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Entry No. : 2020CH70196

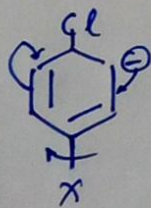**Q1.**

25

(a.) Isotopic effect (i.e H labelling)

C-H/C-D
(As bond is breaking in
RDS step ∴ PKIE)
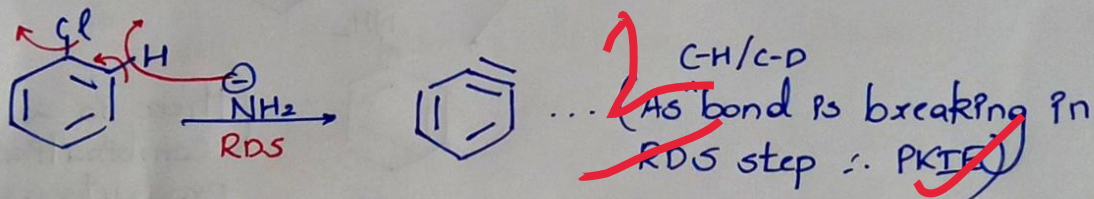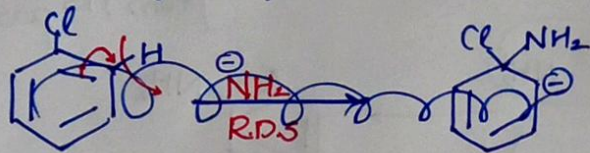
Whereas in the pathway-A there is not breaking of C-H/C-D bond & its involvement. Hence not Kinetic isotopic effect occurs
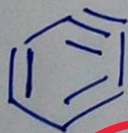
(b.) Sensitivity Const.(s) & its measurent for some substituents.

