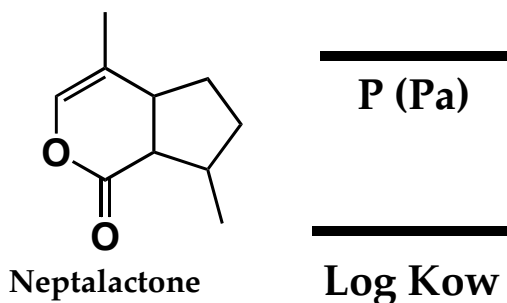
Nucleophilic displacement (aqueous)



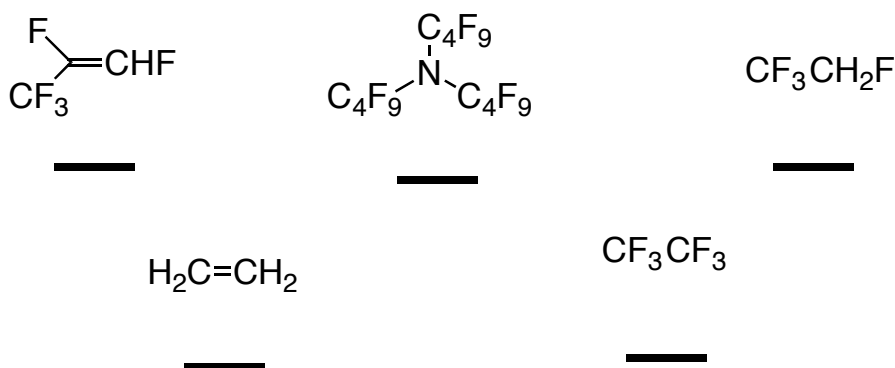
Elimination (sediment)



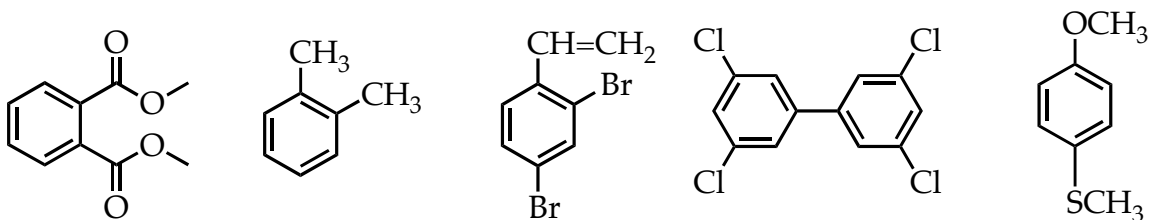
5. (12 Points). **Neptalactone** is the active ingredient in *catnip* responsible for making cats go a bit haywire. Please answer the question of whether it is wise to store your catnip in the freezer instead of the counter, to keep it 'active', by calculating the vapour pressure of this chemical. Provide your answer in Pascals and 'yes or no' to the freezer storage. Secondly, if you managed to spill catnip onto your shirt please suggest whether a quick rinse with water would be effective at removing the active ingredient, and thus avoiding being pursued by all the cats in the neighborhood. To do so it would be best to calculate the  $K_{ow}$  for this compound. [you can do calculations on the back of this sheet or the extra sheets provided]



6. (10 Points). Rank the following chemicals with respect to their global warming potential (where 1 has the HIGHEST global warming potential and 5 the lowest).

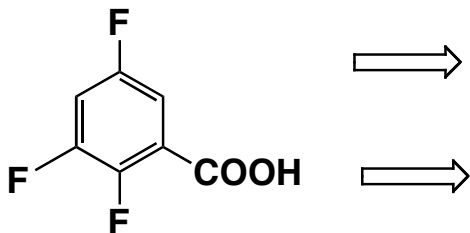


7. (10 Points). Please rank the following compounds with respect to their relative Kow values ~ 1 is the lowest and 5 is the highest:



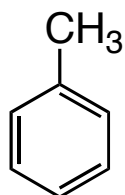
8. (18 Points). Metabolism question ~ please answer the following 2 questions by providing the appropriate *chemical* answers:

a) Please provide two reasons why trifluorobenzoic might be highly persistent:



b) Why might  $\text{CCl}_4$  be problematic for your liver if it were routinely used in Orgo Lab?

9. (7 Points). With respect to the free energy change in dissolving toluene and isopropanol in water, **briefly** compare and contrast (in the space provided) these two chemicals with respect to water solubility:



10. (13 Points). a) Prior to industrialization how was the  $[O_3]_{ss}$  maintained in the stratosphere? Please provide the basic generation and consumption cycles:

b) Two parts: What is a good example of a chemical that disrupted this  $[O_3]_{ss}$ ? What is a good example of a chemical that would be viewed as a 'replacement' to mitigate this problem?

