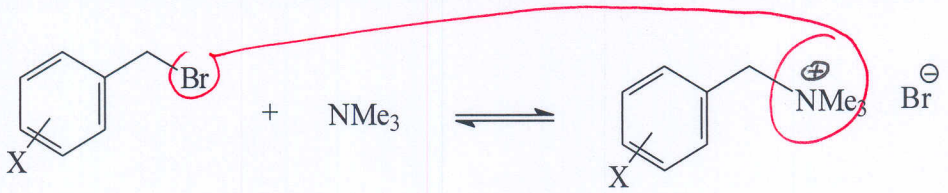
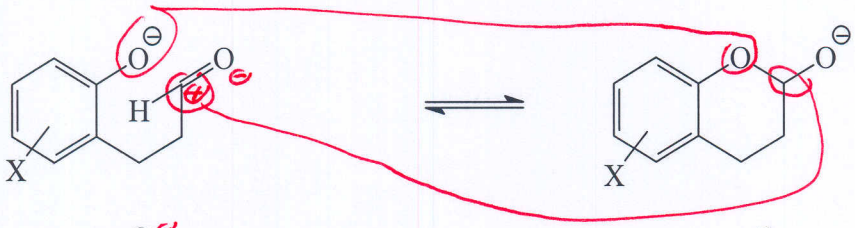
Chemistry 4483a 2009
Midterm Quiz #1
Name: _____

Answer all questions in the space provided. The time allotment is indicated.

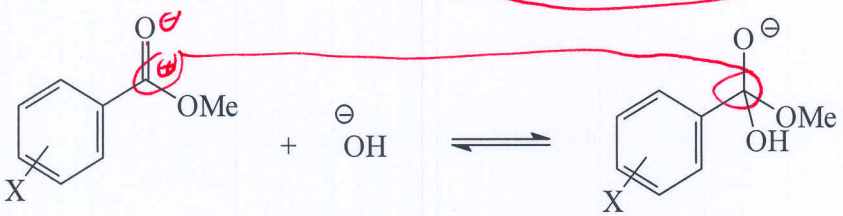
5) 1] Estimate ρ values (sign and magnitude) for log K for each of the reactions below



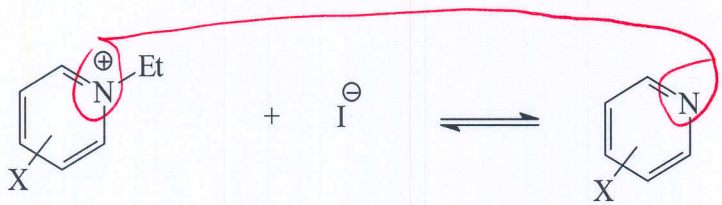
−1



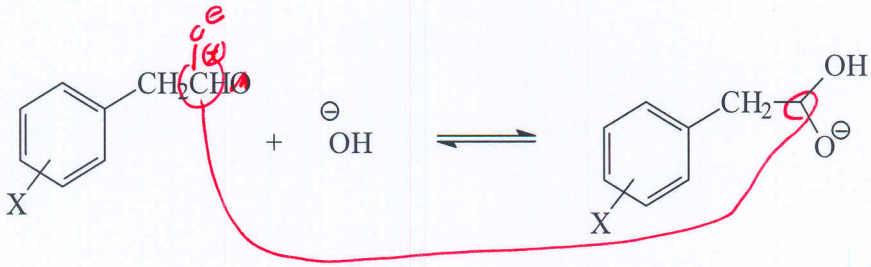
−1.5



+2



+4



+1

5) 2] The pKa for methanesulfonic acid, CH_3SO_3H, is -1.92. Predict the pKa for trifluoromethansulfonic acid, CF_3SO_3H

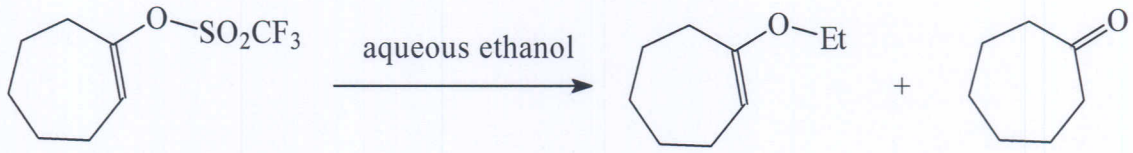
X-SO₂-OH & X-CO-OH ; $\rho^x = 1.6 = \frac{\Delta pK_a}{\Delta\sigma}$; EWG make pKa smaller

$\Delta\sigma^x = \sigma^x_{CF_3} - \sigma^x_{CH_3} = 2.61 - 0.0 = 2.61$

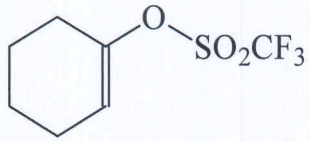
$\Delta pK_a = \rho^x \cdot \Delta\sigma^x = -4.18$