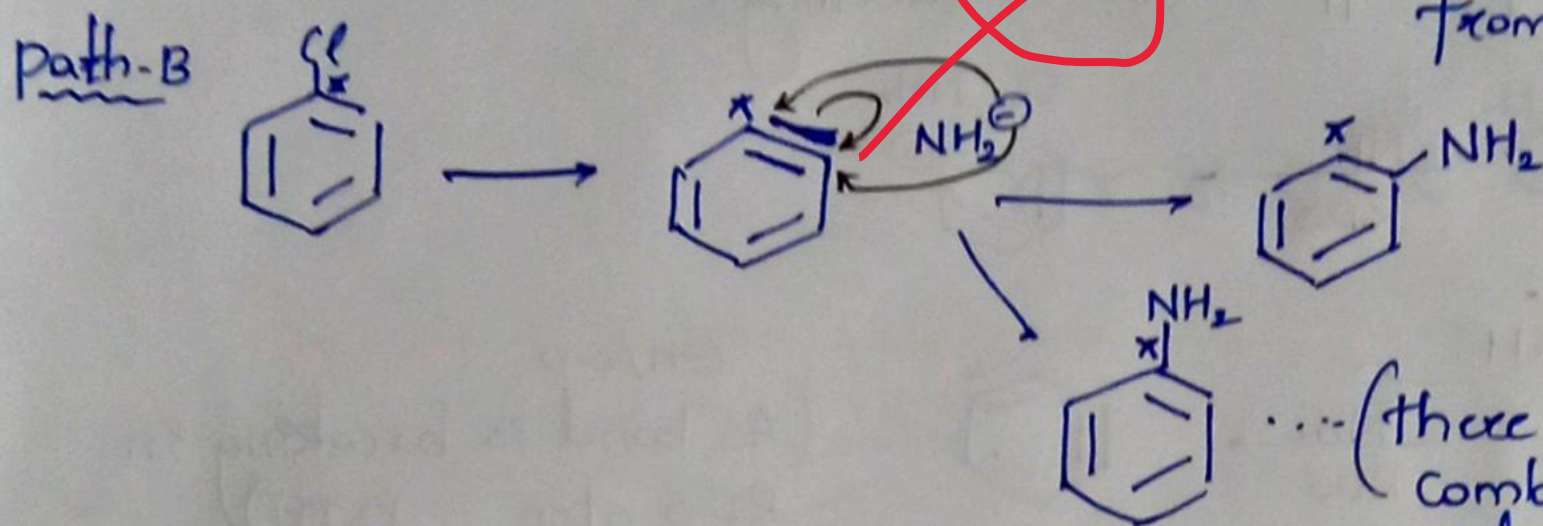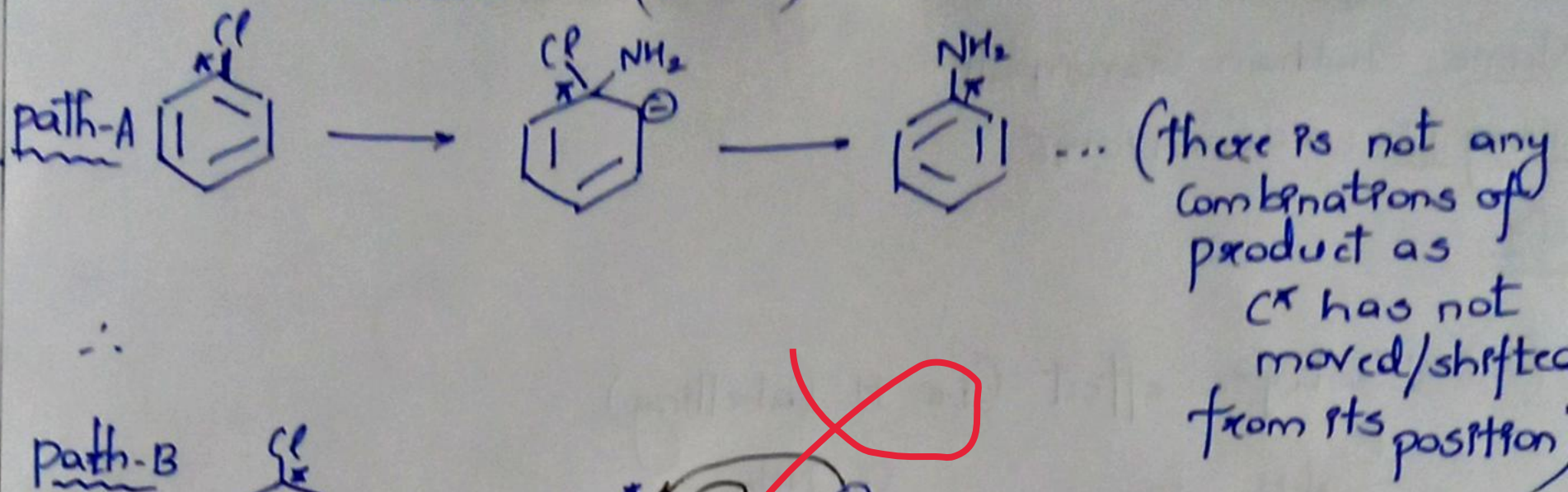As the -ve charge is delocalised in the whole Ar ring (& in the T.s step)
∴ (The value of s = high i.e > 1)

Whereas in pathway-B there is :

not -ve/ charge is involved in the T.s as well as in the step so the s value will be close to zero.

(c.) C^{14} denotation: $(C^{14} \equiv C^*)$

path-A

... (there is not any combinations of product as C^* has not moved/shifted from its position)

∴

path-B

.... (there is a combination 2 products as the attack of $NH_2^{\ominus}$ is possible on both sides of the $\equiv$ bond)

∴ These are three experiments that are devised, for distinguishing between the path-A & path-B

Q2.

(a.)
(b.) ... (Given in questions)
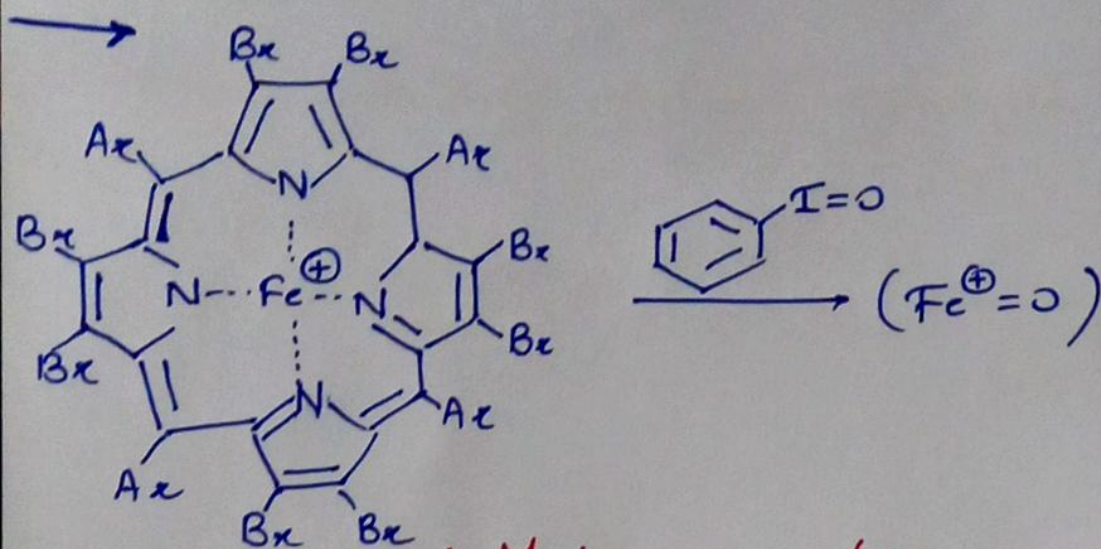
Proposed Mechanism goes/Occurs as follows:-

