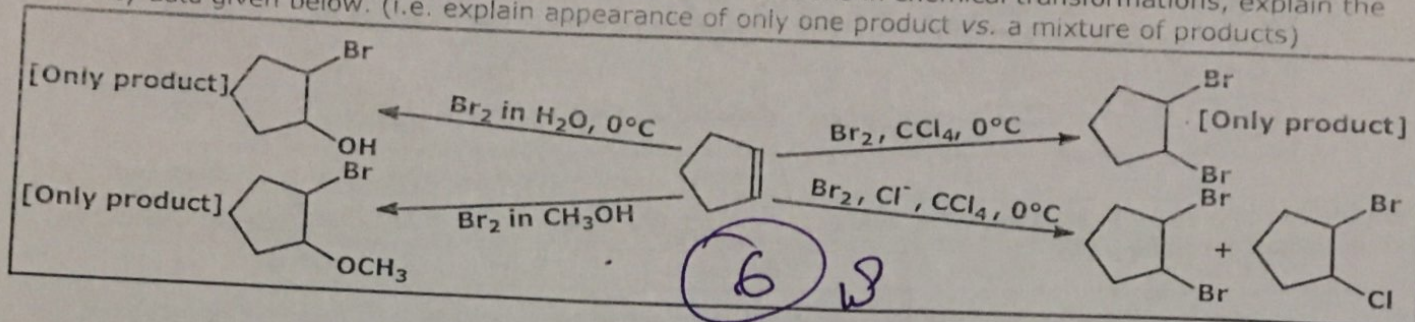
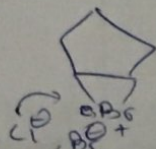
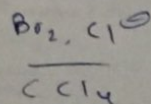
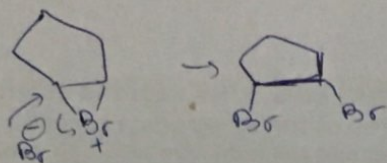
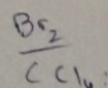


NAME: Sukant Koul

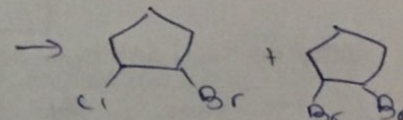
1) Given what you now know about the importance of collisions in chemical transformations, explain the reactivity data given below. (i.e. explain appearance of only one product vs. a mixture of products)



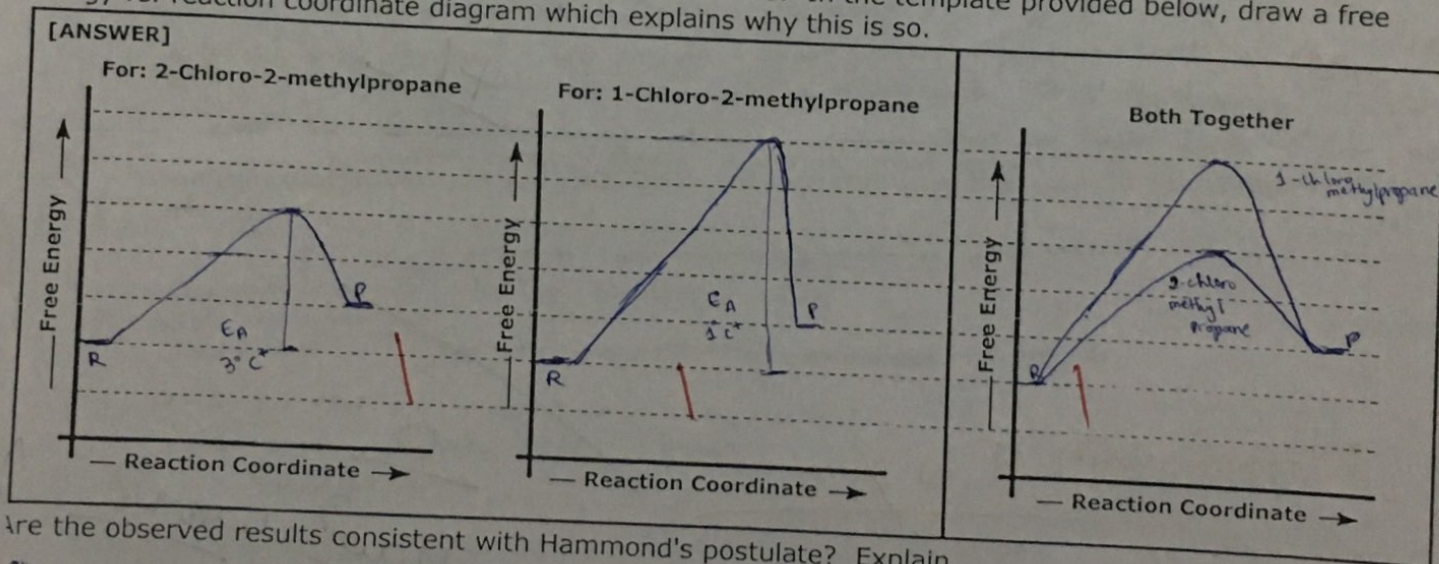
The last case is the only case in which a species other than Br is able to have effective overlap with the π orbitals of the doubly bonded C.



