31-October 2022

1 2019/2020. Exam: 5b

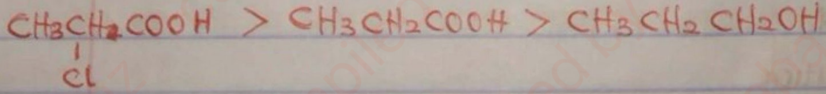
Arrange the following in order of decreasing acid strength

(a) $CH_3CH_2CH_2OH$, $CH_3CHClCOOH$, CH_3CH_2COOH

Recall that; any effect that stabilizes the anion of a compound increases the compound's acitidy.

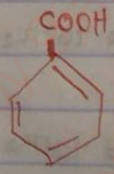
Because of the resonance effect in the $\mathrm{C}\begin{smallmatrix}=O\\ -O^-\end{smallmatrix}$ of the carbonyl group which is absent in the alcohol; also the acids are more acidic than the alcohol due to the $C=O$ electron withdrawing group that stablizes the negative charge on the carboxylate anion.

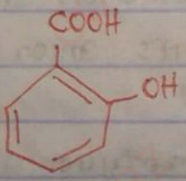
The chloro-acid is a strong electron withdrawing group that withdraws electron density from negatively charged anion and hence increasing stability / acidity of the acid

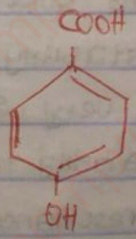


$\therefore\ CH_3\underset{\displaystyle |\atop Cl}{CH}COOH > CH_3CH_2COOH > CH_3CH_2CH_2OH$

(ii)

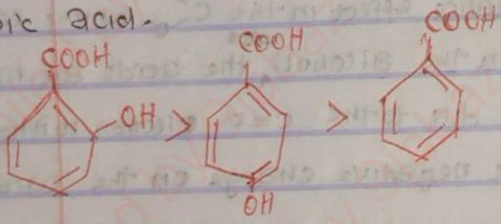






Notice that the ortho-hydroxy benzoic acid will exhibit hydrogen bonding with 'COO⁻ from the acid due to it's proximity to the ~~ox~~ oxygen atom Hence forming a 6-membered ring system which confers on it extra stability, therefore the acid is the most acidic/strongest.

The para-analog is more acidic than Benzoic acid because the Phenolic oxygen is also delocalised over the Benzene ring and this is not readily obtained in the Benzoic acid.



② 2017/2018 Test : Question 1a.

Arrange the following in the order of increasing acidity. $Cl_2CHCOOH$, CH_3CH_2OH, $BrCH_2COOH$, CH_3COOH, $ClCH_2COOH$, C_6H_5OH

solution

The Least acid is the alcohol(ethanol) amongst the list ~~and it's st~~ as the stability of it's anion relative to the other compounds is very small

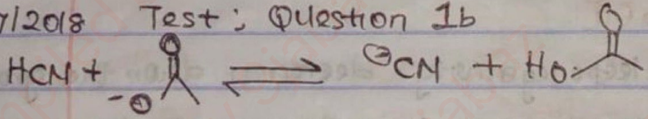
There is increased acidity in carboxylic acid due to the combined effect of resonance and $\overset{\text{negative}}{}$ inductive effect which is found in the carboxylate ion (COO^-) hence increasing the stability and making it ~~stable~~. acidic.

chlorine is an effective electron withdrawing group than Br and a combined effect of the chlorine withdraws more electrons from the center and stabilizes the anion further.

Hence

$CH_3CH_2OH > C_6H_5OH > CH_3COOH > BrCH_2COOH > ClCH_2COOH >$
$Cl_2CHCOOH$

③ 2017/2018 Test; Question 1b



If K_{eq} is 10^{-5}, Predict which direction equilibrium lies and hence suggest which of the acid species is stronger.

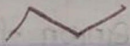
observe that $K_{eq} < 1 [10^{-5}]$, This means that the product is more consumed than the reactants and hence more reactants are Product; this invariably means that the equilibrium lies to the LEFT.

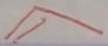
Hence acetic acid is a stronger acid than HCN and it forms a more stable conjugate base.

④ 2017/2018 exam; Question 1a

Question and answer exactly what was asked in no 3 above.

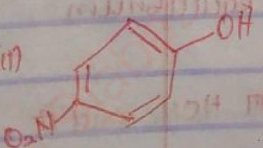
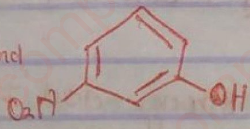
⑤ Indicate which of each pair of compounds is likely to be more acidic and why?

a)  or 

 is more acidic because the H in =C–H has more s-character and hence, electrons of the anions will be lower in energy / more stable, Therefore increasing the acidity of the compound.

(ii) $R_2SH^{\oplus}$ or $R_2O\overset{\oplus}{H}$

Recall that electronegativity decreases down the group, hence S is less electronegative than oxygen and because of the ~~[illegible]~~ small size of oxygen, there will be increased overlapping between the Hydrogen and oxygen making it difficult for it to be deprotonated when compared relative to S–H, hence $R_2SH^{\oplus}$ is more acidic.

(iii)  and 

Despite the fact that the Nitrogroup stabilizes via induction (–ve inductive ~~effect~~) the negative charge from the phenoxide ion in P-analog can be delocalized over the whole compound and hence contributes to it's stability; This is not readily found in m-analog ~~[illegible]~~ and ~~hence~~ Therefore,

P-nitrophenol is more acidic than m-nitrophenol.

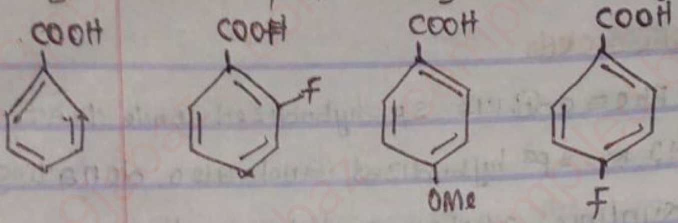
(iv) $PhC\equiv CH$ and $PhC\equiv CCH_3$

The hydrogen in $PhC\equiv C\text{-}Ⓗ$ is sp hybridised while that of $PhC\equiv CCH_3$ $(-C-H)$ is sp^3 hybridised and also donating electrons to the alkynlinic carbon and hence decreasing it's stability! Hence $PhC\equiv CH$ having higher s-character and higher stability of its anion is more acidic

$PhC\equiv CH$ is more acidic

Arrange in order of decreasing acid strength

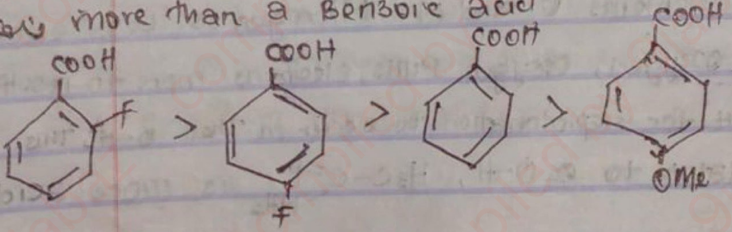
⑦ 2016 .5b



-

The o-fluoro benzoic acid is more acidic then p-fluoro because of the position of the fluoro group which is an electron withdrawing group; and recall that electron withdrawing group stabilises an anion much more and confers on the compound extra stability

The methoxyl group (-OMe) donates electron to a benz ring and decreases the acidity (+ve inductive effect) eve ~~[illegible]~~ more than a Benzoic acid



2016 .5c

⑧ Explain why methanol is much acidic than chloroform in aqueous medium, while their acidities are almost identical in the gas phase

~~Methanol is more acidic than chloroform because it forms a~~ ~~very~~ ~~conjugate base (methoxide) which is weaker than that of chloroform {which d~~

SOLUTION

Methanol is a polar compound and upon solvating in an aqueous medium(water) another polar solvent the entropy decreases and the solvent molecule becomes much more ordered and hence there is an increased stability; unlike CCl_4 a non polar compounds which won't effectively solvate ~~the~~ in the solvent. The compound(methanol) whose conjugate base gave highest stability will be more acidic than chloroform. (In short; they can easily separate into ions in solution compared to chloroform because they are polar) In gas phase, separation of oppositely charged particle is difficult and hence the acidity remains almost identical

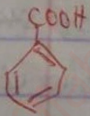
9. Arrange the following in order of increasing acid strength

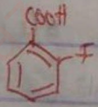
(i) $CH_3CH_2CH_2OH$; $CH_3CHClCOOH$, CH_3CH_2COOH, C_6H_5OH

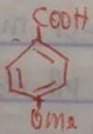
$CH_3CH_2CH_2OH > C_6H_5OH > CH_3CH_2COOH > CH_3CHClCOOH$

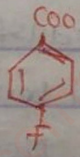
Kindly refer to question 3 for ~~so~~ explanation

(ii)









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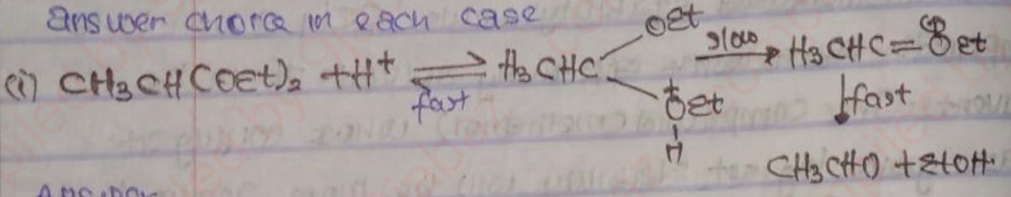
Refer to question number 7 for solution.

03-November

10) 2019/2020; Exam; 5d 5

classify the following as either specific or general acid-catalysed. provide a brief explanation for your answer choice in each case

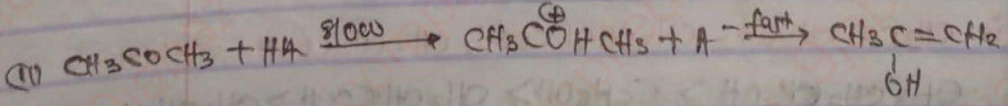


(i) $CH_3CH(OEt)_2 + H^+ \underset{fast}{\rightleftharpoons} H_3CHC(OEt)(\overset{+}{O}HEt) \xrightarrow{slow} H_3CHC=\overset{+}{O}Et \xrightarrow{fast} CH_3CHO + EtOH$

Answer

Specific Acid catalysis

Notice that the protonation of the acetal occured before the slowest step [rate-determining step] in the mechanism above. The acid catalyst is involved in the step prior to the rate determining step and it is not involved in the rate determining (slowest step) itself.



(ii) $CH_3COCH_3 + HA \xrightarrow{slow} CH_3\overset{+}{C}OHCH_3 + A^- \xrightarrow{fast} CH_3C(OH)=CH_2$

Answer

General-Acid catalysis

The proton is/was transfered in the slowest step of the mechanism and hence pH depends on conc of the undissociated acid present in the buffer system.

Summary, The proton-transfer step is the rate-determining step ~~step before the product intermediate~~

Q1 2014, Exam, 1

Assume that the reaction of benzyl diazonium chloride with water to yield benzyl alcohol proceeds by an S_N1 mechanism

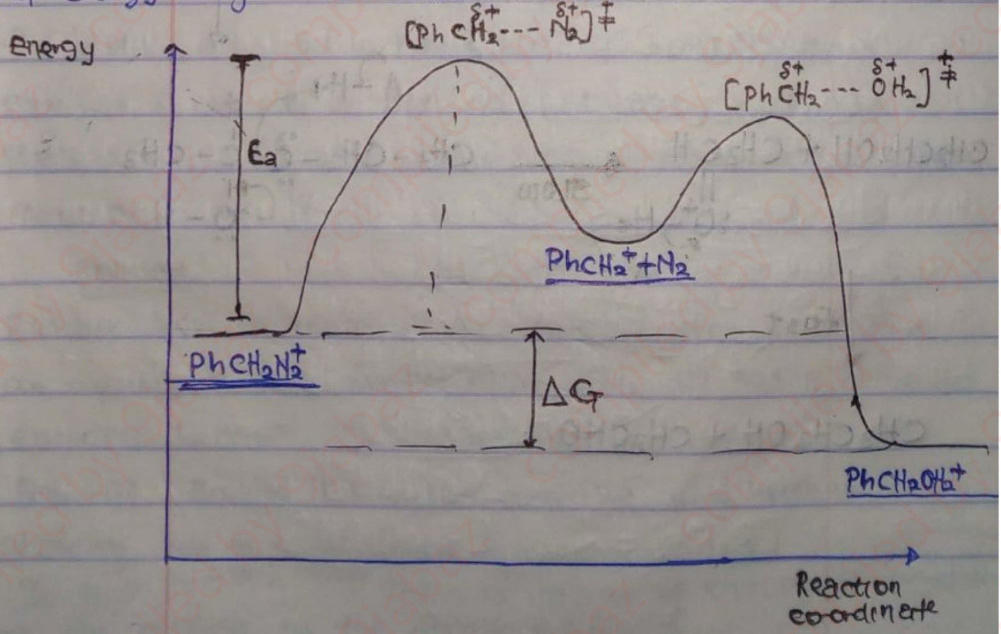
$$PhCH_2N_2^+ \xrightarrow{slow} PhCH_2^+ + N_2$$

$$PhCH_2^+ \xrightarrow[fast]{H_2O} PhCH_2OH_2^+$$

a Draw an appropriate energy diagram for the process, showing the Ea, transition state, ionic intermediates, starting material and product.

Solution

Recall that the slowest step is the rate determining step and it has the highest $\Delta G^\ddagger$ (Activation energy), so the two-step energy diagram is shown below.