"Endo"   "Exo" $\}$
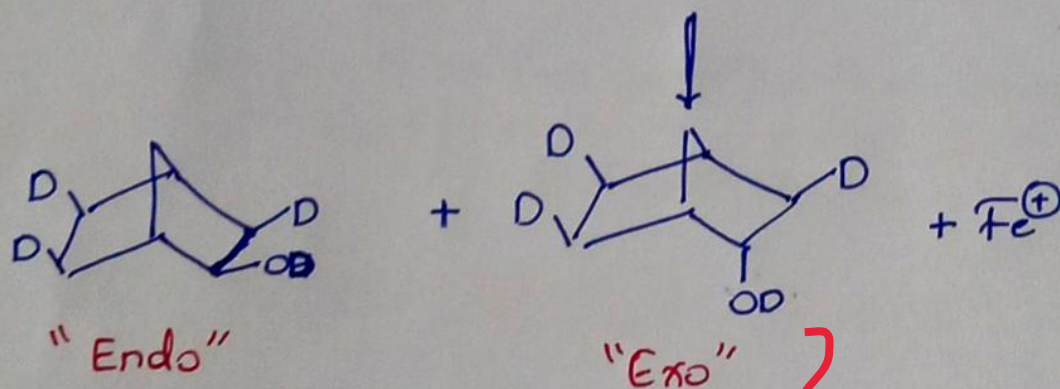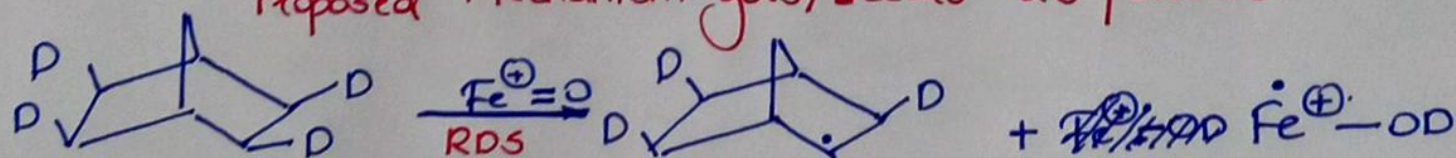
As the (b.) pt. says $R_H/R_D = 5$ i.e Primary Kinetic Isotopic Effects takes place (As from Mechanism also in 1st step (i.e RDS) the C-H/C-D bond is broken.

(This whole concept and problem was taught by Prof. Kuntal Manna & have referred & praticed by that concept)

94.

→ Ethylbenzoates:

1. ~~starting from~~ Acid catalysed Hydrolysis :- ($\rho = 0.14$)

