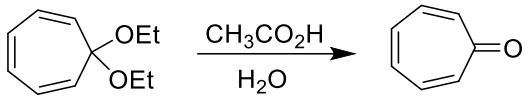
CML 103 (2020-21) Final exam (Total Marks: 70)

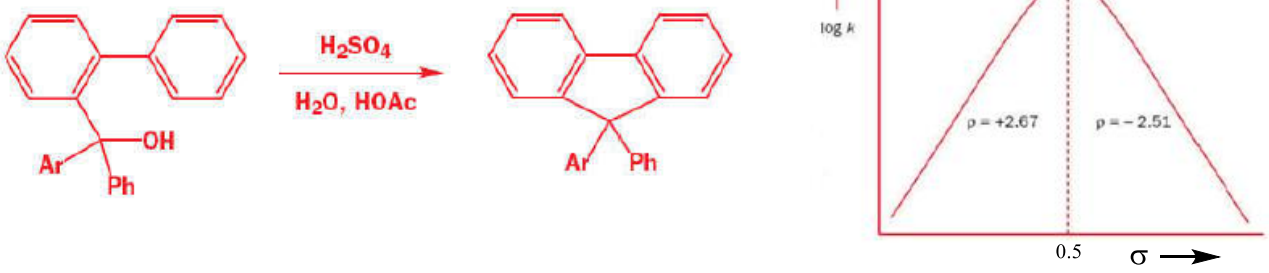
Part-1 (50 marks)

1. Q. The following reaction occurs by a general-acid catalyzed mechanism. Propose a mechanism for this reaction. Draw every step clearly and cite the rate determining step. (3) Propose minimum five experiments you can devise to support your proposed mechanism. (5)



2. Q. Draw the possible mechanism of the following cyclization reaction, and assign the rate determine steps with reasons that follows the non-linear Hammett plot given below. (3+3)

Hammett plot

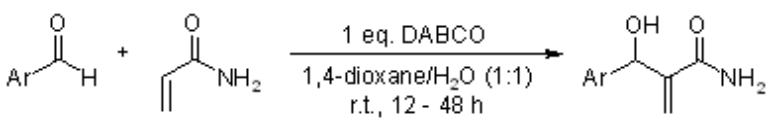


3. In the large-scale industrial production of methylamines, methanol and NH_3 are reacted at 350–500 °C and 20 bar in the presence of Al_2O_3. A mixture of mono-, di-, and trimethylamine is obtained with an equilibrium content of ca. 62% trimethylamine. However, trimethylamine is of only minor economic importance. Suggest how the product spectrum could be modified to favor mono- and dimethylamine. (3)

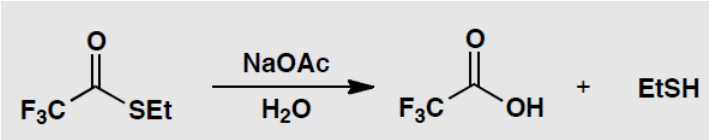
4. Answer each of the following with reference to the corresponding substituent constants considering both inductive and resonance electronic contributions. Illustrate your answer showing resonance structures for substituted benzoic acids, where appropriate.

(a) The σ_{meta} and σ_{para} values for the $–CO_2CH_3$ group are both positive with $\sigma_{para} > \sigma_{meta}$. Why? (2)
(b) The values of σ_{meta} for the methoxy substituent ($–OCH_3$) is positive, whereas the values for σ_{para} is negative. Why? (2)
(c) The picryl (2,4,6-trinitrophenyl) substituent, $-C_6H_2(NO_2)_3$ is relatively large with the ortho nitro groups sterically interfering with atoms in the ortho positions on an adjacent aromatic ring. Predict the sign and relative magnitude of σ_{meta} and σ_{para} for the picryl substituent. (3)

5. Draw the mechanism of the following reaction. Show all the steps clearly. (6)

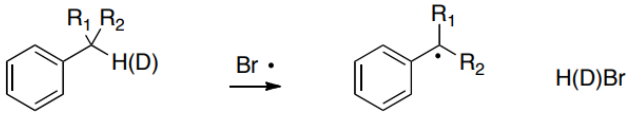


6. Between pH 2 and 7 the rate of hydrolysis of this ester is independent of pH. At pH 5 the rate is proportional to the concentration of acetate ion (AcO^-) in the buffer solution and the reaction goes twice as fast in H_2O as in D_2O. Suggest a mechanism for the pH-independent hydrolysis. (2)
Above pH 7, the rate increases with pH. What kind of change is this? (2) Solved it likewise



