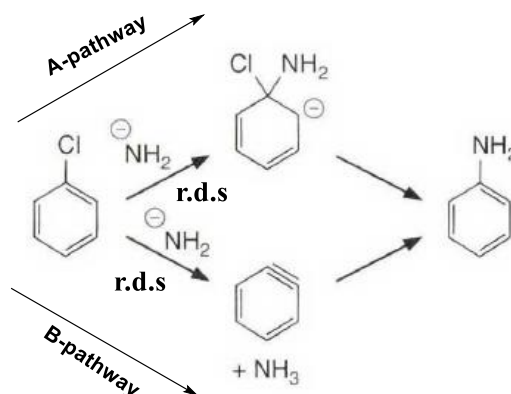


1. The treatment of chlorobenzene with potassium amide in liquid ammonia results in the formation of aniline. Propose **minimum three experiments** you can devise, that can be used to distinguish between the two mechanisms given below. Explain each experiment how it can distinguish one pathway compared to the other pathway. (6)



A. 1 point each for correct 2, 3 and 4; and 1 point for each correct explanation.

Rate law is same for both pathways and therefore it is an incorrect answer.

A pathway:

1. $\text{rate} = k[\text{chlorobenzene}]^1[\text{amide}]^1$; as both substrates are involved in the rds
2. $\Delta S^\ddagger = \text{large } (-) \text{ value}$
3. $k_{\text{C-H}}/k_{\text{C-D}} = 0$; no kinetic isotope effect; as no C-H/C-D bond is breaking in the rds
4. ρ is (+) 4.0 or larger value as the negative charge build up in the aromatic ring

B pathway:

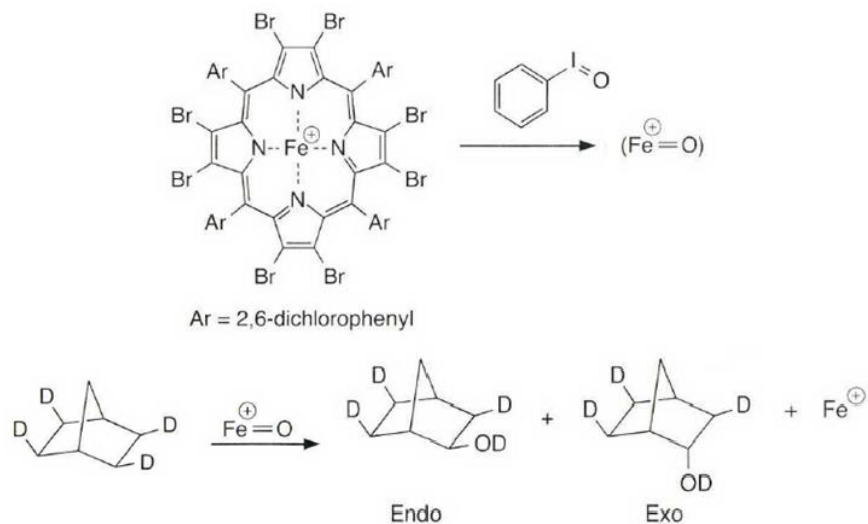
1. $\text{rate} = k[\text{chlorobenzene}]^1[\text{amide}]^1$; as both substrates are involved in the rds
2. $\Delta S^\ddagger = 0$
3. $k_{\text{C-H}}/k_{\text{C-D}} > 3$; Primary kinetic isotope effect; as C-H/C-D bond is breaking in the rds
4. small ρ value and the value is close to 0 as no charge build up in the aromatic ring