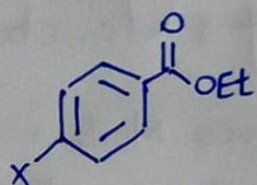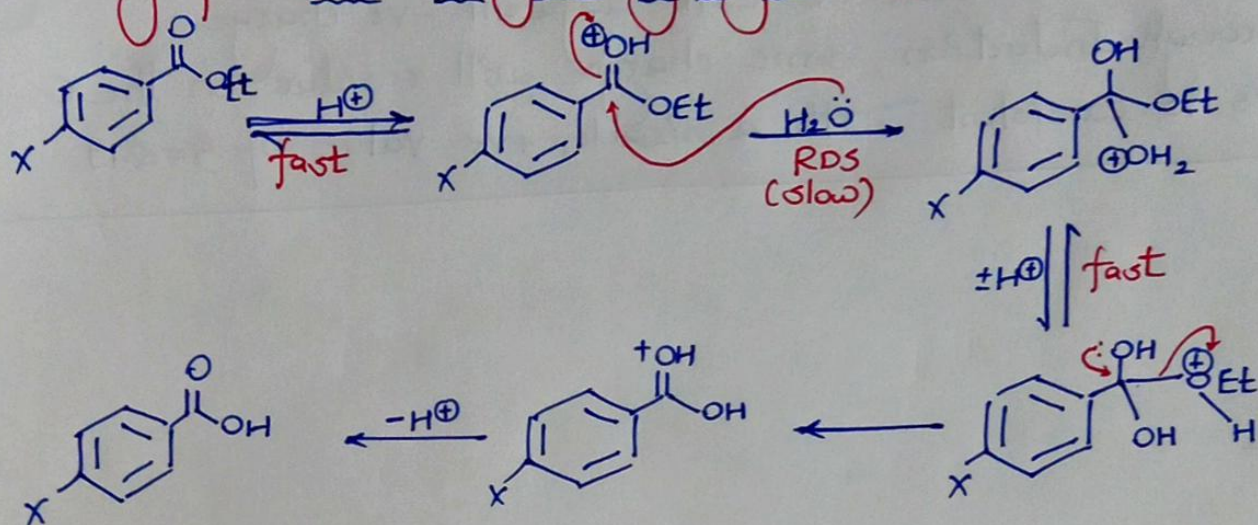(Sensitivity const.) $\rho = 0.14$ (i.e it is less sensitive than benzoic Acid (Reference Rxn)) [As it is just close to O i.e. A less, EWG is Attached to the Ar ring which /weak gives small +ve value]

2. For Base catalysed Hydrolysis : ($\rho = 2.19$)
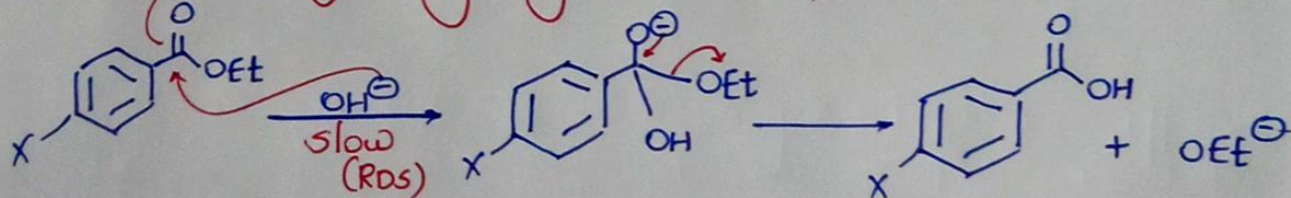
$\rho = 2.19$ (i.e It is more sensitive than

2 ✓
No T.S
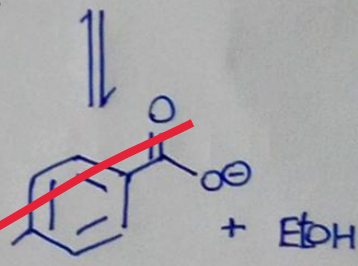
In Acid catalysed Hydrolysis Mechanism:
i.e In the RDS step, a very significant +ve charge at the Carbonyl C of $\overset{O}{C}-OEt$ (i.e Resonance through) has a much weaker +ve charge.
There is a weakening of the +ve charge in the same direction as conversion of a positive to a negative

as observed from the base catalysed rxn., so this is consistent with positive value of s. $\therefore$ observed value is $+0.14$.

For base catalysed Hydrolysis Mecha:

In the RDS step, the carbonyl C, with a partial +ve charge leads to tetrahedral C with adjacent -ve charge Through Induction, some charge will resi'duc on the C This is consistent with a sizable, +ve value of $s = 2.19$.