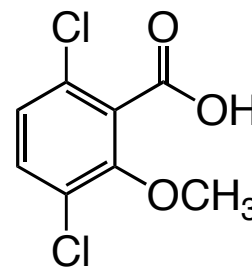
c) What is the main problem that results from reducing  $[O_3]_{ss}$  in the stratosphere?

11. (10 Points). Dicamba is a widely used herbicide. Please predict, from structure, its Log Kow and V.P. (Pa) and suggest which "sphere" you expect this compound to be found in under typical environmental conditions.

Log Kow =

V.P. =

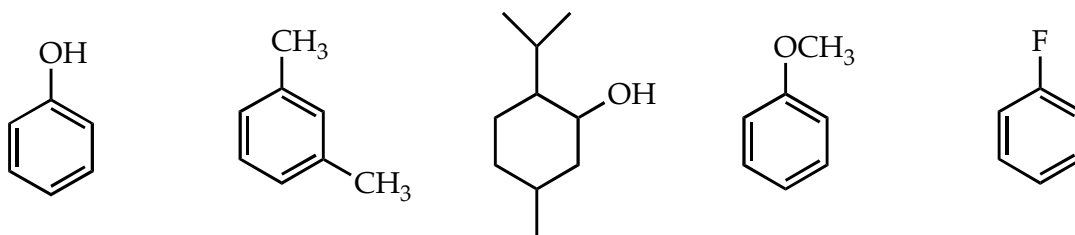
sphere =



Dicamba  
m.p. = 115C

Dicamba is capable of undergoing photonucleophilic displacement. Upon irradiation with actinic light at a suitable pH, it was found that only one of the two Cl groups is effectively replaced by OH. Which chlorine group is more likely to react and give a brief explanation why.

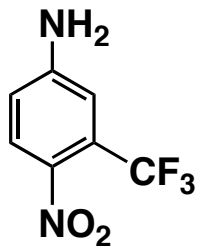
12. (10 Points). Please rank the following compounds with respect to their relative vapour pressure values ~ 1 is the lowest and 5 is the highest: [all are liquids]



13. (6 Points). It has been claimed there are natural sources of chlorinated dioxins. One hypothesis, if this is true, involves microorganisms that have high haloperoxidase activity; haloperoxidases produce HOCl as a highly reactive reagent. You have not seen this reagent in class before but realize that the O is more electronegative than Cl and thus a nucleophilic attack on HOCl can lead to the creation of a carbon chlorine bond. Consider the bogs of Nova Scotia and posit a plausible pathway for the production of the following chlorinated dioxin starting with phenol and HOCl.

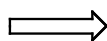
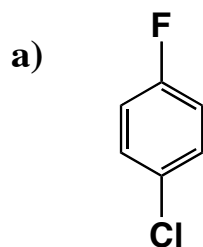


14. (6 Points). The aromatic amine shown below is similar to degradation products of a number of pesticides. With clear chemical illustrations, please describe the sorption mechanisms (three) by which this compound may associate with soil or soil constituents.



15. (18 Points). Dichlorobenzene (DCB) is used widely as a disinfectant in toilet bowls. Please provide the structures you expect for the following conditions:

a)



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First Stable Atmospheric Product

Scavenged  
by  
rain

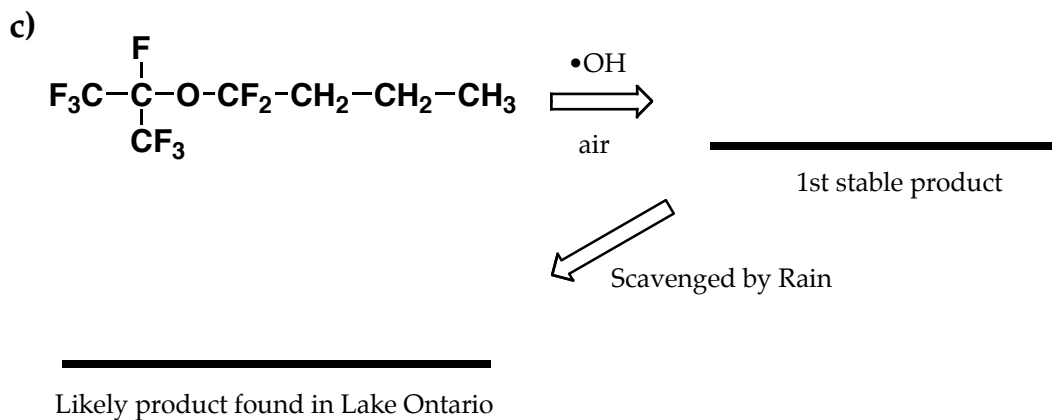
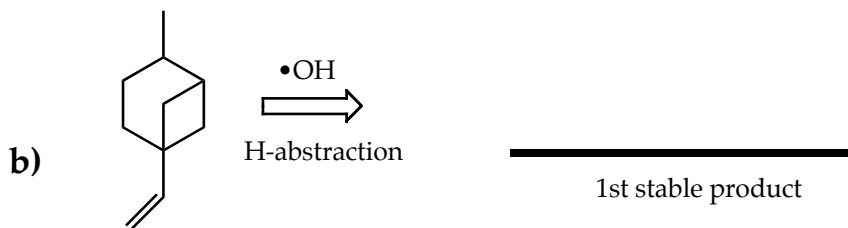