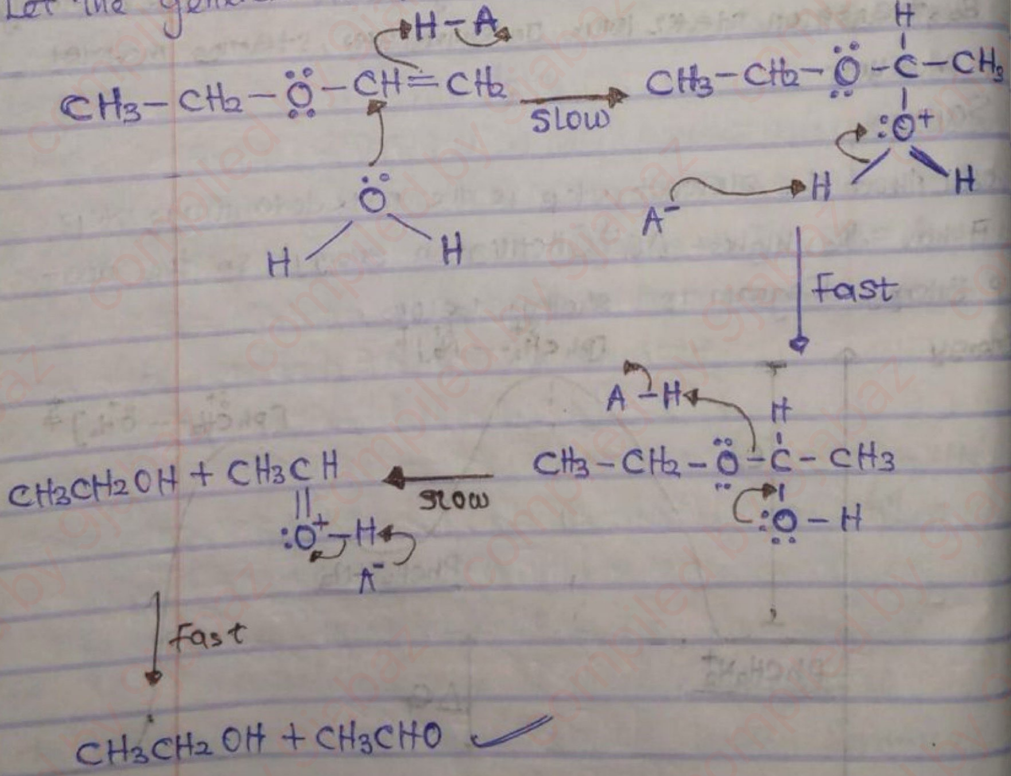


(12) Assuming the following reaction is general acid catalyzed, propose a mechanism for it, indicating the rate limiting step and the fast step

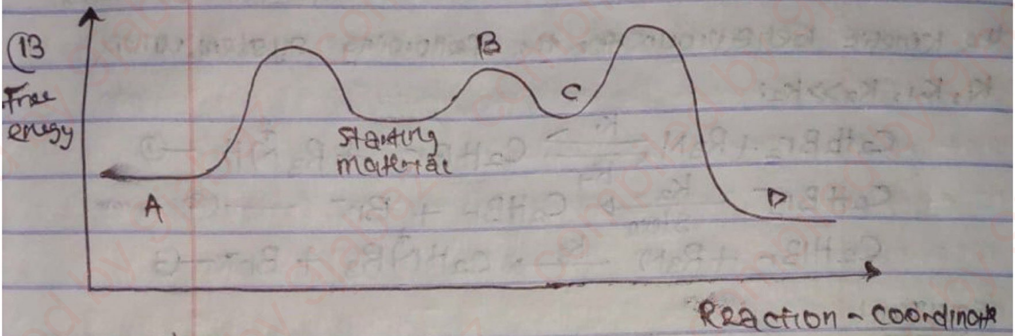
$$CH_3CH_2OCH=CH_2 + H_2O \longrightarrow CH_3CH_2OH + CH_3CHO$$

Solution

Let the general acid be H—A.



(13)



What ~~pass~~ do letters A—D represent?.

A = Reactants

B = Transition state of starting material

C = Intermediate

D = Product.

More diss

(14) Explain why the dissociation of benzoic acid exhibits a positive entropy of activation in the gas phase but a negative entropy of activation in the aqueous medium

Solution

Benzoic acid being a polar compound upon solvating in an aqueous medium (another polar molecule) has a decreased entropy because the solvent molecules becomes more ordered around the polar compound and hence increasing stability due to strong bond formation.

In gas phase; ~~they~~ there is increased entropy of activation as the reverse of the former happens!

(5) Write the rate law that would be expected to desorse the Kinetic behaviour for the following system, where $K_1, K_{-1}, K_3 >> K_2$:

$$C_2H_2Br_2 + R_3N \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} C_2HBr_2^- + R_3\overset{+}{N}H \quad ①$$

$$C_2HBr_2^- \xrightarrow[slow]{K_2} C_2HBr + Br^- \quad ②$$

$$C_2HBr + R_3N \xrightarrow{K_3} C_2H\overset{+}{N}R_3 + Br^- \quad ③$$

SOLUTION.

Since $K_1, K_{-1}, K_3 >>> K_2$; The slowest step in the reaction is one leading to formation C_2HBr [rate-determining step]

$$\frac{d[C_2HBr]}{dt} = K_2[C_2HBr^-]$$

from ①

$$K = \frac{[C_2HBr_2^-][R_3\overset{+}{N}H]}{[C_2H_2Br_2][R_3N]}$$

$$[C_2HBr_2^-] = \frac{K[C_2H_2Br_2][R_3N]}{[R_3\overset{+}{N}H]}$$

$$\frac{d[C_2HBr]}{dt} = \frac{K_2K[C_2H_2Br_2][R_3N]}{[R_3\overset{+}{N}H]}.$$

For a Base accepting a Proton

$$R_3N + H^+ \longrightarrow R_3\overset{+}{N}H$$

$[B^- + H_2O \overset{K_b}{\rightleftharpoons} BH + O$

$$K_{a_{RH}} = \frac{[R_3\overset{+}{N}H]}{[R_3N][H^+]}$$

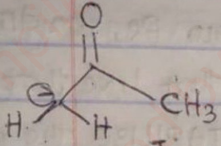
$$[R_3\overset{+}{N}H] = K_{a_{RH}}[R_3N][H^+]$$

$$\frac{d[C_2HBr]}{dt} = \frac{k_2 K [C_2H_2Br_2]\cancel{[R_3N]}}{K_{a_{RH}}\cancel{[R_3N]}[H^+]}$$

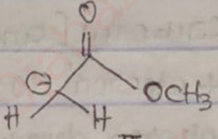
$$\frac{d[C_2HBr]}{dt} = \frac{k_2 K}{K_{a_{RH}}} \frac{[C_2H_2Br_2]}{[H^+]}.$$

Tutorial questions 4

⑯ Which of the following is more basic and why?


I

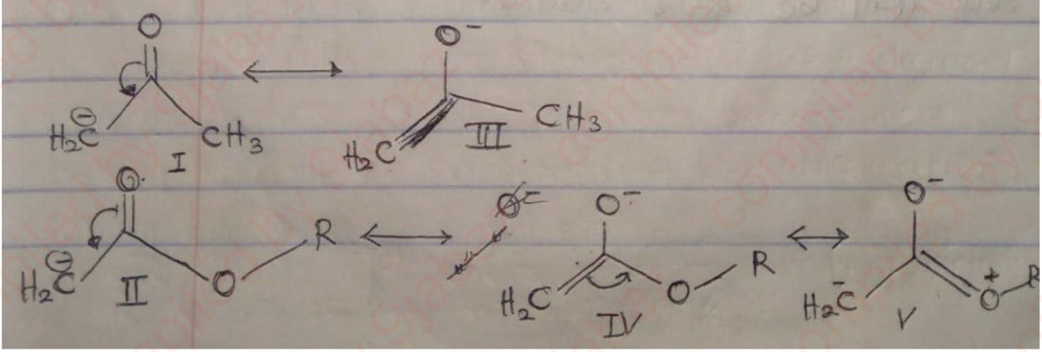
or


II ✓ more basic

~~Ester ion is more basi~~

II is more basic than I because the enolate ion is less stabilized in the ester compared to the ketone, hence the ester is less acidic than ketone and subsequently the conjugate base formed from esters [II] will be more basic than that of ketones [I].

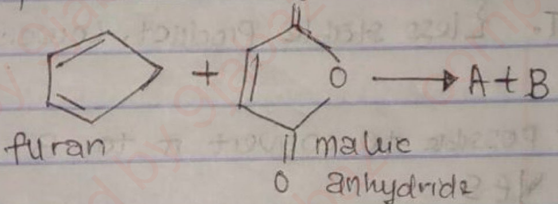
Want More Precise explanation Peace:? Oya lez go.

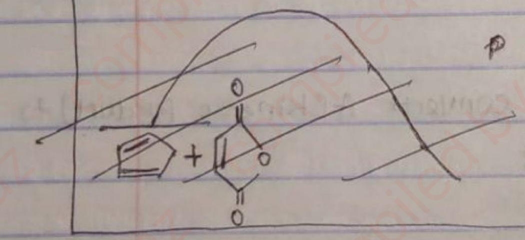


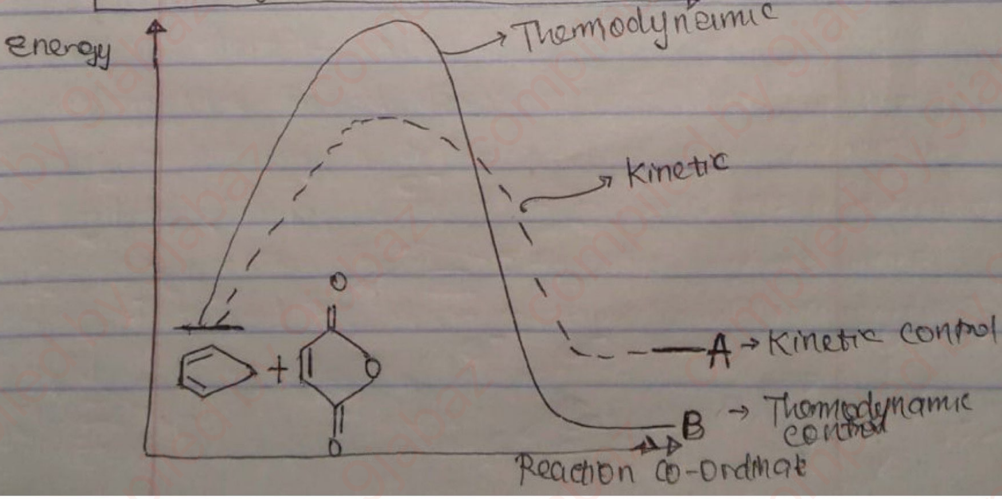
The figure shows resonance structures for the enolate
anion of a ketone and an ester. Resonance structures
III and IV stabilise the enolate anion [and you know
that if the anion is stable. The ~~acid~~ cpd that formed it
is ~~more~~ acidic, Yes, I agree] in ketone and ester
respectively. But in the ester ion (II), there is an
additional resonance structure, V. Through resonance
structure V, the alkoxy group in the ester donates
electrons to the carbonyl [and you know pe, we don't
like the effect of electron donating like that like that],
The movement of electron density will DESTABILISE the
formation of any negative charge; [fano| taa, ba, ti
destabilise anion/ - o mean pe / cpd to form le yen
maa doa basic] on the carbon attached on the
other side of the carbonyl [electrostatic repulsion]. This
reduces the likelihood of the formation of an enolate
anion on that carbon. Hence making it more basic
and the compound that formed that ester enolate ion
self will be ~~more~~ less acidic.

⑰ Tutorial question no 9, many many years in PQ

ⓐ Maleic anhydride react with furan to give two possible tricyclic products; a sterically crowded endo product A and/or a less crowded exo product B. Under some specific lab conditions, A is obtained exclusively as the product of this reaction. Using a Simple energy profile diagram, explain what type of control is in effect







Because A is obtained exclusively as the Product, being a sterically crowded endo Product, it will be the kinetic Product as a sterically crowded compound is less stable. So we can just summarise like this:

A, being sterically crowded endo Product is a less stable Product and since it is also exclusively Produced, ~~Meaning~~ It means that the Product was Obtained faster than B. Hence the type of control in this effect is KINETIC PRODUCT. {less stable Product, lower Actuation Energy}

(b) Is it possible to convert A to B

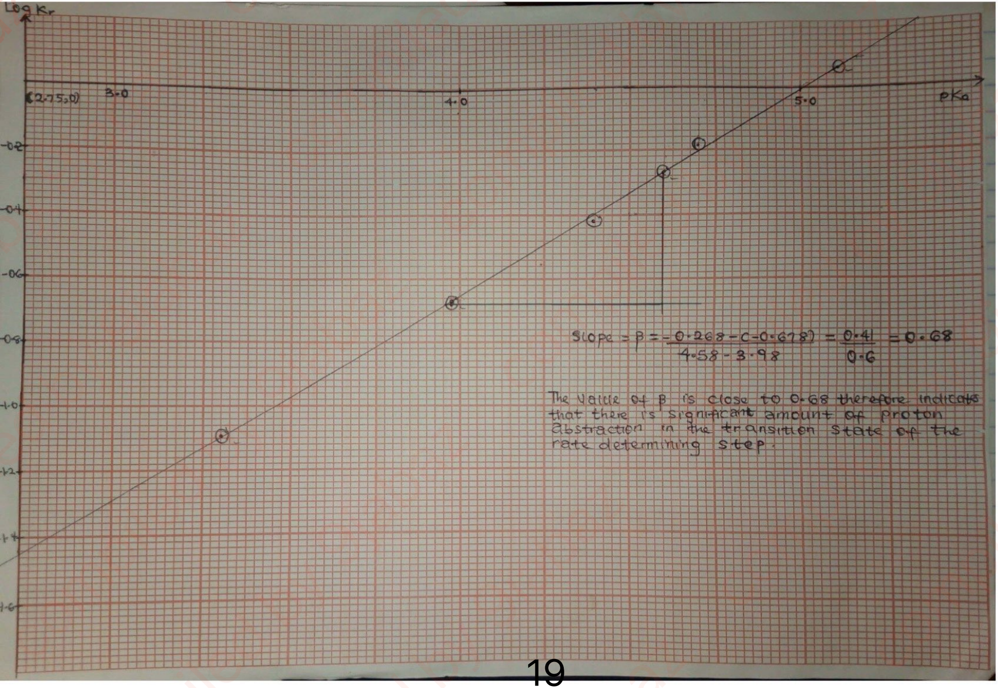
YES

How?