2. The hydroxylation of deuterionorbornane catalyzed by the following iron-oxo complex gives

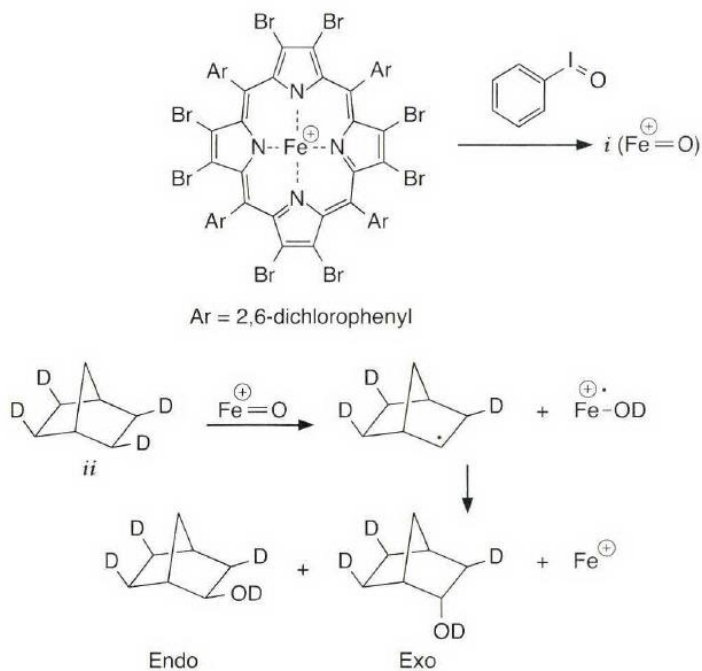
a) A mixture of endo- and exo-norboran-2-oIs is produced

b) Shows a primary kinetic isotope effect of $(k_H/k_D) = 5$

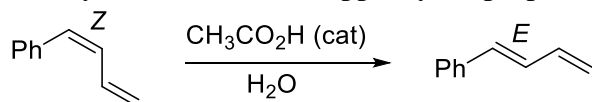
What mechanism might account for this? (3)



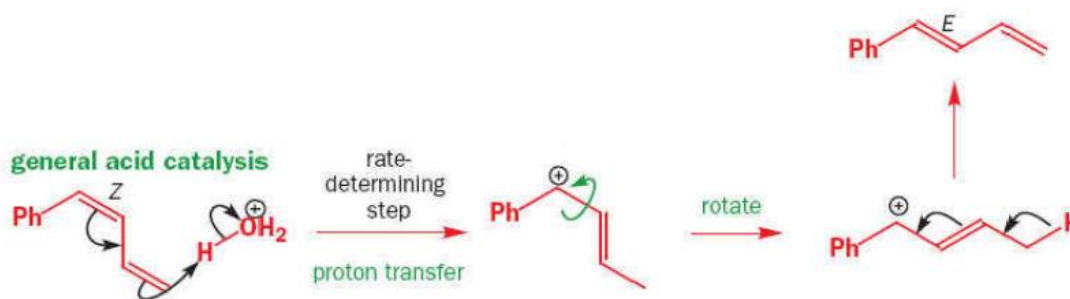
A.



3. 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**). Propose minimum three experiments you can devise to support your proposed mechanism. (3+3)



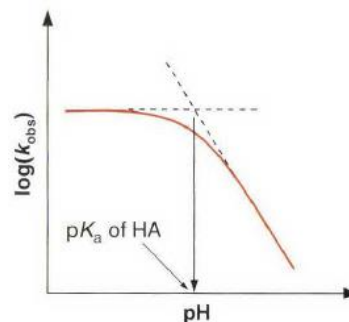
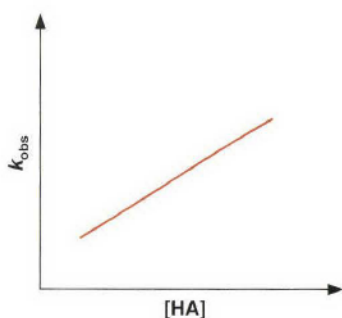
A. a) RDS: 1point, 2 point for each step correctly.