Q5.

$$\log\left(\frac{K}{K_0}\right) = S \times \sigma \quad \cdots \quad \left(K_0 = k_{kk}, \, P_{ka}(H)\right)$$

$$\log\left(\frac{K_{P-Br}}{K_0}\right) = \sigma_{Br} \times S \quad \text{same for } X = Br, NO_2, \cdots$$

$$= 0.26 \times (-1.31) = -0.3406 \quad \cdots (1)$$

$$\log\left(\frac{K_{P-NO_2}}{K_0}\right) = \sigma_{NO_2} \times S$$

$$= 0.81 \times (-1.31) = -1.0611 \quad \cdots (2)$$

$$\therefore \log\left(\frac{K_{P-Br}}{K_{P-NO_2}}\right) = \log\left(K_{P-Br}\right) - \log\left(K_{P-NO_2}\right)$$

$$= \log\left(\frac{K_{P-Br}}{K_0}\right) - \log\left(\frac{K_{P-NO_2}}{K_0}\right)$$

$$= \log -0.3406 - (-1.0611) \cdots \left(\text{from } 1 \, \& \, 2\right)$$

$$\log\left(\frac{K_{P-Br}}{K_{P-NO_2}}\right) = 0.7205$$

$$\therefore \boxed{\frac{K_{P-Br}}{K_{P-NO_2}} = 10^{0.7205} = 5.254}$$

4

Q6.

$$\therefore \log\left(\frac{K}{K_0}\right) = S \times \sigma \quad ; \quad K = 2 \times 10^{-4} \, /Ms$$

$$\therefore \log\left(\frac{K}{K_0}\right) = 2.38 \times (0.70) = 1.66$$

$$\frac{K}{K_0} = 10^{1.66} = 46.3445 \quad \cdots \left(\text{Here } K_0 = 2 \times 10^{-4}\right)$$

$$\therefore \boxed{K = 46.3445 \times K_0 = 9.2690 \times 10^{-3} \, /Ms}$$

3

Q7.

(A) + (B) $\xrightarrow[\text{DMSO, rt, 4h}]{\text{30 mol%}}$ product

68%   76%
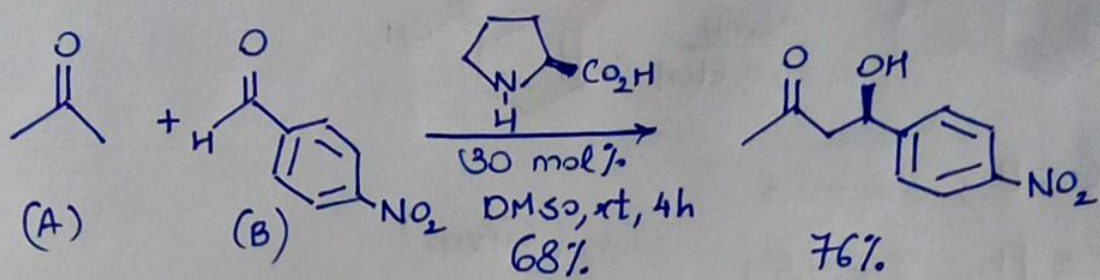
→ The Rxn is Acid Catalysed aldol reaction

$\overset{\ominus}{O}$ ≈ more Acidic Than Ketone ($\overset{O}{\underset{\|}{C}}$)

(B.)

H, Aldehyde grp.

:O: ⟶ H⁺

$\overset{\oplus}{OH}$ ⟶ OH (c)

$NO_2 -$ $\overset{O}{\underset{H}{C}}$ + :OH: ⟶ $NO_2 -$

(B)   (c)   ⊝O, OH⁺

H exchange

$\overset{\ominus}{NO_2} -$ OH, O

Q8.

$$X \text{—} \overbrace{}^{R} C\text{-}Cl \xrightarrow[H_2O, EtOH]{NaOH} X \text{—} \overbrace{}^{R} C\text{-}OH$$

S_{N_1} V/s S_{N_2}
Draw

∴ $R \equiv H$; $S = -0.3$

..... (Given)