Increased Temperature converts A[kinetic product] to [B]-thermodynamic Product

Base	pKa	$k [L mol^{-1} min^{-1}]$	log k_r
p-toluidine	5.12	1.16	0.06446
m-toluidine	4.69	0.64	-0.1938
aniline	4.58	0.54	-0.2676
o-toluidine	4.39	0.34	-0.4685
p-chloroaniline	3.98	0.21	-0.6778
m-chloroaniline	3.34	0.081	-1.0915
o-Chloroaniline	2.64	0.018	-1.7447

Table of values for graph of log k_r vs pKa

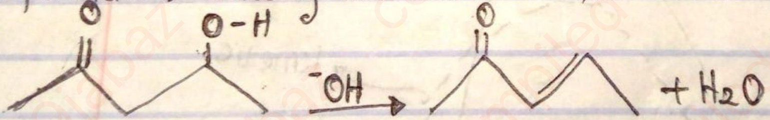


$$\text{Slope} = \beta = \frac{-0.268-(-0.678)}{4.58-3.98} = \frac{0.41}{0.6} = 0.68$$

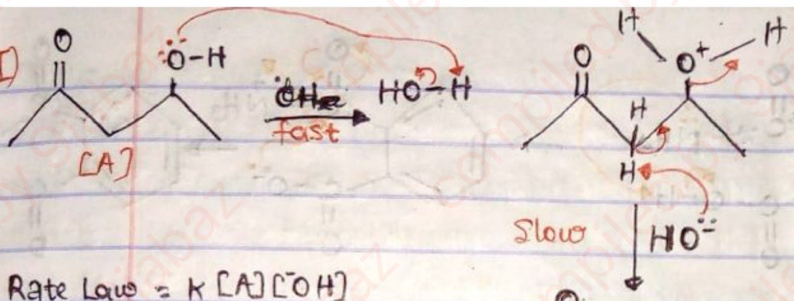
The value of β is close to 0.68 therefore indicate that there is significant amount of proton abstraction in the transition state of the rate determining step.

Tutorial question 1

(18) Propose two possible mechanism for the following transformation, showing the rate law for each



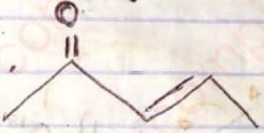
(i) (I)



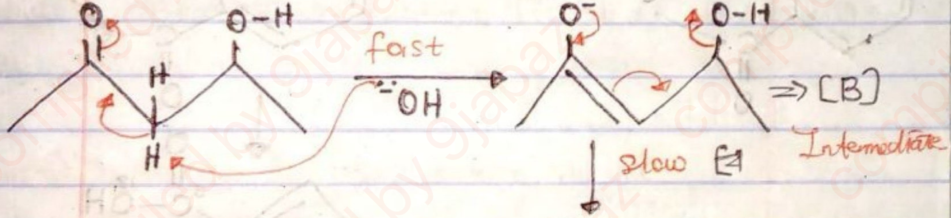
Rate Law = k [A] [⁻OH]

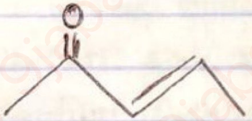
The rate is second-order overall.

E2 Mechanism.

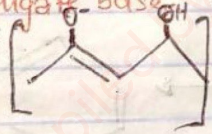


(II)



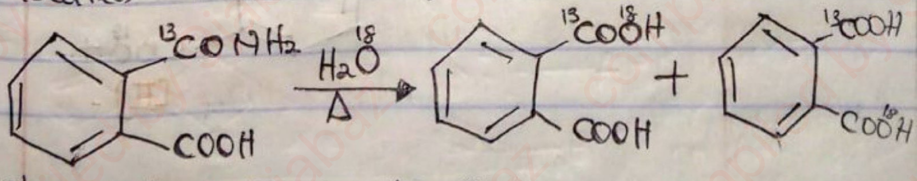


E1 – CB Mechanism
↳ Conjugate base

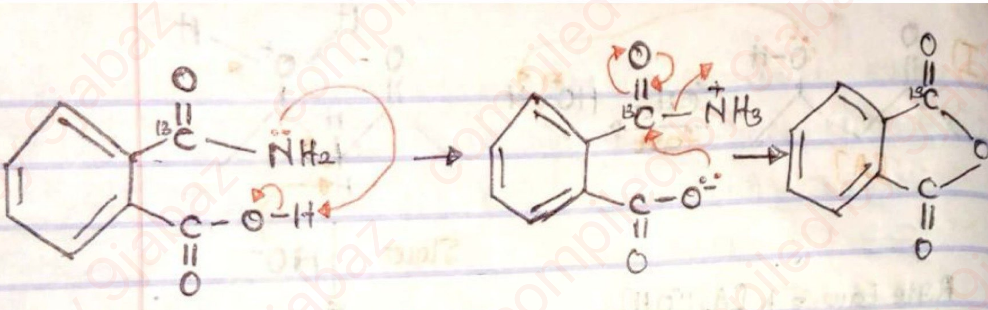
Rate = k[B] = k 

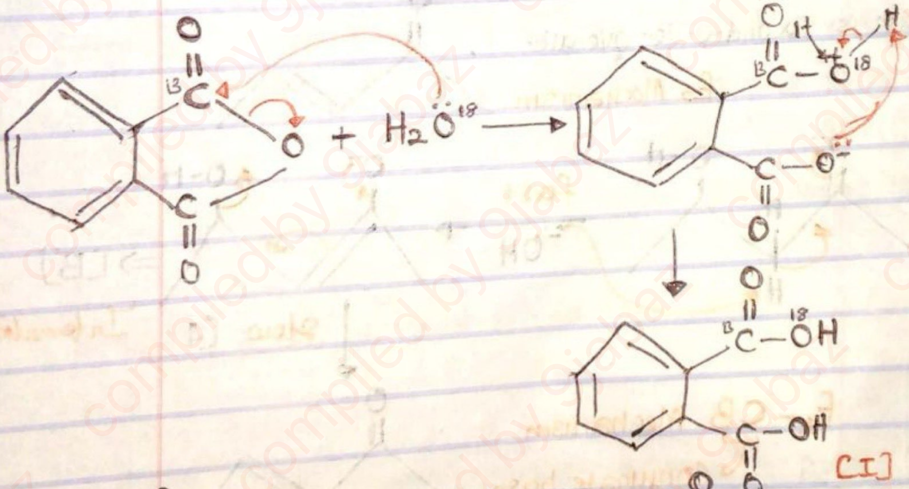
(19) Tutorial question 6

Hydrolysis of ^{13}C labelled o-phthalamic acid in water enriched in ^{18}O gives phthalic acid with the ^{18}O label equally located on each carboxyl group as shown below

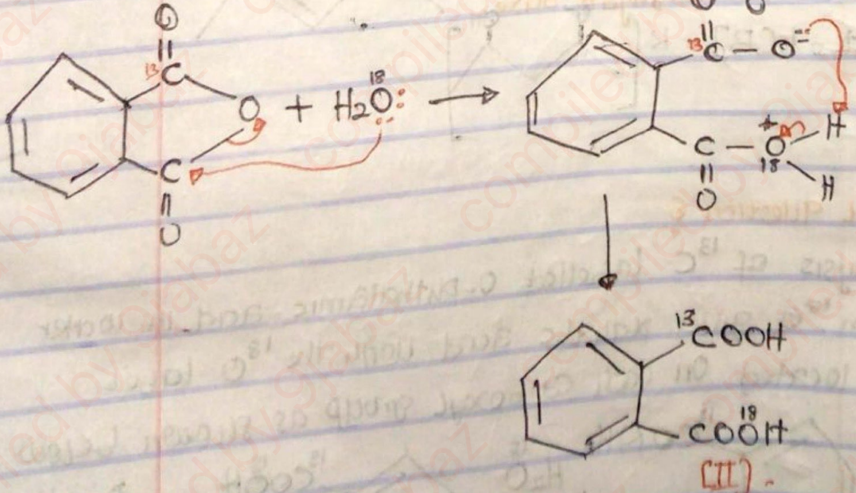


Explain with a reasonable mechanism





[I]



[II].

⑳ Tutorial question; NO 5

The Elimination reaction of 2-bromopropane could Proceed by either of the following mechanisms:

(i) $(CH_3)_2CHBr + C_2H_5O^-Na^+ \longrightarrow CH_3CH=CH_2 + C_2H_5OH + NaBr$ (1 step)

(ii) $(CH_3)_2CHBr \xrightarrow{slow} (CH_3)_2\overset{\oplus}{C}H \xrightarrow{C_2H_5O^-Na^+} CH_3CH=CH_2 + C_2H_5OH + NaBr$.

Outline two different experiments to decide which mechanism is actually operating, stating clearly what results you expect

(I) Kinetic study- By determining the rate Law.

Notice that the first reaction is a 1-step "concerted" mechanism which involves no intermediate while the second reaction has an intermediate; The first mechanism follows an E_2 mechanism [2nd order] while the ~~first~~ 2nd mechanism follows a first order mechanism [due to formation of intermediate]

~~The~~ If the kinetic data obtained experimentally gives a 2nd order overall reaction, the first mechanism is operating

$$Rate = k[C_2H_5O^-Na^+][(CH_3)_2CHBr]$$

If the kinetic data obtained shows ~~dependent~~ a first order overall reaction, then the second mechanism is operating ~~and~~

$$Rate = k[(CH_3)_2\overset{\oplus}{C}H].$$

(II) Isotopic Labelling ~ Kinetic Isotope effect

- Notice that the ~~first~~ second mechanism involves the breaking of the bonds at ~~[illegible]~~ the rate determining step while this is (C–Br) not readily observed in the first mechanism. The kinetic Isotope experiment | Isotopic labelling can also be used to monitor the reaction as a

(21)

Acid	pKa	
$CH_3CH_2CH_2CO_2H$	4.88	(I)
$CH_3CH_2CHClCO_2H$	2.80	(II)
$CH_3CHClCH_2COOH$	4.06	(III)
$ClCH_2CH_2CH_2COOH$	4.52	(IV).

Explain the trend above?

ANSWER

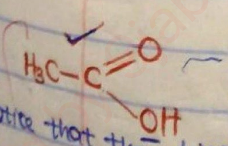
A small value of pKa indicates that the compound is acidic. ~~And~~ The trend above can be explained by ~~the~~ concept of inductive effect on the -vely charged centre produced when the ~~Prot~~ compound loses a proton.

The closer the electronegative element is to the centre, the more pronounced will be the -ve inductive effect on that centre hence spreading the charge and stabilizing the anion any

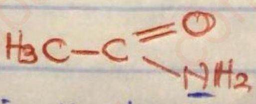
As the EWG moves far away from the charged centre, the stabilizing effect is less pronounced and acidity decreases.

This explains why II is more acidic than (III) and (IV) and then (I) which has no EWG at all.

(22)



and

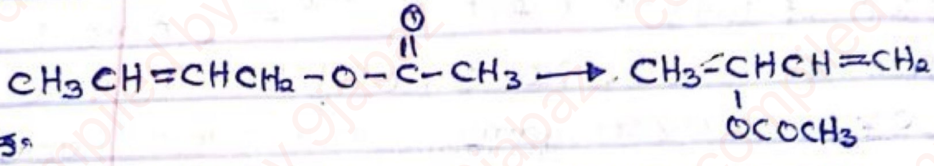


Notice that the difference in the two compounds are the electronegative elements O and N, Across the Periodic (from left to right) acidity increases due to increased electronegativity which makes O withdraw electrons to itself making the anion much stable.

Hence CH_3COOH is more ~~stable~~ acidic

(23) Tutorial question 1

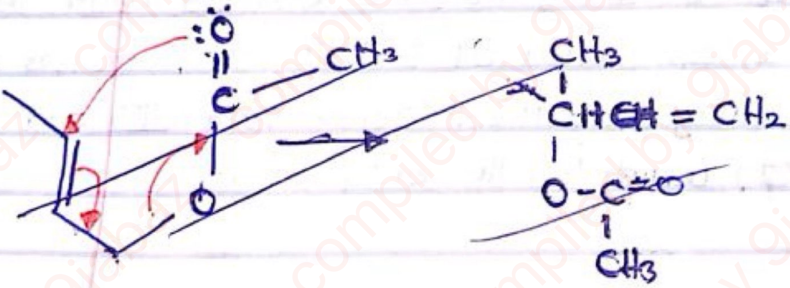
Suggest two possible mechanisms for the following reaction, — a 1-step intramolecular and a 2-step ionic mechanism.

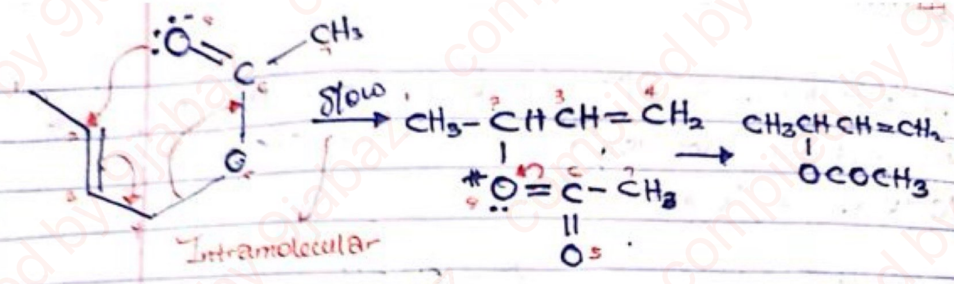


$$CH_3CH=CHCH_2-O-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow CH_3-\underset{\underset{OCOCH_3}{|}}{C}HCH=CH_2$$

~~Cters~~:

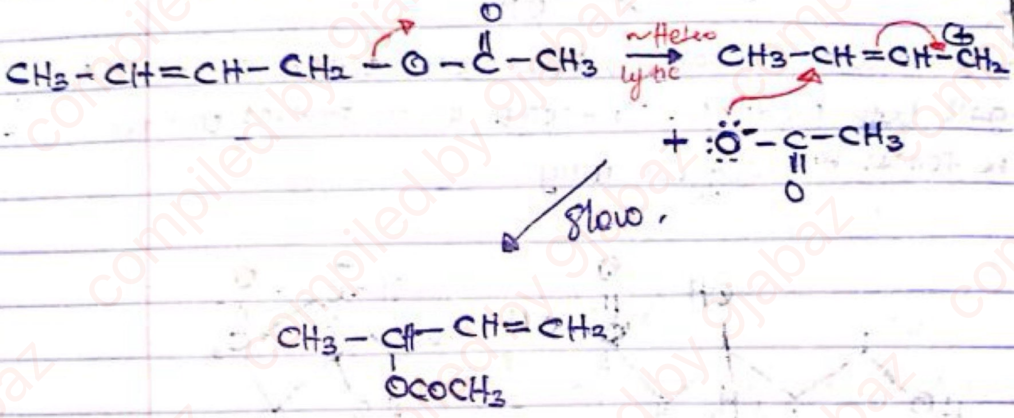
(i) How would you differentiate between the two mechanisms





$CH_3CH(OCOCH_3)CH=CH_2$

1-STEP INTRAMOLECULAR



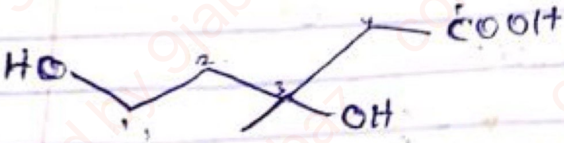
$CH_3-CH=CH-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{lytic}]{\text{~Hetero}} CH_3-CH=CH-\overset{+}{C}H_2 + {:}\ddot{O}^{-}-\underset{\underset{O}{\|}}{C}-CH_3$