Isomerization of the allylic alcohol is SAC—NO protonation in the slow step.

b) 3 points for any correct three experiments among 5 options given below

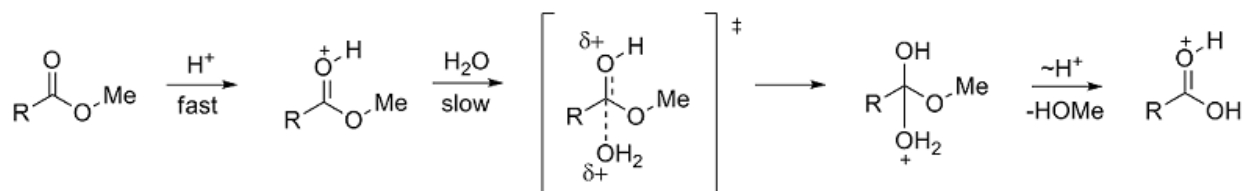
1. ΔS^\ddagger = large – value
2. $k_{\text{O-H}}/k_{\text{O-D}} > 2.0$; primary KIE or rate in H_2O is faster than in D_2O
3. $\rho = (-)$ vs
4. Rate = $k [\text{substrate}][\text{HA}]$
- 5.



4. Q. The acid-catalyzed hydrolysis of substituted ethylbenzoates has a ρ value of 0.14, whereas the base-catalyzed hydrolysis of the same series of compounds shows a ρ value of 2.19. Why is there such a difference? **Explain with mechanisms** (3)

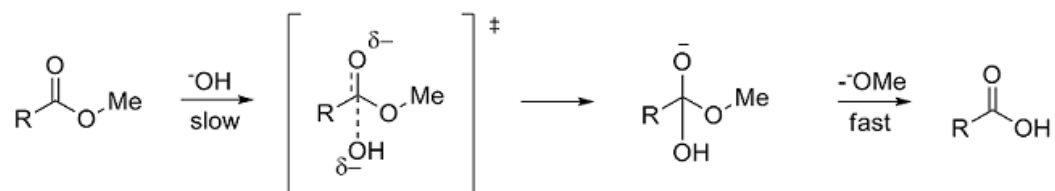
A. for each mechanism, showing the correct TS is 0.5 mark. Rest of the mechanism: 0.5 mark each.

Acid Catalyzed Ester Hydrolysis:



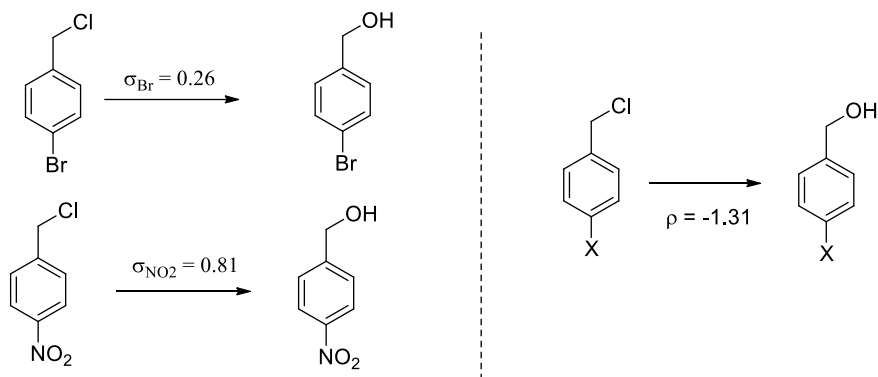
A slight of negative charging is building in the slow rate determining step due to the diffusion of the positive charge, thus ρ value is positive and less.

Base Catalyzed Ester Hydrolysis:



A lot of negative charging is building in the slow rate determining step thus ρ value is positive and high.

5. Q. Determine the value of k_{p-Br}/k_{p-NO_2} . **Show detailed calculation.** (4)
Which reaction is faster? (1)



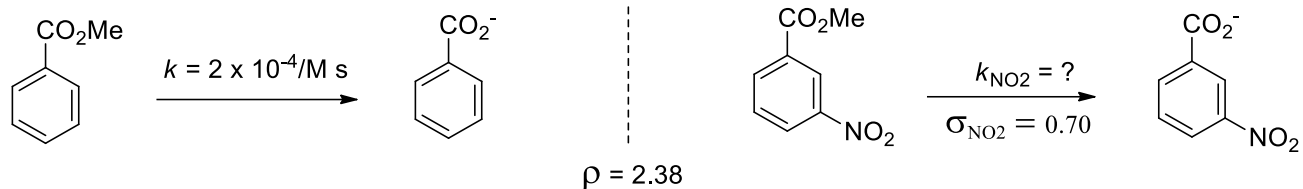
$$\log(k_{p-Br}/k_H) = \sigma\rho = -1.31 \times 0.26$$

$$\log(k_{p-NO_2}/k_H) = \sigma\rho = -1.31 \times 0.81$$

$$k_{p-Br}/k_{p-NO_2} = 5.25$$

2. p-Br reaction is faster.