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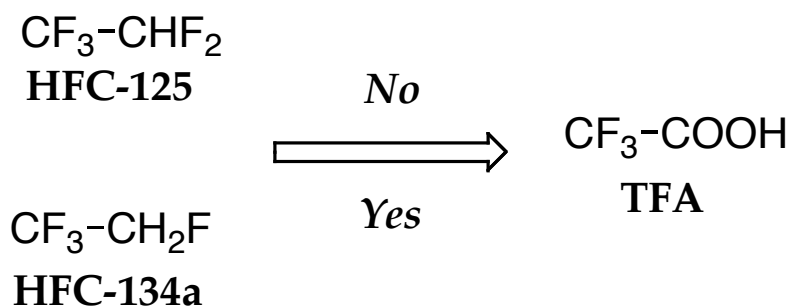
..and the product of one more  
cycle of that reaction?

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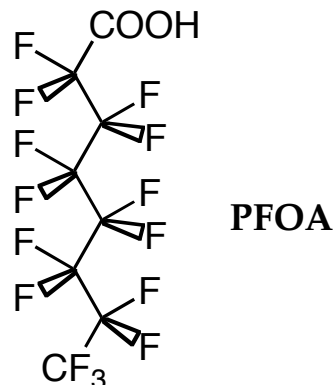
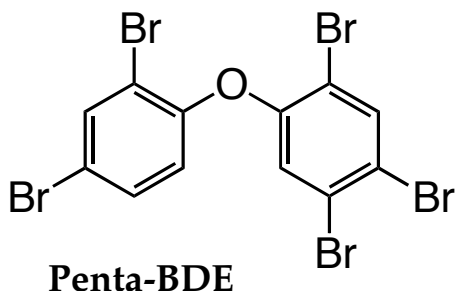
First stable product in sunlit  
Lake Ontario



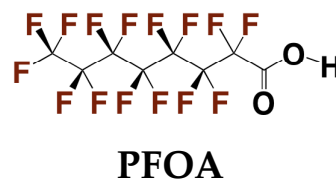
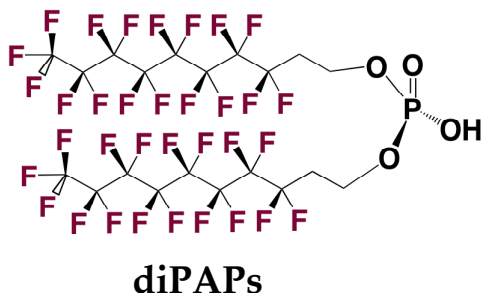
16. (7 Points). Interestingly, HFC 134a does produce TFA upon atmospheric oxidation while HFC-125 apparently does not. Can you briefly describe a plausible reason why? A structure or two might help you illustrate and is all that is required.



17. (8 Points). Pentabrominated diphenyl ether (penta-BDE) and perfluorooctanoate (PFOA) are two persistent organic pollutants (POPs) that have been detected, in relatively high concentrations, in polar bears from the Canadian Arctic in relatively high concentrations. Compare and contrast transport pathways of these compounds to the Canadian Arctic.



18. (8 Points). The eight carbon version of the polyfluoroalkyl phosphoric acid diesters (diPAPs) and perfluorooctanoic acid (PFOA) are observed in human blood at similar concentrations (1-4 mg/L). DiPAPs is a commercial product used to greaseproof paper food packaging. PFOA is not a commercial product, but the recalcitrant degradation product of a variety of fluorochemical commercial products.



Questions for 6 are on next page.....**10/11**

a) Could the diPAPs in human sera be responsible for some of the observed PFOA contamination? To probe this hypothesis, propose a metabolic pathway to produce PFOA from diPAPs. For every step provide appropriate structures and identify the metabolic reaction occurring.

b) Compare the bioaccumulation of diPAPs and PFOA, which would you expect to be longer-lived in the body and why?

*The End*  
**Have a Great Summer**

## **Work Sheet (if needed)**

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