$\xrightarrow{\text{Slow}} CH_3-\underset{OCOCH_3}{\underset{|}{CH}}-CH=CH_2$

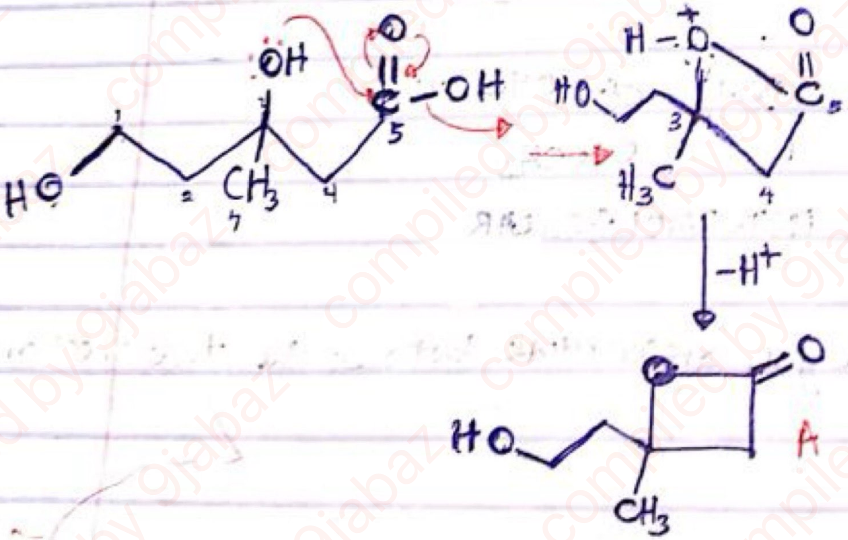
2-STEP INTERMOLECULAR

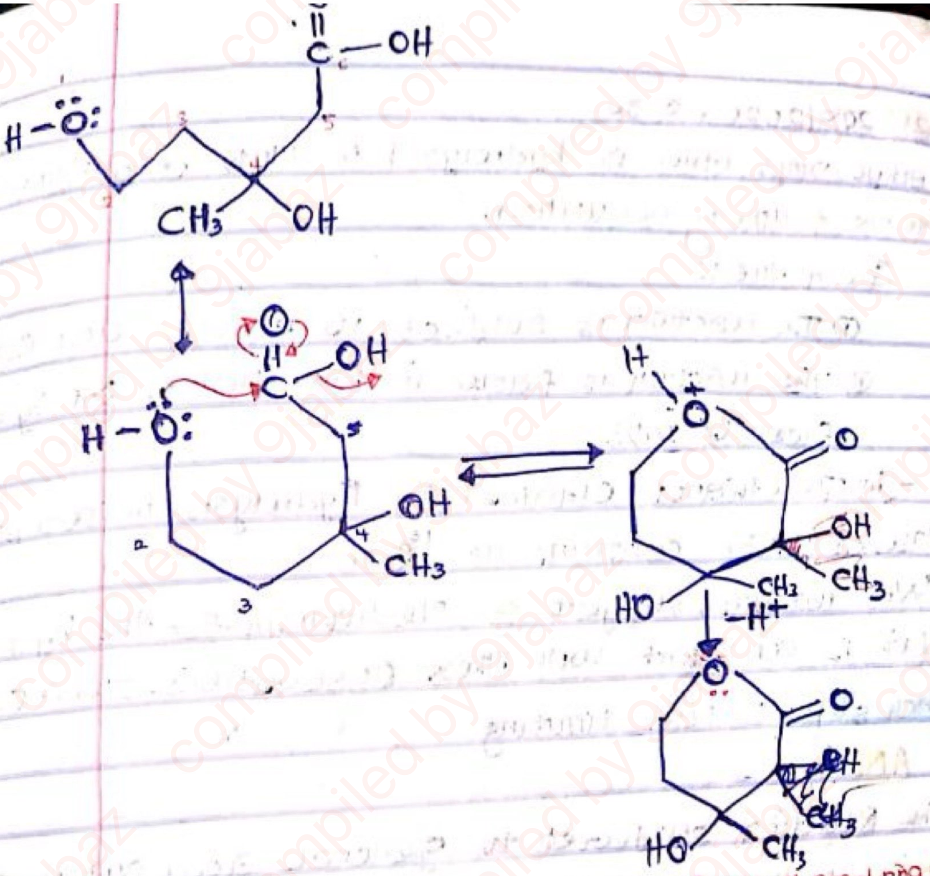
(ii) How would you differentiate between the two mechanism

24) Mevalonic acid [shown below] can potentially form two possible lactones. however in nature, just one of these lactones is formed



Show with mechanism, how lactonization can occur to give both products. Indicate which product will not be formed and suggest why





6-membered ring: stable

(25) 2019/2020, Q 8a.

Ethyl vinyl ether is hydrolysed in dilute acid according to the following equation.

Given that:

(i) The reaction is subject to general acid catalysis

(ii) The reaction is faster in H_2O than in D_2O by a factor of 2.93.

(iii) The ethanol obtained by hydrolysis in isotopically labelled water contains no ^{18}O.

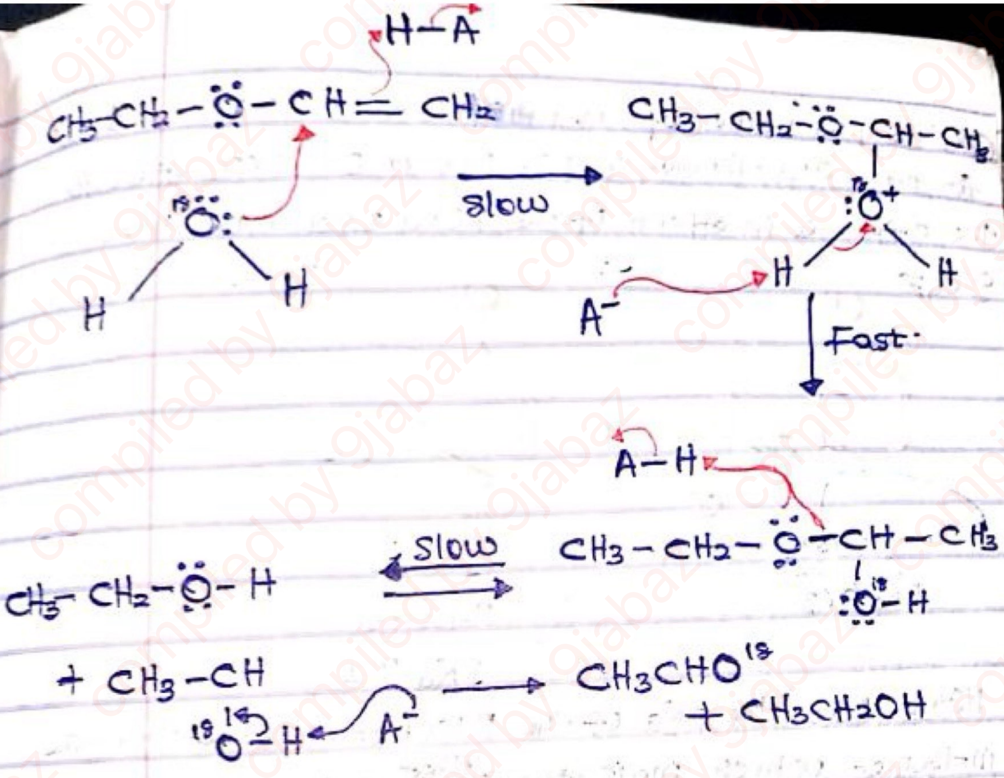
With reasons, suggest a mechanism for the hydrolysis which is consistent with these observations. state clearly which step is rate limiting

ANS:

The Reaction subjected to general acid catalysis is an indication that the Protonation of the substrate by an acid (H-A) occurs in the slowest step and it is the rate determining step

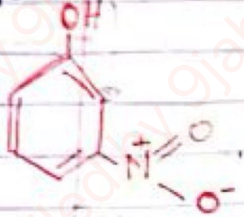
The k_H/k_D value of 2.93 is an evidence that C-H bond was FORMED at the rate determining step.

The Consistent mechanism for these observations are:



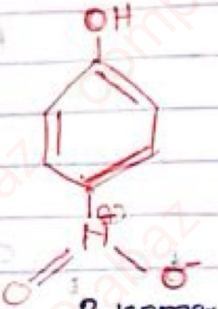
The Ethanol contains no ^{18}O according to mechanism shown.

(26) The pKa value of m-nitrophenol is 9.3, and that for the para-isomer is 7.2. Provide an explanation for the difference in effect of the para and meta nitro groups



m-isomer

pKa 9.3

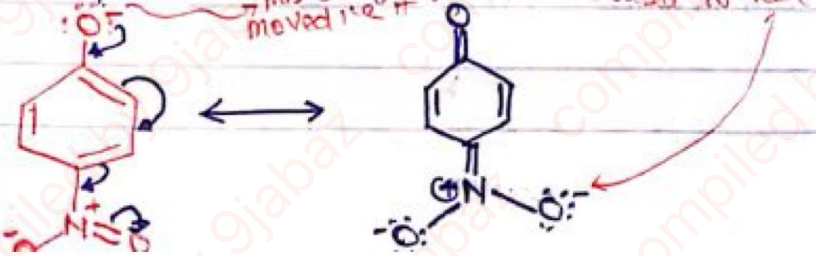


P-isomer

PKa 7.2

Notice that the pKa of the p-isomer is lesser than the m-isomer which indicates ~~or~~ that p-isomer is more acidic than the m-isomer.

Even though there is an inductive event on the nitro-group due to resonance, the ability of the p-isomer to decolalize the -ve charge (spread the charge) from the phenoxide anion to the nitro group contributes more to its stability as this is absent n the m-nitrophenol



This charge was delocalised to here moved i.e it

(27) Without relying using a pK_a table, rank the following Sets of compounds in order of increasing basicity

$(CH_3)_2\boxed{P}-H$ $CH_3\boxed{S}-H$ $H-\boxed{Cl}$

In the periodic table, acidity increase from left to right (basicity decreases from left to right) due to the increased electronegativity. ~~element~~ Hence arrangement o

$HCl < CH_3S-H < (CH_3)_2P-H$

Another angle;

That phosphorus has two CH_3 groups attached to it, so they are donating electrons into its centre and making it more basic.

(28) Rank 1.0M solutions of HBrO, HIO and HClO in order of increasing pH.

$HBrO, K_a = 2.1 \times 10^{-8}$

$HIO, K_a = 2.3 \times 10^{-11}$

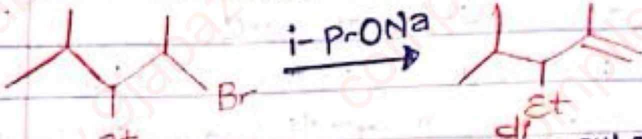
$HClO, K_a = 3.0 \times 10^{-8}$

The ~~lower~~ the K_a, the more acidic, Hence decreasing ~~increasing~~ pH higher

$$\underset{\text{Increasing acidity}}{HIO < HBrO < HClO \xrightarrow{\qquad}}$$

$$\underset{\text{Increasing pH}}{HClO < HBrO < HIO \xrightarrow{\qquad}}$$

(㉙ The elimination reaction shown below gives predominantly the terminal olefin. Is this reaction under kinetic or thermodynamic control? Why?



~~mono~~ di-substituted alkene

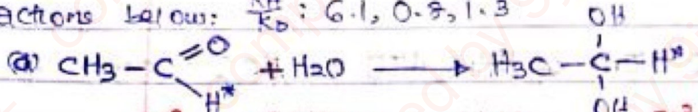
(less stable)

The Reaction is under <u>Kinetic Control</u>..

Why?

30) Exam, 2019/2020, 5c.

Match the following $\frac{K_H}{K_D}$ values with the appropriate reactions below: $\frac{K_H}{K_D}$: 6.1, 0.8, 1.3

(a)


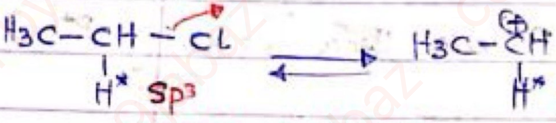
$CH_3-C(=O)H^* + H_2O \longrightarrow H_3C-C(OH)(OH)-H^*$

$\frac{K_H}{K_D} = 0.8$

INVERSE α-2° KIE.

(b)


$H_3C-CH(H^*)-Cl + H_2O \longrightarrow H_3C-CH(H^*)-OH + HCl$



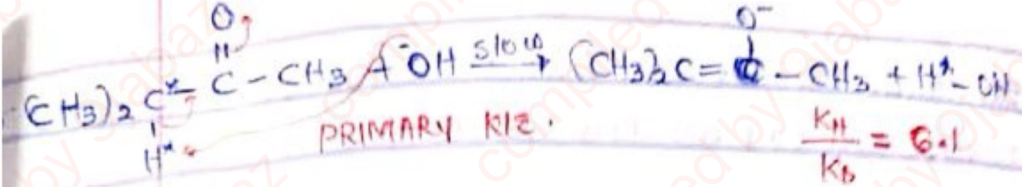
$H_3C-CH(H^*)-Cl \rightleftarrows H_3C-\overset{\oplus}{C}H(H^*)$

sp² (planar carbocation)

$\frac{K_H}{K_D} = 1.3$

NORMAL α-2° KIE

#*. Neighboring H* experiences a decreased existence
o out-of-plane bending (Higher frequency for C–H) hence the
bserved value.

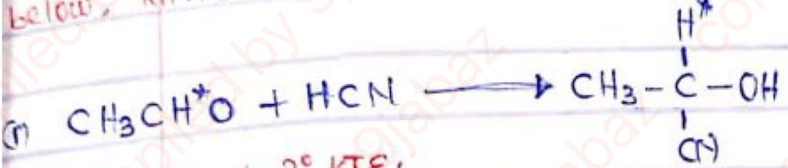


$(CH_3)_2C^*H-C(=O)-CH_3 + {}^-OH \xrightarrow{slow} (CH_3)_2C=C(O^-)-CH_3 + H^*-OH$

PRIMARY KIE.

$\frac{K_H}{K_D} = 6.1$

③. Match the following K_H/K_D Values with the appropriate reactions below. $K_H/K_D = 1.3, 0.8, 4.66, 1.1$

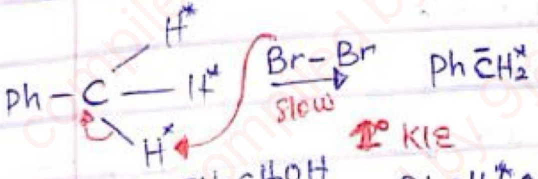
(i) 

$CH_3CH^*O + HCN \longrightarrow CH_3-CH^*(OH)-CN$

$\frac{K_H}{K_D} = 0.8$

Inverse α-2° KIE.