7. What can you infer about the nature of the transition state based on the KIE data of the following reaction? (3)

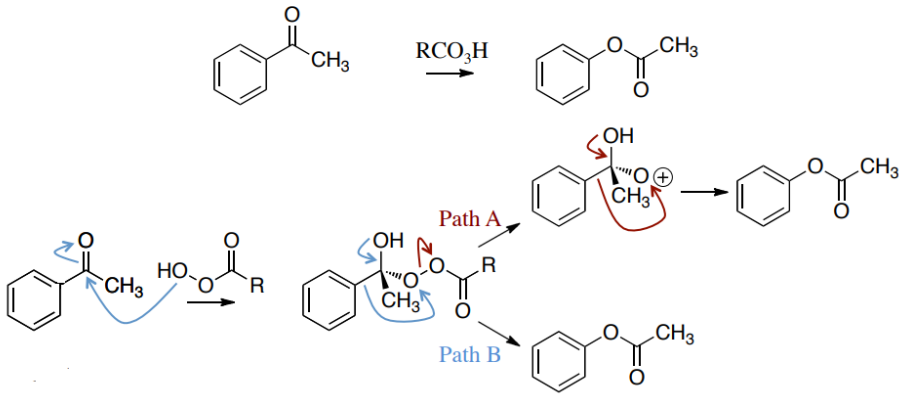
Consider the KIE data for the following reaction



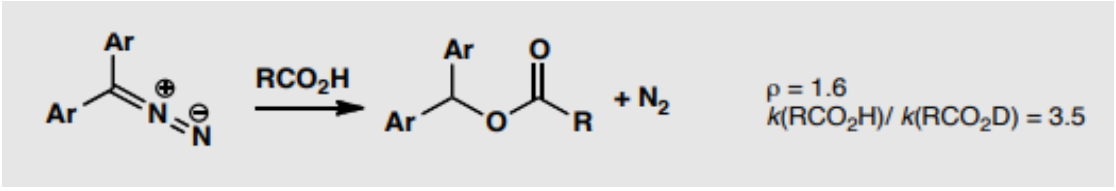
R_1	R_2	k_H/k_D
H	H	4.9
CH_3	H	2.7
CH_3	CH_3	1.8

8. Propose minimum two experiments you can devise, that can be used to distinguish between A- and B-pathway given below. Explain each experiment how it can distinguish one pathway compare to the other pathway. (3+3) 1. reason is unique one could be asked again

Consider a Baeyer-Villiger oxidation



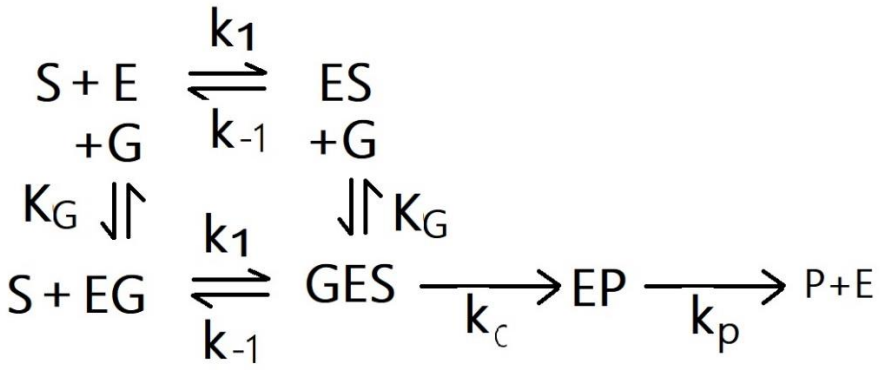
9. The reaction of diazo compound with carboxylic acid give gaseous nitrogen and esters as products. Based on the experimental data given below, draw a suitable mechanism and cite the rate determining step. (4)
Also, draw the energy profile diagram of the same reaction pathway. (3)



Part-2 (20 marks)

(1) 50 mL of a fluid with 50% of ethanol was taken by pet dog Sheru mistaking it for wine. Oxidation of methanol by Liver alcohol dehydrogenase (ADH), an enzyme, produces formaldehyde which is toxic. Ethanol can act as competitive inhibitor of ADH, his doctor decided to give him a wine having 12% Ethanol. How much of wine Sheru should consume in order to lower the activity of his ADH on methanol to 5% of its normal value. K_M values of canine ADH for ethanol and methanol are 1 mM and 10 mM respectively. Assume methanol and ethanol to distribute quickly throughout Sheru body fluid which is around 15 L. Density of 50% ethanol and the wine are both 0.9. (Hint: KI for ethanol for oxidation by ADH is same as its K_M) [8]

(2) The ribozyme (an enzyme, E) uses a guanosine cofactor (G) to cleave a ribo-oligonucleotide substrate [S]. A simplified mechanism for the reaction is:



Derive an expression for the steady state concentration of GES and d[P]/dt in terms of total concentration of enzyme, $[E_0]$, [S], [G], rate constants k_1, k_{-1}, k_c, k_p and dissociation constant K_G (Remember that $[E]_0=[E]+[ES]+[GE]+[GES]$. [8]

(3) Derive the rate equation for a bimolecular reaction occurring between A and B and inhibited by a diatomic molecule X_2 which is adsorbed with dissociation into atoms. What equation applies if A and B are adsorbed very weakly and X_2 very strongly. [4]

Important Note: There will be step wise marking. Make sure that every step is written in answer sheet. Skipping of any step will result into deduction of mark. Answer sheet will be checked strictly for plagiarism.