∴ $R \equiv Ph$; $S = -5.1$
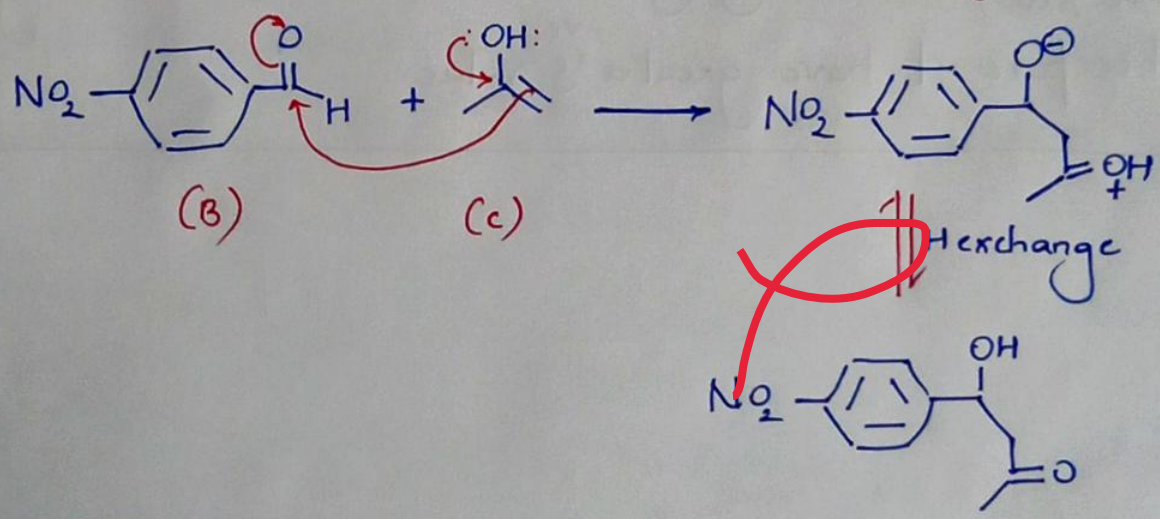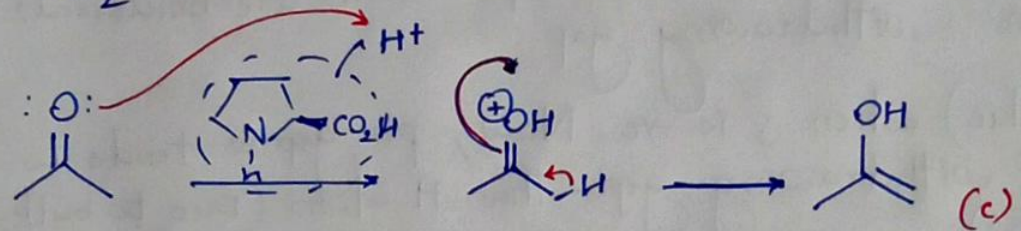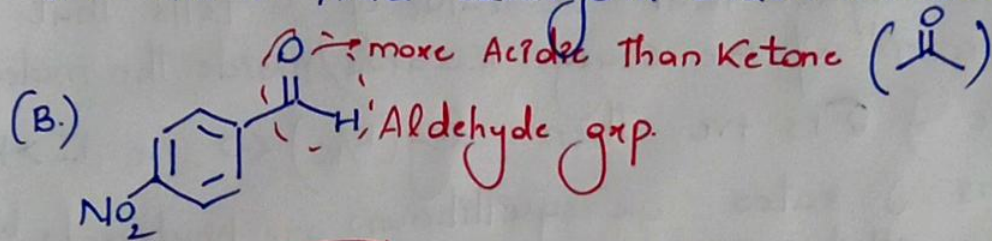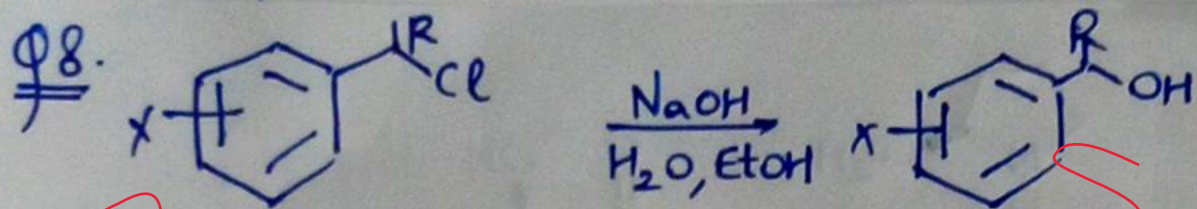
We know the fact that -ve value of S tells that there is an involvement of +ve charge towards / inside the molecule. If S is -ve & σ is +ve then $\log(K/K_0) < 0$ i.e $K_0 > K$. This means S rates or equillibrium are hindered, by electron withdrawing grp.