(ii) $PhC\overset{*}{H_3} + Br_2 \longrightarrow PhCH_2^*Br + H^*Br$.



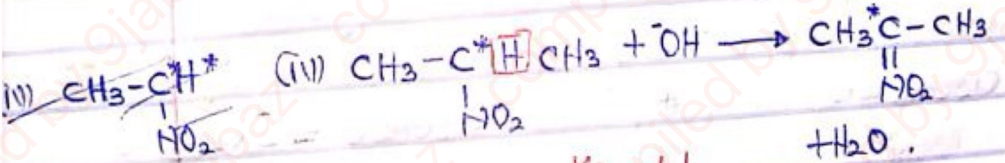
$K_H/K_D = 4.66$

1° KIE

(iii) $PhCH_2^*Cl \xrightarrow[H_2O]{CH_3CH_2OH} PhCH_2^*OH$ S_N1.

NORMAL α-2° KIE

$\frac{K_H}{K_D} = 1.3$



(iv) $CH_3-C^*H^*(NO_2)$ (iv) $CH_3-C^*\boxed{H}(NO_2)CH_3 + {}^-OH \longrightarrow CH_3\overset{*}{C}(=NO_2)-CH_3 + H_2O$.

$\frac{K_H}{K_D} = 1.1$

~~The~~

~~The effect~~

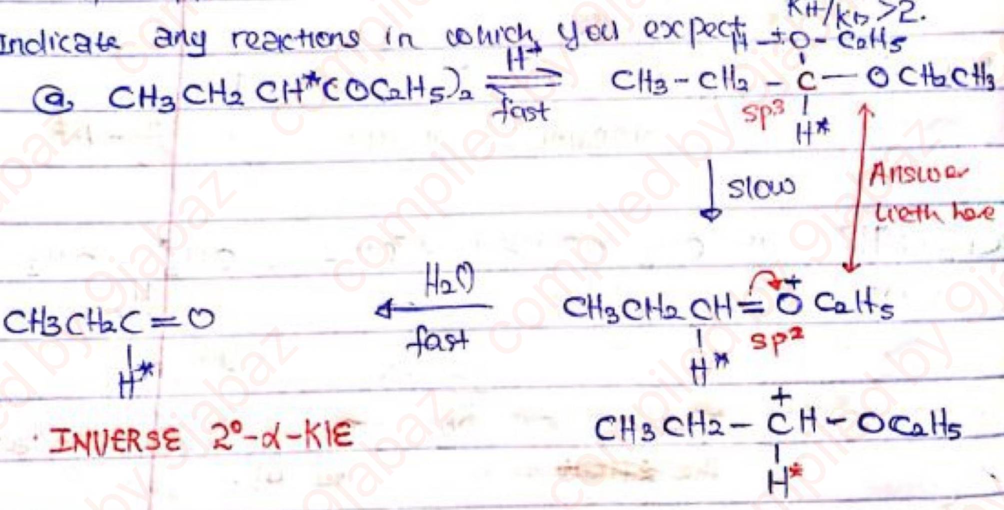
The rds in not removal of H!.

(32) What are the two main modes of studying reaction kinetics and explain how each of these is carried out?

If you know it, abeg send answer

(33) Predict and explain whether normal, inverse, or no isotope effects will be observed for each reaction below. Indicate any reactions in which you expect $k_H/k_D > 2$.

(a)

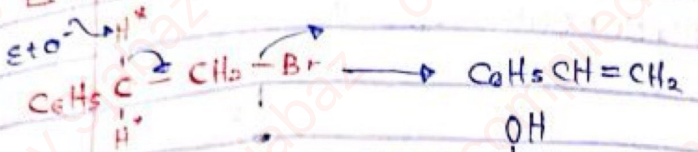


INVERSE 2°-α-KIE

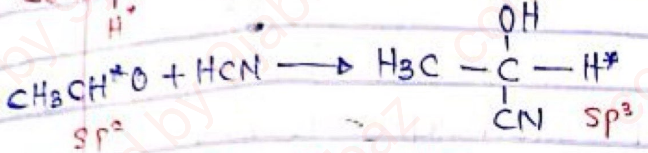
ⓑ $C_6H_5CH_2^*CH_2Br \xrightarrow[1step]{^-OEt} C_6H_5CH=CH_2 + EtOH^* + Br$

Primary KIE Effect

E_2 mechanism involves breaking of C–H bond at rds



$\frac{k_H}{k_D} >> 2.$

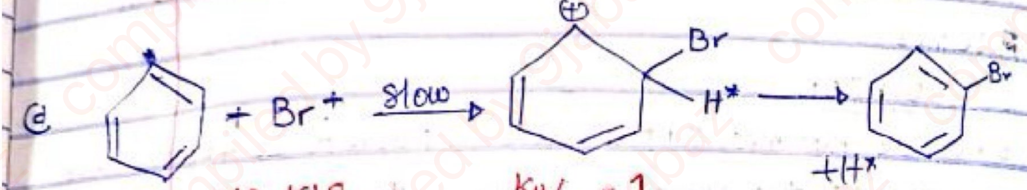


ⓒ $CH_3CH^*O + HCN \longrightarrow H_3C-\overset{OH}{\underset{CN}{C}}-H^*$

sp^2 sp^3

INVERSE – 2° – α – KIE.

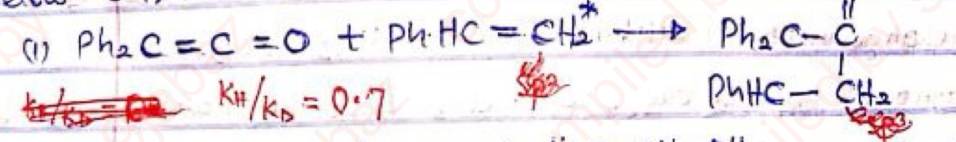
ⓓ



NO KIE $k_H/k_D = 1$

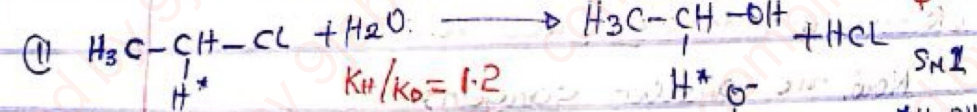
The Reaction ⓑ will have $k_H/k_D > 2$.

㉞ Match the following values with the appropriate reactions below: 6.1, 0.7, 1.2



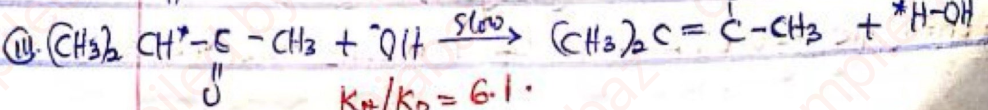
(i) $Ph_2C=C=O + Ph{\cdot}HC=CH_2^* \longrightarrow Ph_2C-\overset{O}{\overset{\|}{C}}$ / $PhHC-CH_2$

~~k_H/k_D = [illegible]~~ $k_H/k_D = 0.7$



(ii) $H_3C-\underset{H^*}{CH}-Cl + H_2O \longrightarrow H_3C-\underset{H^*}{CH}-OH + HCl$ S_N1

$k_H/k_D = 1.2$



(iii) $(CH_3)_2CH^*-\underset{O}{\overset{\|}{C}}-CH_3 + {}^-OH \xrightarrow{slow} (CH_3)_2C=\overset{O^-}{C}-CH_3 + {}^*H-OH$

$k_H/k_D = 6.1$.

35) The mechanism of semicarbazone formation from substituted benzaldehyde is shown below

$$ArCHO + NH_2NHCONH_2 \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} ArCHOH-NHNHCONH_2 \xrightarrow{K_2} ArHC=N-NHCONH_2 + H_2O$$

The Hammet plot is acid dependent. At pH = 7, P = +0.07, but at pH = 1.75, P = +0.91. explain the difference in P values

ANSWER

P is the Reaction/Sensitivity constant and it gives a measure of how susceptible a reaction is to the electronic characteristic of substituents.

The P value is +ve, It only tells us that the reaction is accelererted by electron withdrawing group. Nothing extra.

Now, the main deal;

The Hammet plot ~~is~~ being acid dependent suggests that The reaction Proceeds favorably/more sensitive to acidic condition and This inturn increases the magnitude of |P|.

At pH = 7, the solution is neutral, but at pH = 1.75, the solution s acidic and the reaction is more sensitive to the electronic characteristics of the ~~solvent~~ substituents attached, which xplains why the value increases from 0.07 to 0.91 in an cidic condition[solution].

36 Explain the wide difference in the values of the substituents constants σ_m and σ_p which are 0.337 and +0.062 respectively for the F substituent of fluorobenzene-

Soln

See question (37) for answer.

(38) Match P values with the appropriate reaction

$P = -3.3, -8.06, +1.00, +2.61$

(i) $ArCH_2CO_2Et + {}^-OH \longrightarrow ArCH_2CO_2^- + EtOH$

(ii) $ArNMe_2 + MeI \longrightarrow ArNMe_3^+I^-$

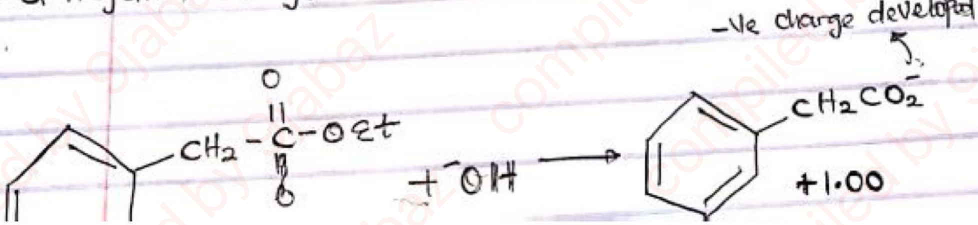
(iii) $ArCO_2Et + {}^-OH \longrightarrow ArCO_2^- + EtOH$

(iv) $ArH + Cl_2 \longrightarrow ArCl + HCl$

P measures the ability of the substituent to stabilize or destabilize charge; it depends on proximity of the substituent to the charged centre.

If ~~an~~ a positive charge is developed at the TS, the value of P is negative.

If a negative charge is developed at the TS, the value of P is +ve.

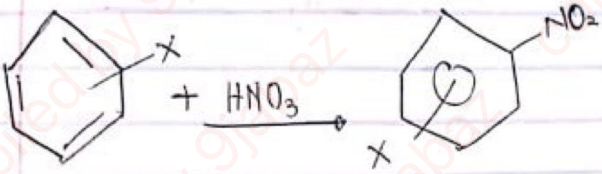


Q9 Match the ρ values with the appropriate reactions. explain your reasoning

$\rho = +2.45, +0.75, -2.39, -7.29$

Reactions:

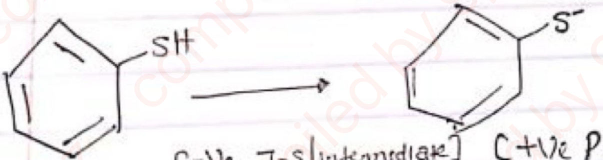
(i) Nitration of substituted benzenes.



+ve intermediate [−ve ρ] ~

close proximity ; definitely −7.29.

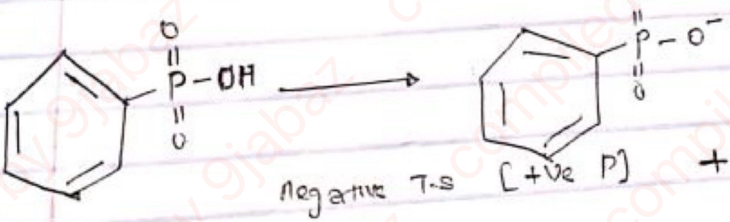
(ii) Ionization of substituted benzenethiols



[−ve T-S | intermediate] [+ve ρ]

close proximity; definitely +2.45

(iii) Ionization of substituted benzene phosphonic acid

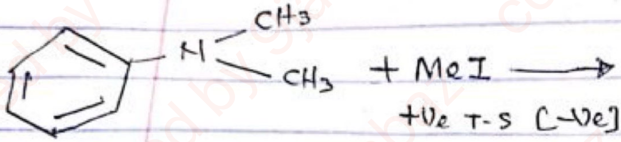


negative T-S [+ve ρ] +0.75.

go

(iv) Surely -2.39 must be for this one lol

(Reaction of substituted N,N-dimethyl anilines with methyl Iod



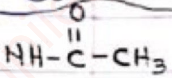
+Ve T-S [-Ve]

Good Proximity -2.39-

(37) Explain the difference in values of σ_m and σ_p for each of the following groups in terms of the electronic character of each group

Substituent	σ_m	σ_p
$NHCOCH_3$	+0.21	0.00
F	+0.337	+0.062
Cl	+0.373	+0.227

NB → A +ve value of σ suggests that the substituents are more electron withdrawing than Hydrogen and a more -ve value of σ means that the substituents are Electron donating. A value of 0 indicates that the +ve effects and -ve effects cancel out'

For 
$NH-\overset{O}{\overset{\|}{C}}-CH_3$

At the meta position, there is an increased -ve inductive effect felt/observed ~~for~~ ~~by~~ from the Reaction centre, by the EWG hence the observed value

But at the Para Position; The $NHCOCH_3$ group is an electron donating group and they donate electrons to stabilise the ring via +ve mesomeric effect, but due to the keto group adjacent to it, The electron donating capability is decreased significantly since the C=O will withdraw electrons by -ve inductive effect [due to their polarity], hence cancelling out the effect of the substituent on the ring and giving observed value of 0, and a much decreased value compared to σ_m.

For F

At the meta position, there is a ~~Strong~~ Large ~~-ve~~ -ve inductive effect observed due to the strong electronegative nature of fluorine, ~~and also a +ve~~ and at the meta position, he mesomeric effect is strongly reduced or does not even xists hence a more +ve σ value

At the para position, even though the inductive effect is till observed to be -ve inductive effect, the mesomeric ffect is +ve [F has lone electrons on it and hence electron onating to the ring], hence there will be a partial cancellation eading to a reduced value.

Note that:

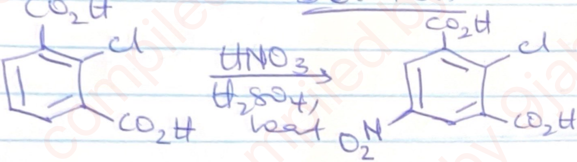
NB→The same effect is felt in chlorine as well, only that in chlorine, the σ_p is a little bit close to σ_m because ~~Cl is more. electronwithdrawing on a ring~~ Cl has a much lesser mesomeric effect (+ve) compared to F to the ~~chlor~~ ring

That is → chlorine will prefer to withdraw electrons via mesomeric effect than donate electrons into a ring to stabilise. You get?