both can collide effectively

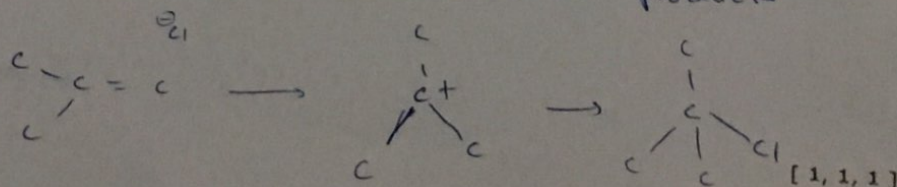


2) The addition of HCl to 2-Methylpropene gives 2-chloro 2-methylpropane as the only product. The other possible product, 1-chloro 2-methylpropane is not formed. In the template provided below, draw a free energy vs. reaction coordinate diagram which explains why this is so. [1, 1, 1]



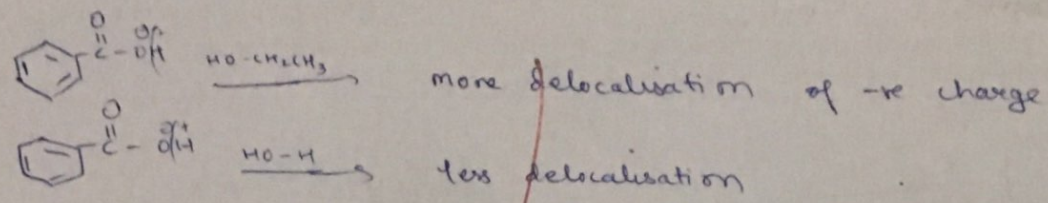
Are the observed results consistent with Hammond's postulate? Explain.

Reaction is endothermic (energy reqd to break C=C bond) ⇒ TS<sup>‡</sup> should resemble products

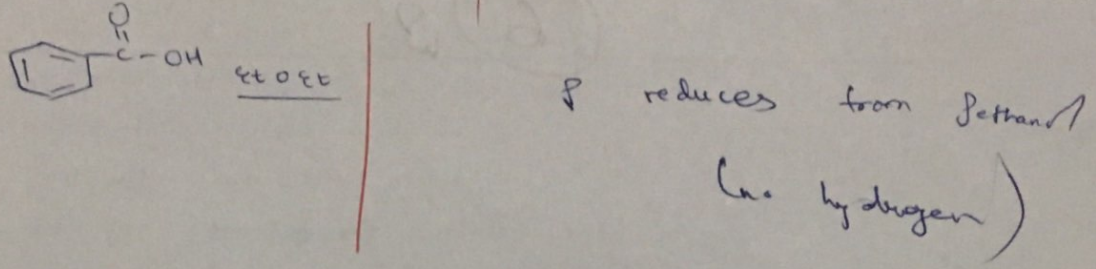




3) For  $C_6H_5COOH$ , in ethanol,  $p$  for the acid dissociation is 1.96 as compared to 1.00 in  $H_2O$ . Explain origin of this difference in  $p$  values.



Relative to the  $p$  value in ethanol, what would you expect the value of  $p$  for  $C_6H_5COOH$  to be in  $C_2H_5OC_2H_5$ ? Explain your reasoning.



4) By comparing the inductive and delocalisation (resonance) effects, explain the difference in the  $\sigma$  values between each pair of substituents in the table below in terms of the electronic character of each group. [Draw the delocalised forms for the resonance effect and the inductive effect (if applicable).]