(i.e +6 value) when S is -ve. Now, ph grp is tends to be more $e^\ominus$ withdrawing grps. than H atom (Due to bulky nature Also)
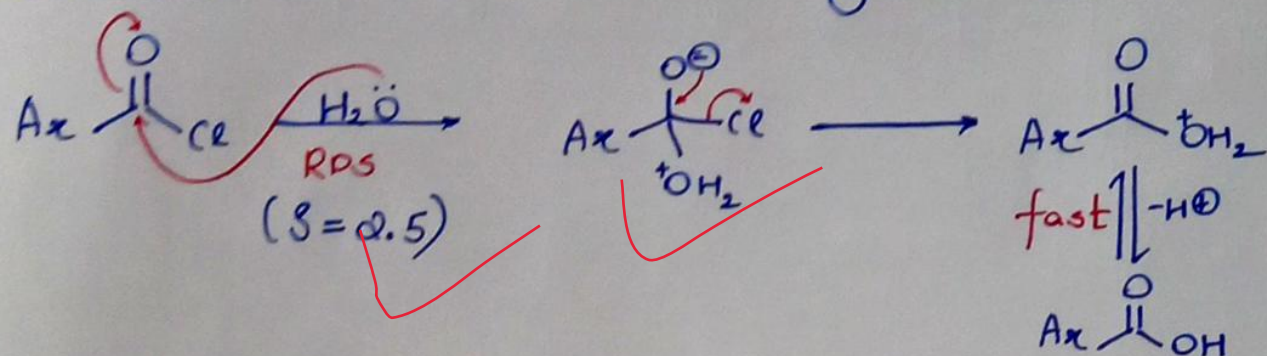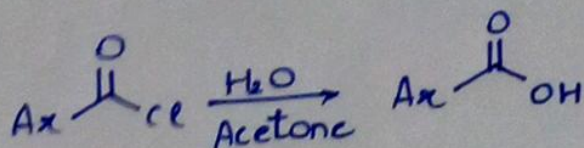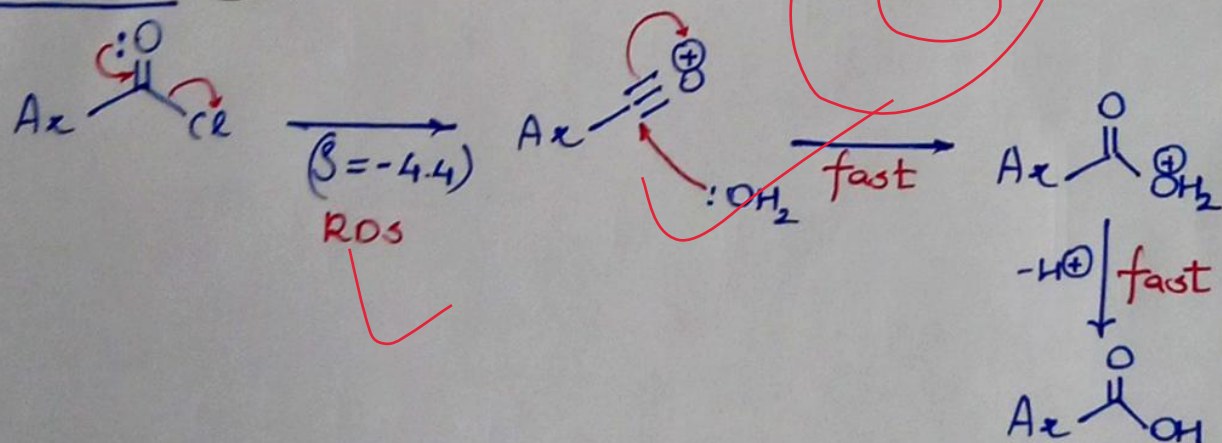
∴ Therefore it have greater ^S value
-ve

Q 9.

$\log k$ (Aryl acyl hydrolysis) vs σ graph: $S = -4.4$, $S = +2.5$, S-cl

$$Ar\overset{O}{\underset{}{C}}-cl \xrightarrow[\text{Acetone}]{H_2O} Ar-\overset{O}{\underset{}{C}}-OH$$
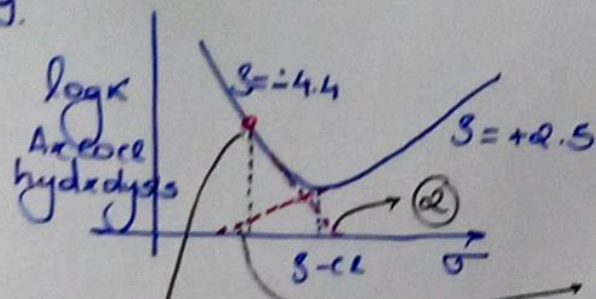
Any compound reacts at the faster of 2 rates ... ①