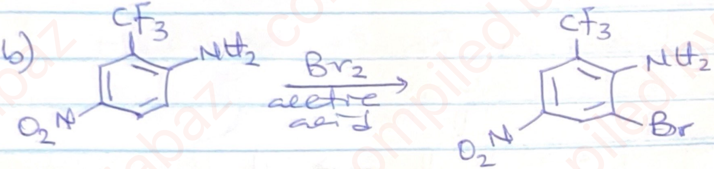
But then if you give the same reason for fluorine, you are okay.

Solution

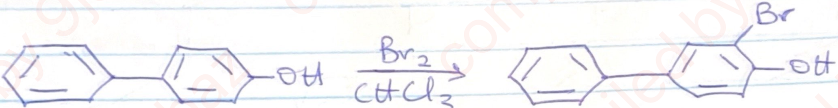
a)



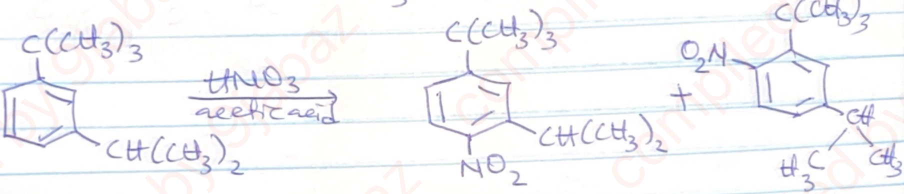
b)



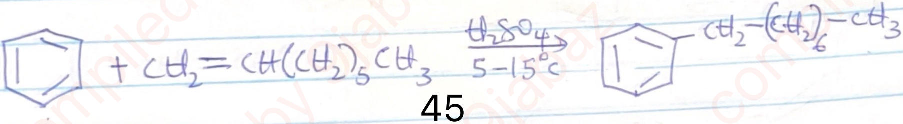
c)



d)

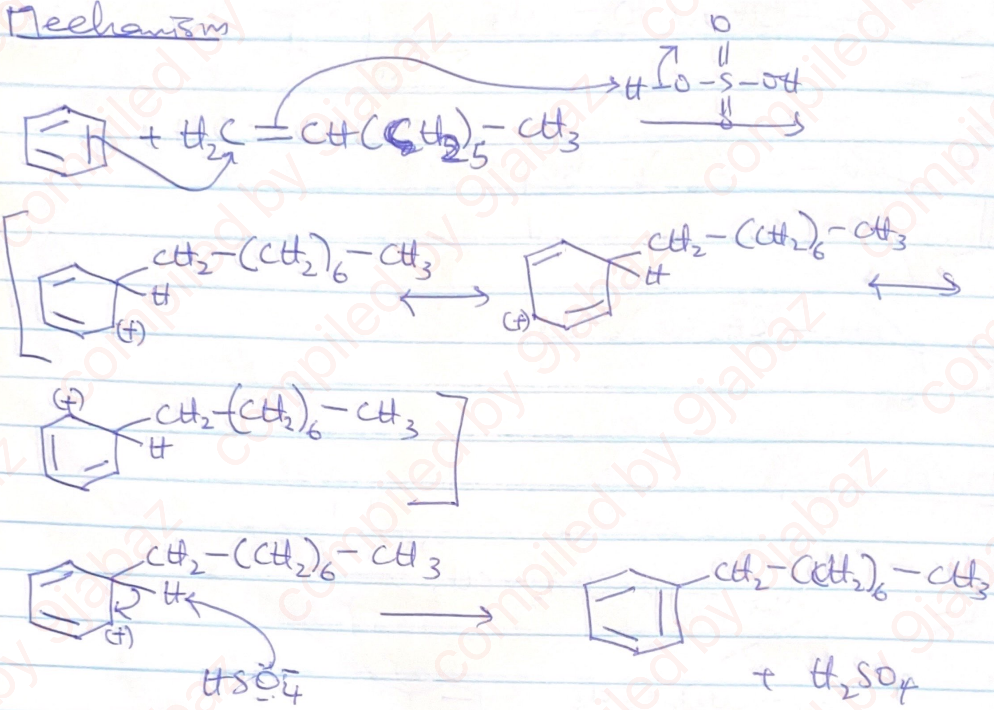


e)



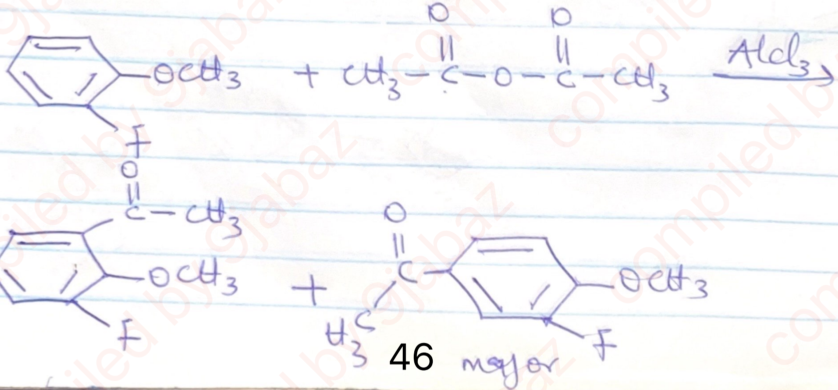
Mechanism

Mechanism



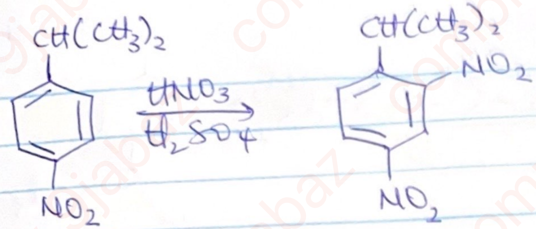
+ H₂C=CH(CH₂)₅–CH₃
H–O–S(=O)(=O)–OH
CH₂–(CH₂)₆–CH₃
H
(+)
HSO₄⁻
+ H₂SO₄

f)

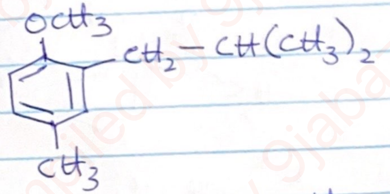


OCH₃
F
+ CH₃–C(=O)–O–C(=O)–CH₃
AlCl₃
C(=O)–CH₃
OCH₃
+
H₃C
OCH₃
F
major

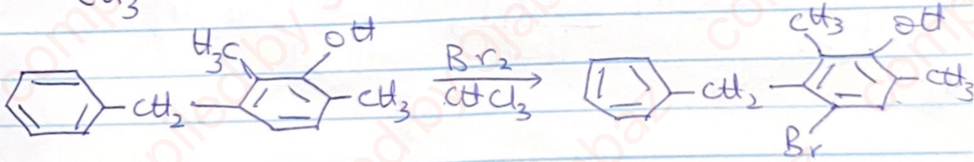
g)


CH(CH3)2
NO2
HNO3
H2SO4
CH(CH3)2
NO2
NO2

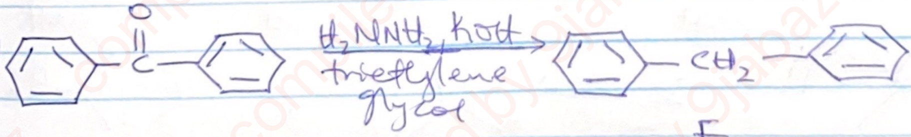
h)


OCH3
CH2 – CH(CH3)2
CH3

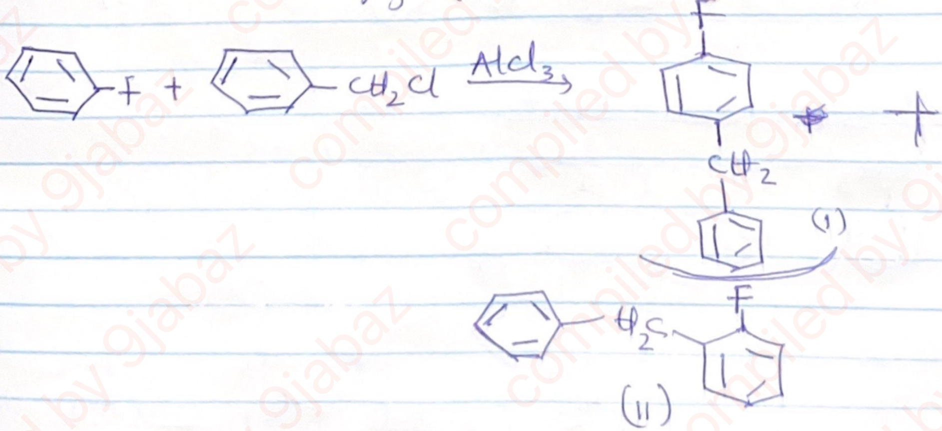
(i)


H3C
OH
CH2
CH3
Br2
CHCl3
CH2
CH3
OH
CH3
Br

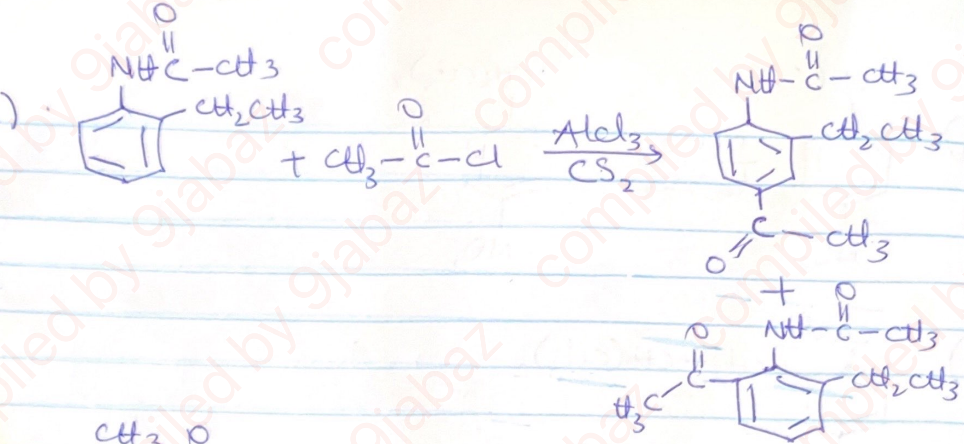
j)


O
C
H2NNH2, KOH
triethylene glycol
CH2

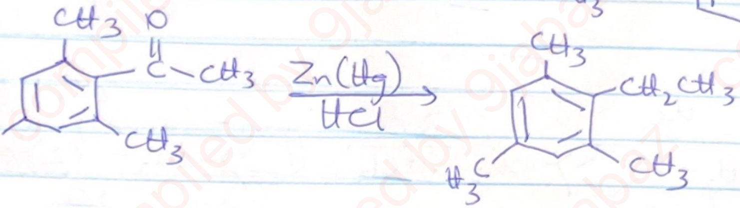
k)


F
+
CH2Cl
AlCl3
F
CH2
+
(1)
F
H2C
(11)

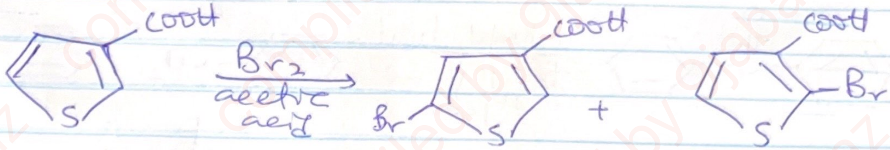
l)



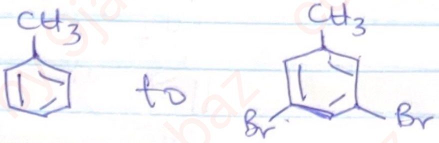
m)



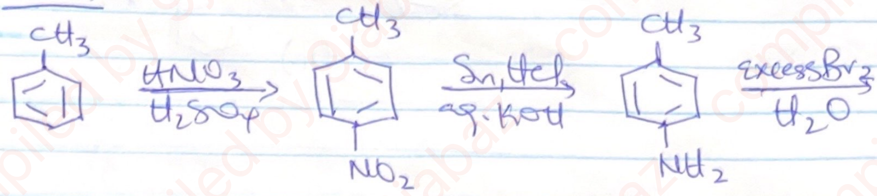
n)

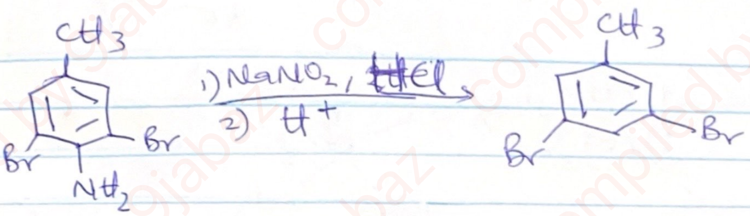


solved problem 19-4



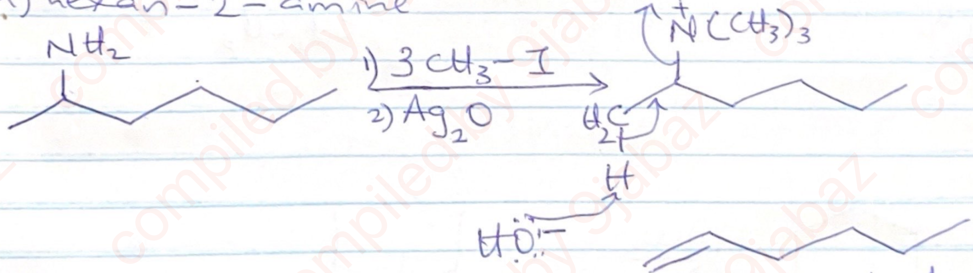
soln





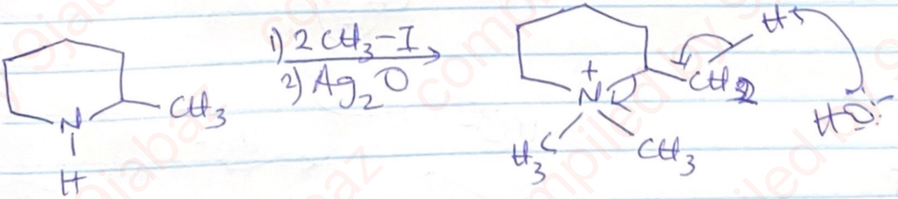
predict major product from exhaustive methylation