6. Q. What is the value of k_{NO_2} ? (3)



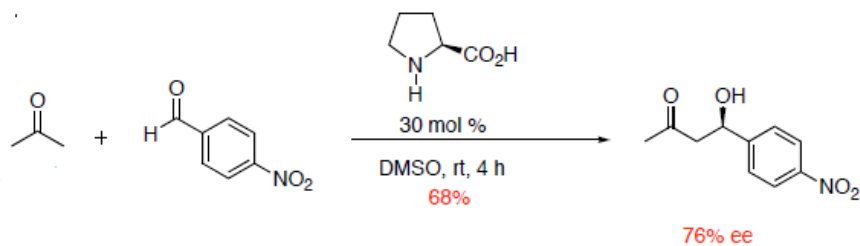
A. one point for correct formula and put data correctly (first line). 1 marks for correct calculation. 1 point for correct final value of k_{NO_2} .

$$\log(k_m/k_H) = \sigma\rho = 0.70 \times 2.38 = 1.666$$

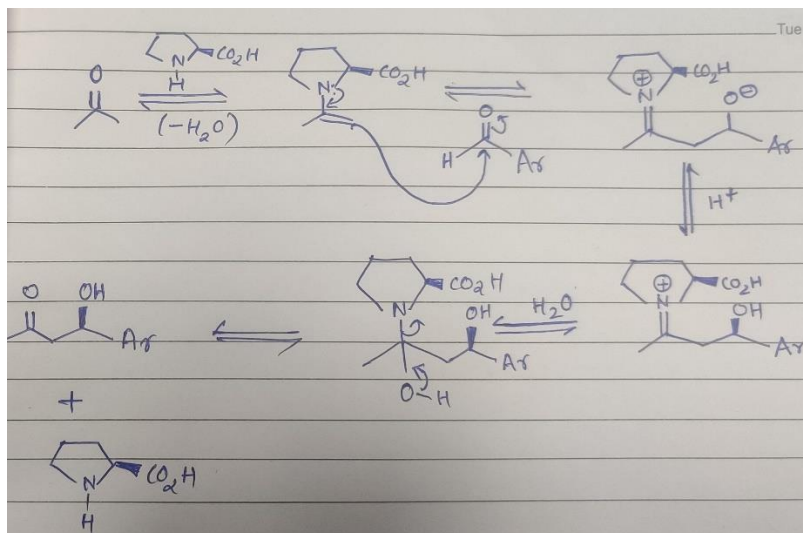
$$k_m/k_H = 10^{1.666} = 46.345$$

$$k_m = 46.345 \times k_H = 92.69 \times 10^{-4} / \text{M s}$$

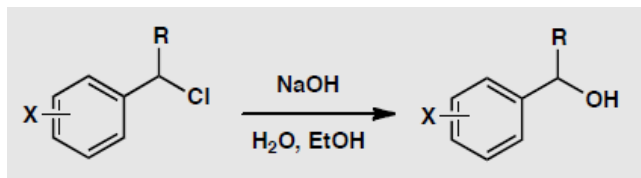
7. Draw the mechanism of the following reaction. Show every step clearly. (4)



A.