(There are 2 possible mechanism for the Given hydrolysis Rxn Hence it is also understandable by the non-linear Graph)

Mechanism ① :

$$Ar-\overset{O}{\underset{}{C}}-cl \xrightarrow[\text{RDS}]{H_2\ddot{O}} Ar-\overset{O^{\ominus}}{\underset{^+OH_2}{C}}-cl \longrightarrow Ar-\overset{O}{\underset{}{C}}-\overset{+}{O}H_2$$

$(S = 2.5)$

$$\xrightarrow[\text{fast}]{-H^{\oplus}} Ar-\overset{O}{\underset{}{C}}-OH$$
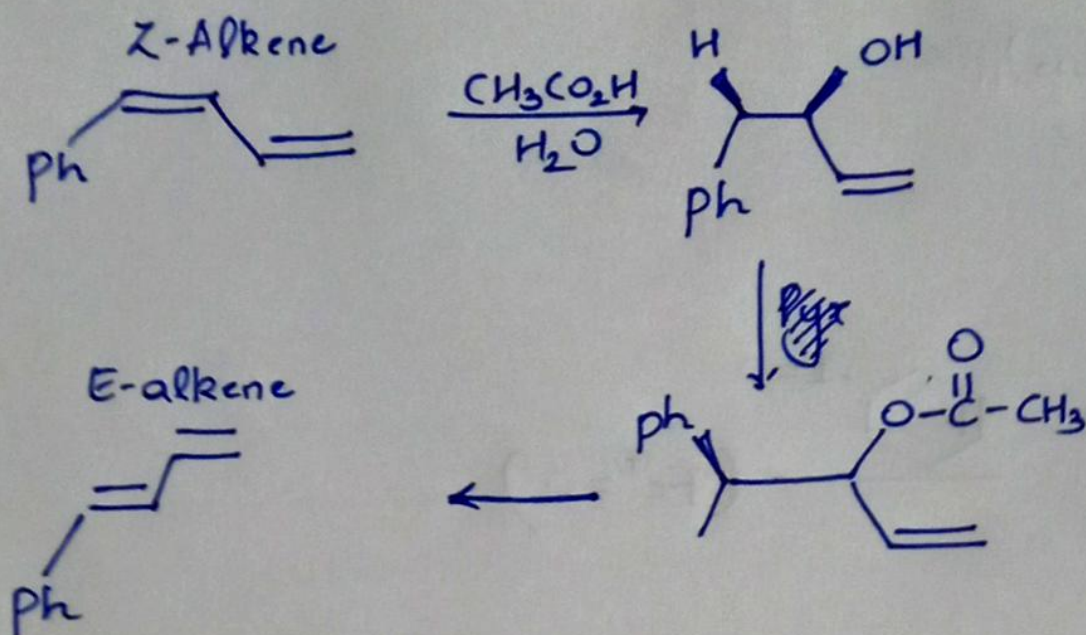
∴ The S value explains that $S = 2.5$ is more sensitive than reference Rxn of benzoic acid. (i.e EWG increases the sensitivity for $S > 1$)

Mechanism ② :

$$Ar-\overset{O}{\underset{}{C}}-cl \xrightarrow[\text{RDS}]{(S = -4.4)} Ar-\overset{+}{\equiv}O \xrightarrow[\text{fast}]{:OH_2} Ar-\overset{O}{\underset{}{C}}-\overset{\oplus}{O}H_2$$

$$\xrightarrow[\text{fast}]{-H^{\oplus}} Ar-\overset{O}{\underset{}{C}}-OH$$

Q3.

Z-Alkene

$$\xrightarrow[H_2O]{CH_3CO_2H}$$

(product with H, OH, Ph, and alkene)

↓ Pyr

$$Ph \quad O-\overset{O}{\overset{||}{C}}-CH_3$$

←

E-alkene

(Ph substituted alkene)

Experiment:

1.) ~~Rate const~~ (NMR spectroscopy)

2.) Rate Const.

3.) KIE is due to clevage (Primary) ✓

4.) Activation parameter (ΔS will negative ✓

5.)

K_{obs} vs [HA]

$\log(k_{obs})$ vs ph