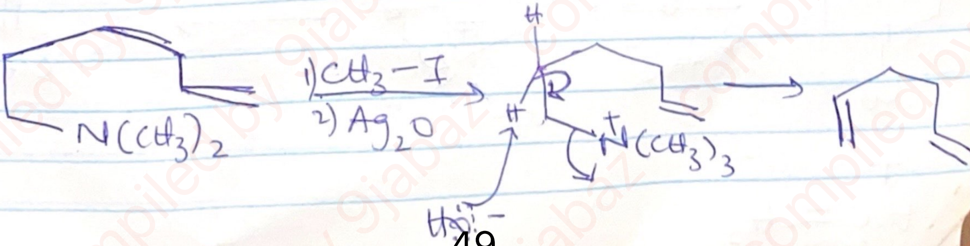
a) hexan-2-amine



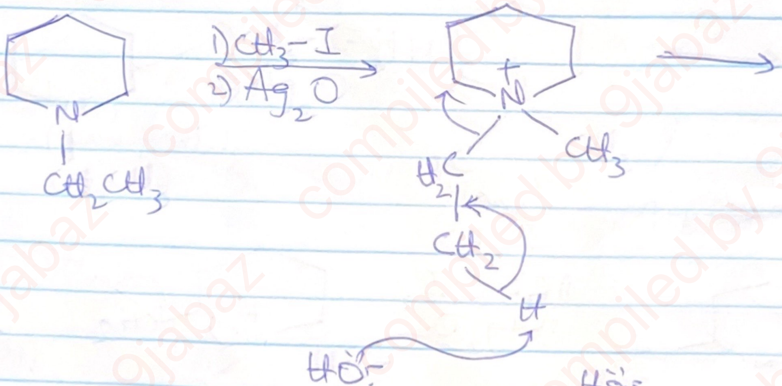
major product (Hoffman)

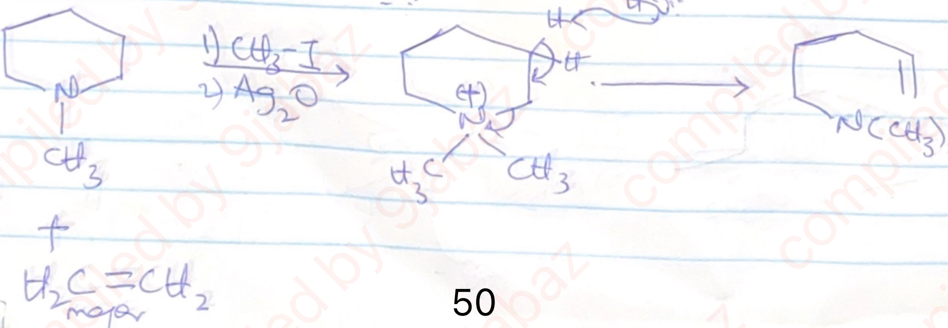
b) 2-methylpiperidine

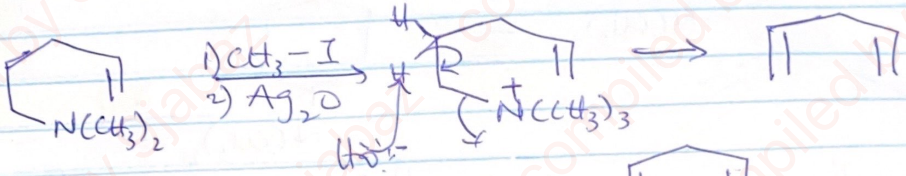




c)

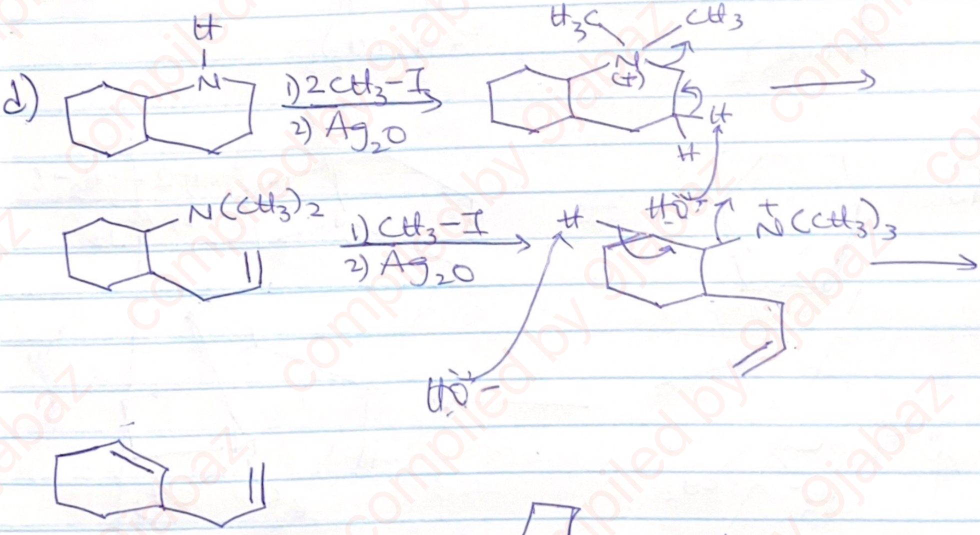

N
CH2CH3
1) CH3-I
2) Ag2O
+
N
CH3
H2C
CH2
H
HO:-


N
CH3
1) CH3-I
2) Ag2O
HO:-
H
H
(+)
N
H3C
CH3
N(CH3)2
+
H2C=CH2
major

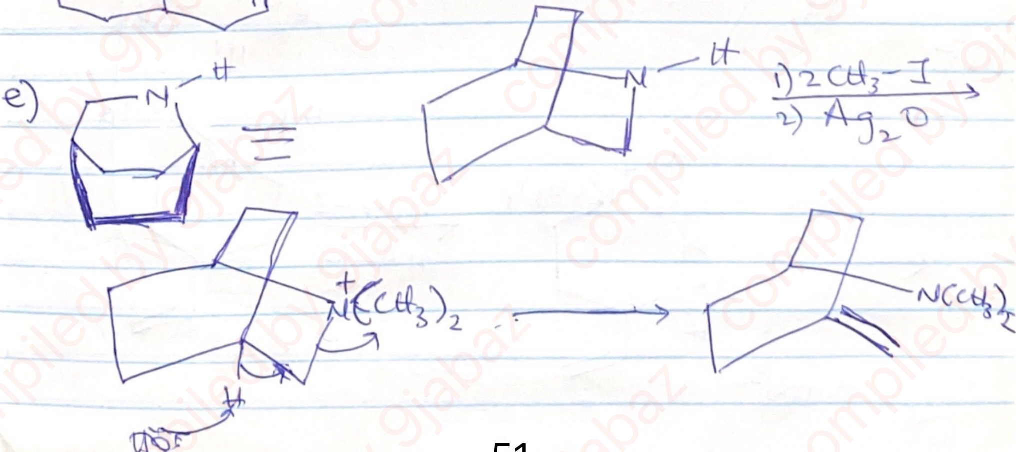


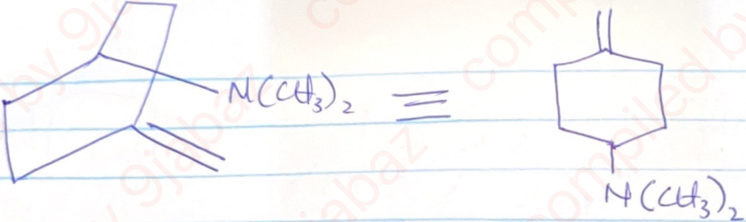
products are; $H_2C=CH_2$ + 
major minor

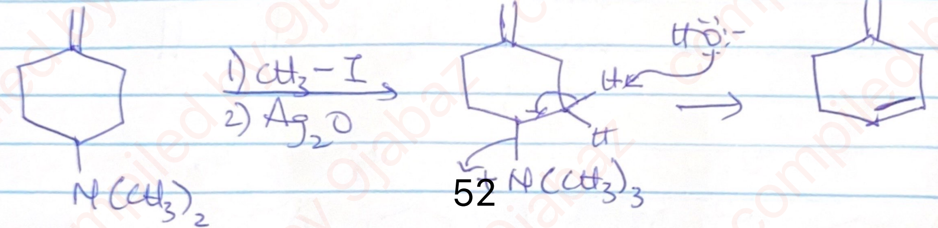
d)



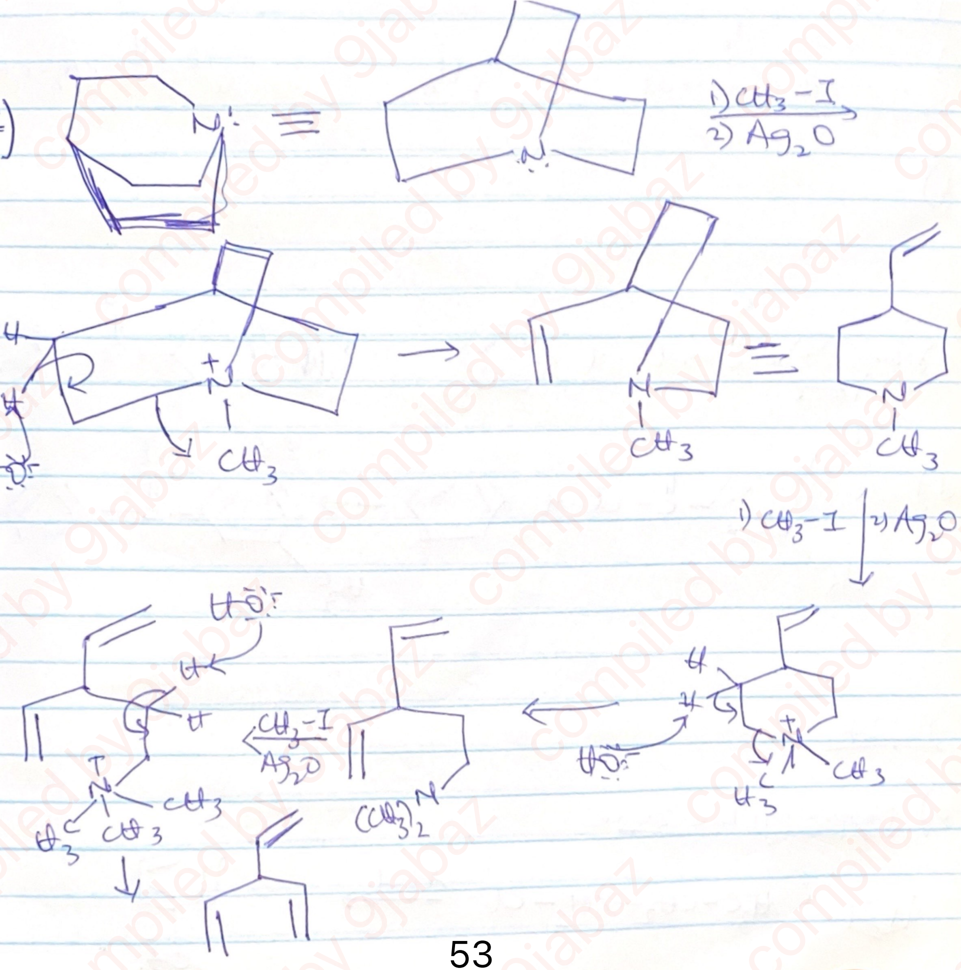
e)




N(CH3)2
≡
N(CH3)2

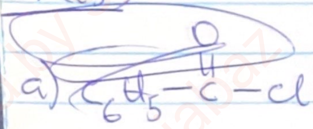

N(CH3)2
1) CH3-I
2) Ag2O
HO:-
H
H
+N(CH3)3

f)


N:
≡
N:
1) CH3-I
2) Ag2O
H
H
HÖ:
+
N
CH3
→
N
CH3
≡
N
CH3
1) CH3-I
2) Ag2O
H
H
HÖ:
+
N
CH3
CH3
←
N
(CH3)2
CH3-I
Ag2O
HÖ:
H
H
+
N
CH3
CH3
CH3

12.33

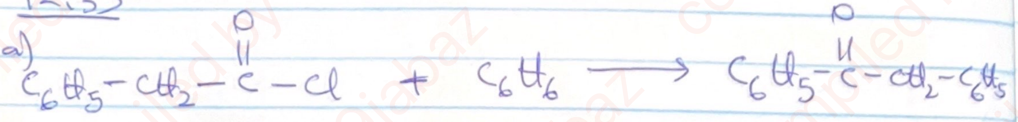
a)



$C_6H_5-\overset{\overset{O}{\|}}{C}-Cl$

12.33

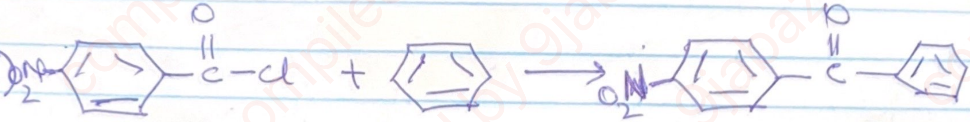
a)



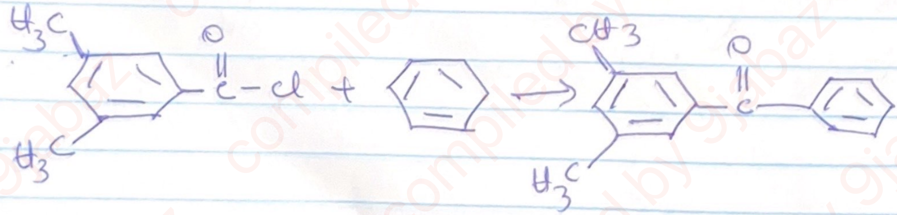
$C_6H_5-CH_2-\overset{\overset{O}{\|}}{C}-Cl + C_6H_6 \longrightarrow C_6H_5-\overset{\overset{O}{\|}}{C}-CH_2-C_6H_5$

b)

c)

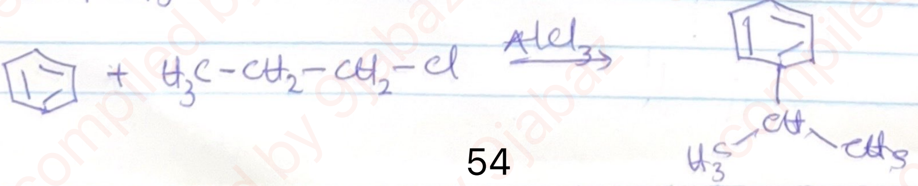


d)