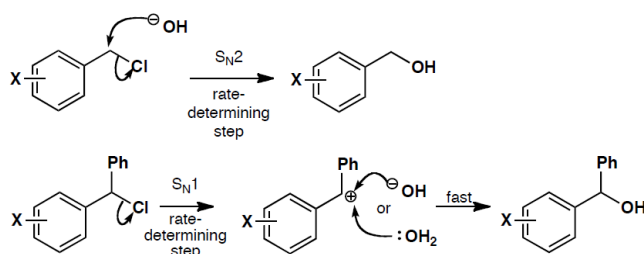


8.Q. Explain the difference between these Hammett ρ values by **drawing mechanisms** for the two reactions. In both cases the ring marked with the substituent X is varied. When R = H, $\rho = -0.3$ but when R = Ph, $\rho = -5.1$. (4)

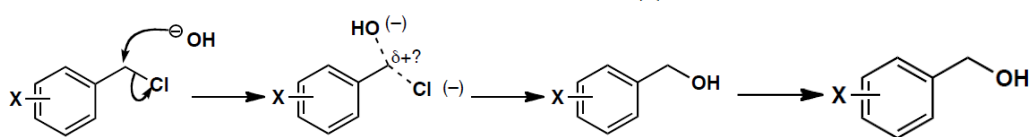


A.

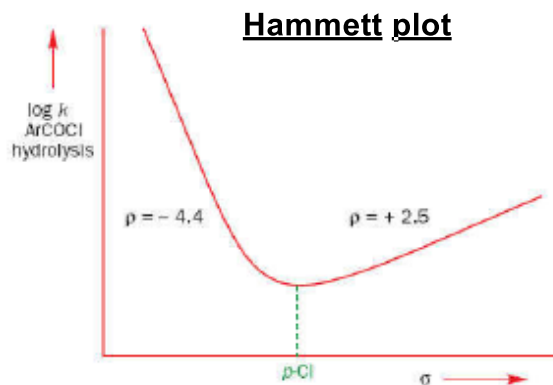
1.



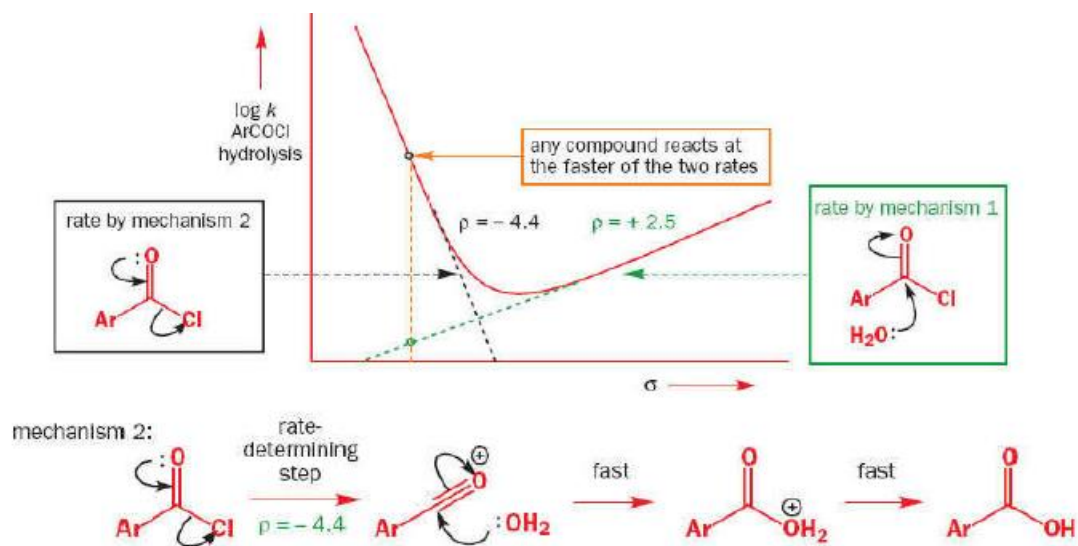
2.



9. Q. The hydrolysis of the following acyl chloride displayed a non-linear Hammett plot. Draw the possible mechanisms of the hydrolysis reaction and assign the rate determine step that follows this non-linear Hammett plot. (6)



A.



2+2 marks for each mechanism for all correct pathways.

One point for showing carbocation in first mechanism ($\rho = -4.4$) and one point showing anion in second mechanism.