$pK_a(CF_3SO_3H) = -6.10$

20) 3] An investigation of the mechanism of the following reaction

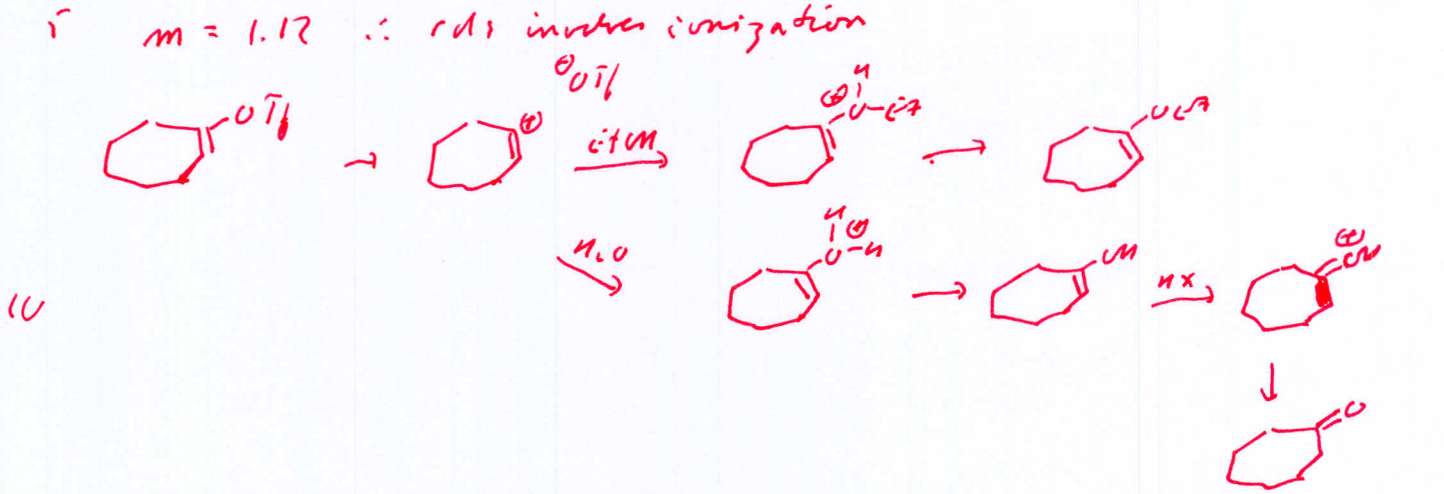


in various aqueous ethanol mixtures at 75°C led to a Grunwald-Winstein *m* value of 1.12, based on Y_{OTs} values for the solvents. These reactions are slow, but

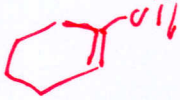


is much slower.

Write a mechanism for this reaction which is consistent with all the evidence. Indicate the rate determining step. Explain how your mechanism is consistent with each bit of evidence

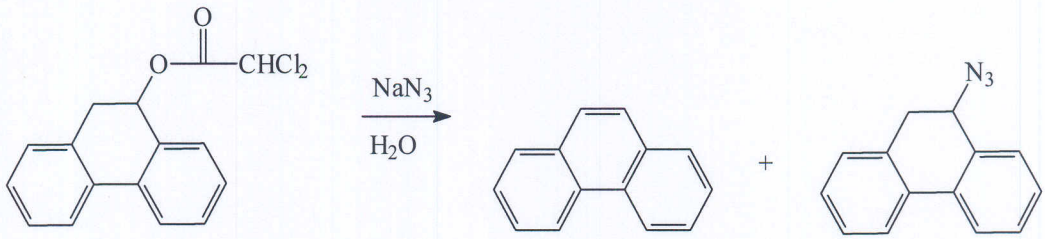


reaction is slow because
a) bad cation ($sp^2 \rightarrow sp$) - charge on electronegative carbon
b) cation wants to be linear, ∴ strained ring



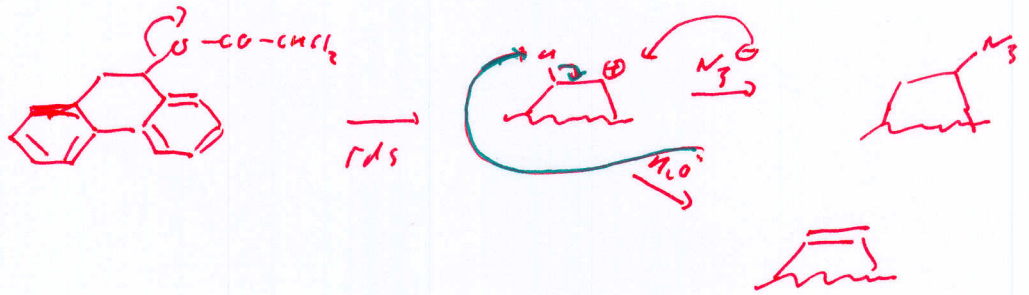
is slower because a smaller ring ∴ linear is much more

20) 4] The reaction shown below was studied in aqueous solution. Addition of NaN_3 did not change the rate of disappearance of starting material but led to formation of the azide product, 9,10-dihydrophenanthryl-9-azide. A plot of [9,10-dihydrophenanthryl-9-azide]/[phenanthrene] vs. $[N_3^-]$ gave a slope of 0.135 M^{-1}. The rate constant for diffusion controlled reaction of an anion and a cation is $5x10^9$ $M^{-1}s^{-1}$.



Phenanthrene 9,10-dihydrophenanthryl-9-azide

a) Write a mechanism consistent with the facts presented. Indicate the rate determining step.



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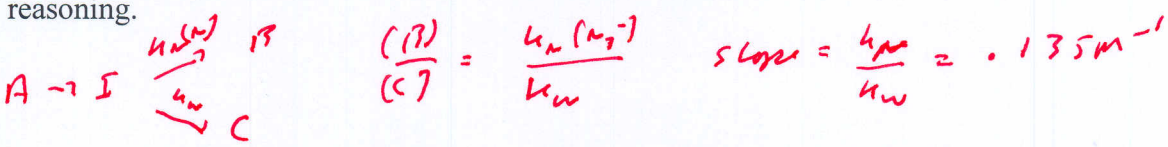
b) Calculate the rate constant for loss of a proton to give phenanthrene. Explain your reasoning.



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$$k_w = \frac{k_N}{.135} = \frac{5\times10^9}{.135} = 3.7\times10^{10}\ s^{-1}$$