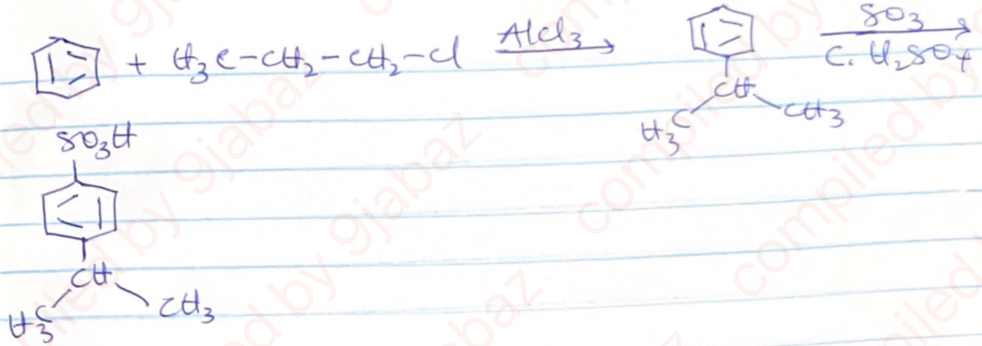


12.27

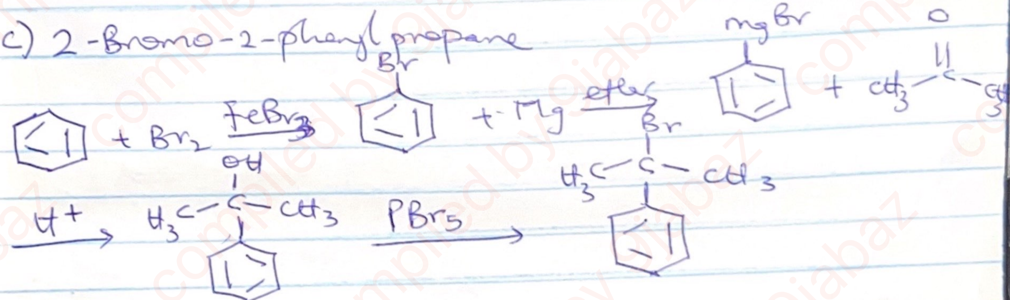
a) Isopropyl benzene



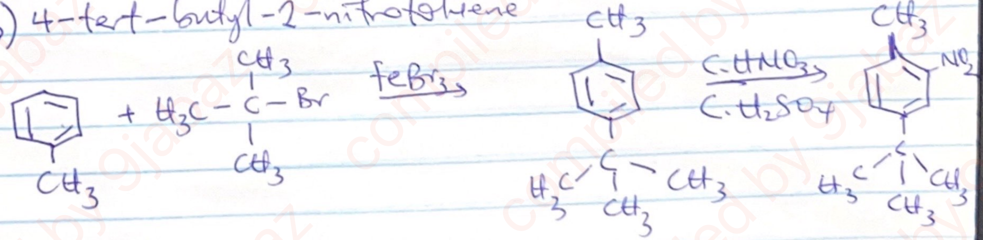
b) p-Isopropylbenzenesulfonic acid



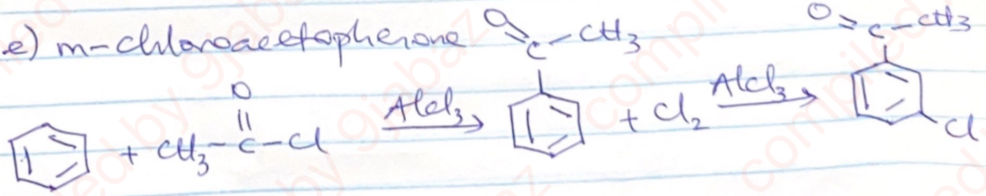
c) 2-Bromo-2-phenyl propane



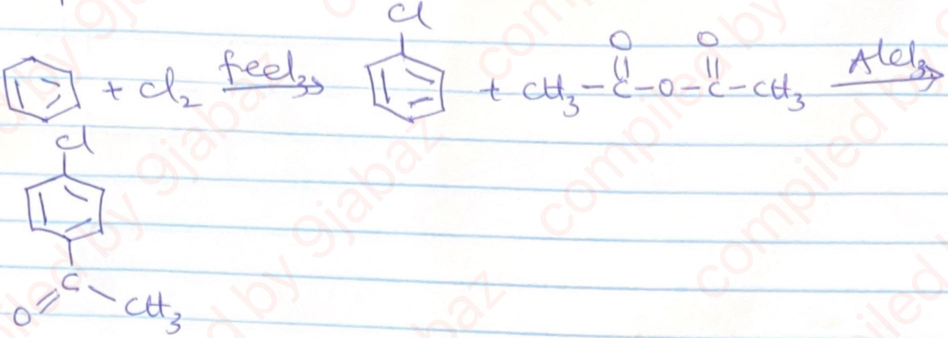
d) 4-tert-butyl-2-nitrotoluene



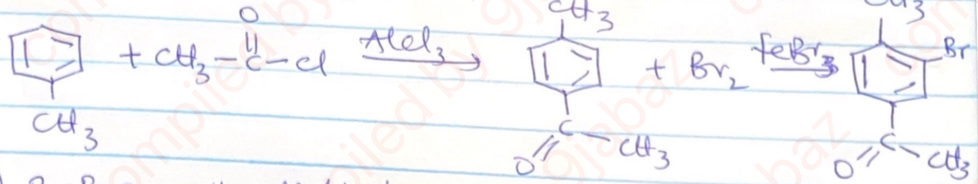
e) m-chloroacetophenone



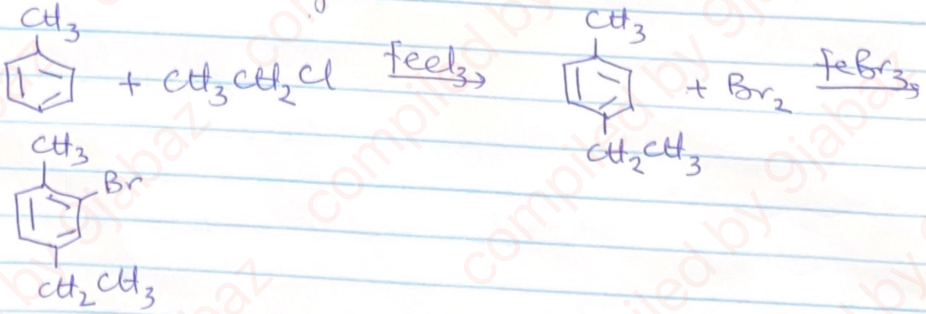
f) p-chloroacetophenone



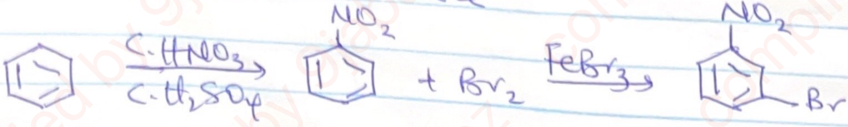
g) 3-Bromo-4-methylacetophenone.



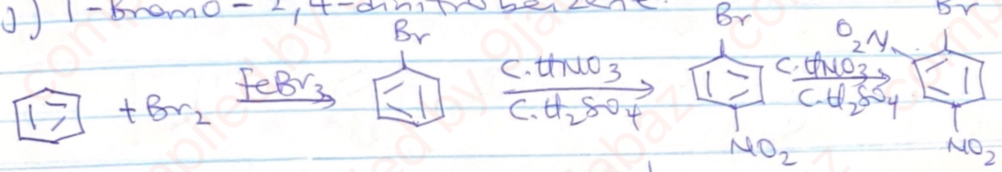
h) 2-Bromo-4-ethyltoluene.



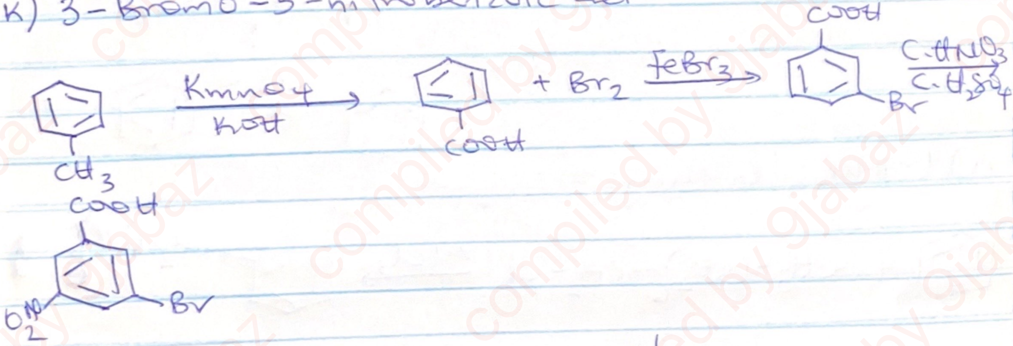
i) 1-Bromo-3-nitrobenzene



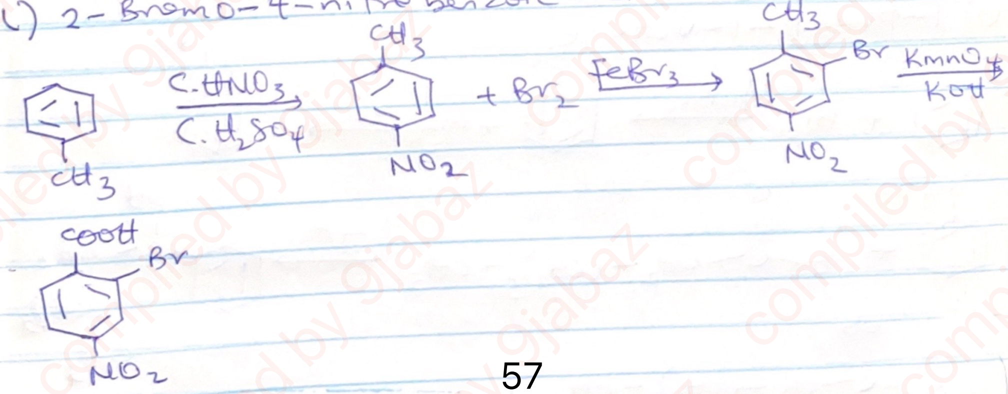
j) 1-Bromo-2,4-dinitrobenzene.



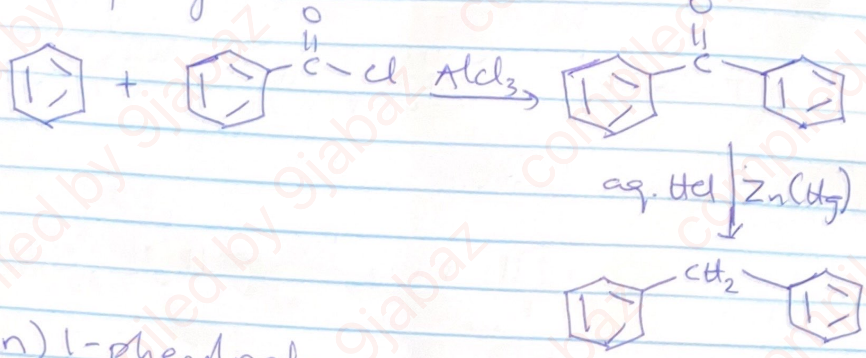
k) 3-Bromo-5-nitrobenzoic acid



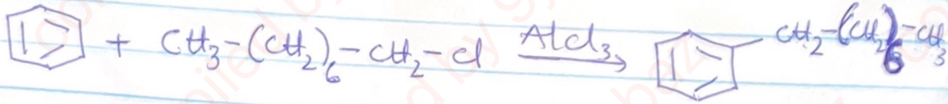
l) 2-Bromo-4-nitrobenzoic acid



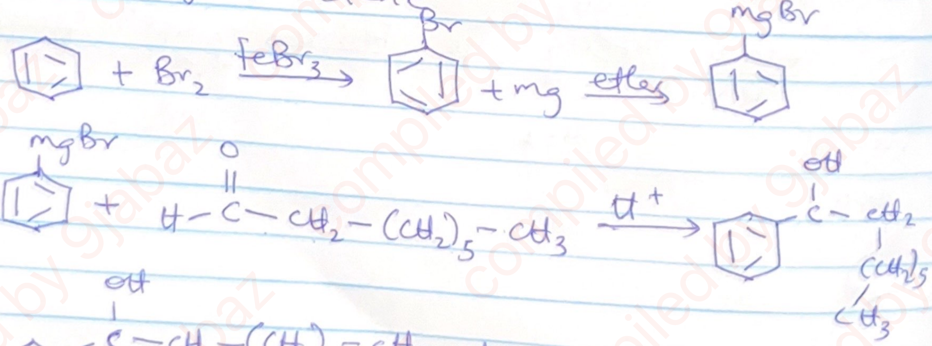
f) m) Diphenylmethane

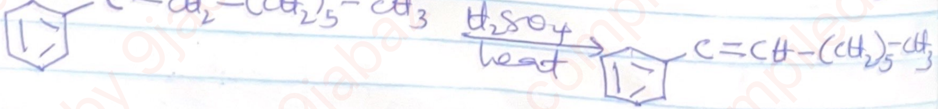


g) n) 1-phenyloctane

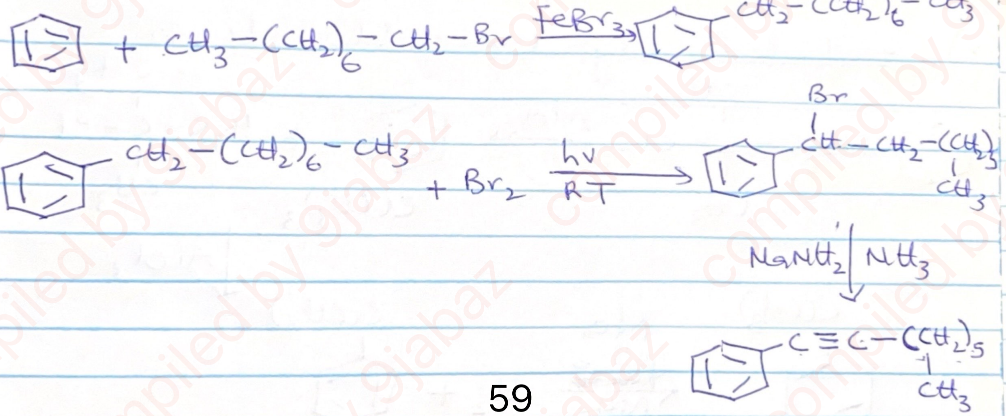


h) o) 1-phenyl-1-octene



i)


P) 1-phenyl-1-octyne



f

g) 1,4-di-tert-butyl-1,4-cyclohexadiene.