Substituent	$\sigma_{meta}$	$\sigma_{para}$	Substituent	$\sigma_{meta}$	$\sigma_{para}$
$OCH_3$	0.07	-0.24	$OCF_3$	0.40	0.35
$OCOCH_3$	0.39	0.31	$NHCOCH_3$	0.21	0

$\sigma$  -  $pK_a$  (unsub)  
 $\sigma$  -  $pK_a$  (sub)  
 $\sigma > 0 \Rightarrow$  sub is stronger acid

Why do  $\sigma_{meta}$  and  $\sigma_{para}$  have opposite signs for  $-OCH_3$  but NOT for  $-OCF_3$ ?

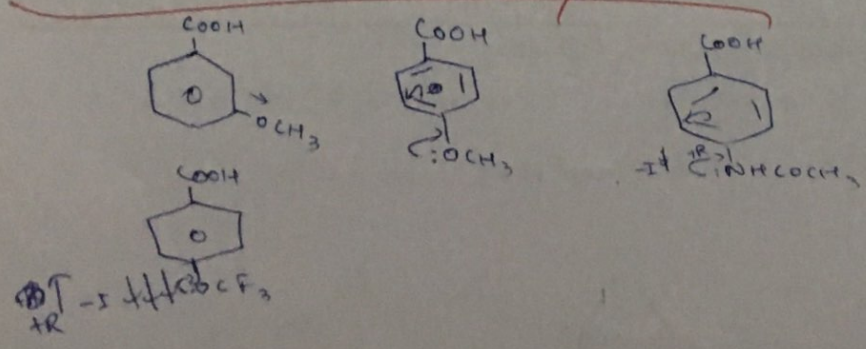
For  $-OCH_3$ , the electrons it donates into the ring make the acid weaker (ve charge sent on already -ve species). However, this delocalisation only occurs from o & p, not from m. From meta, it is just a weak inductive effect that makes the acid slightly stronger. The acid-weakening R-effect exists for  $-OCF_3$  as well, but because of the OCF<sub>3</sub> (stronger), it can overpower the -R effect considerably and hence moving from meta to para (ie from no R to R) does not have much of an effect.

Electronegativity Concept

As the -I-effect is enormously strong, it can overpower the -R effect considerably and hence moving from meta to para (ie from no R to R) does not have much of an effect. In  $OCH_3$ , the I-effect is much weaker, and so cannot overpower R and thus moving from no R to R makes a large difference. Why are the magnitudes of  $\sigma_{meta}$  and  $\sigma_{para}$  different for  $-NHCOCH_3$  but approximately similar for  $-OCOCH_3$ ?

$NHCOCH_3$  is an EDG  $\Rightarrow$  donates  $e^-$  by +R and withdraws by -I  $\Rightarrow$  it is stronger, hence the large difference. I-effect dominates for  $-OCOCH_3$  & it is stronger, hence not much difference.  $OCOCH_3$  is an EWG  $\Rightarrow$  both -I & -R apply, I is stronger, hence not much difference.

Electronegativity of N & O



How? why?  
 3 extremely electro -ve F atoms, the -I-effect is much stronger and hence overpowers the R-effect.

[1, 1, 2]

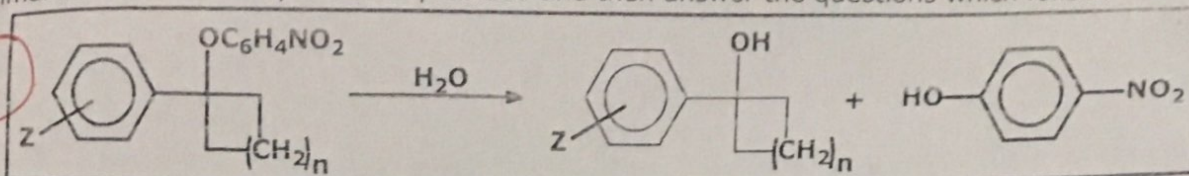


NAME: \_\_\_\_\_

Sukant Koul

ENTRY #: 2015CH10190

Hammett data for a solvolysis reaction that involves nucleophilic attack by water to replace the excellent leaving group  $p\text{-O}_2\text{N-C}_6\text{H}_4\text{O}^-$  with a  $\text{HO}^-$  group to give a tertiary alcohol and paranitrophenol in all the cases is summarized below. Study the data provided and then answer the questions which follow.



$\rho$  for solvolysis reaction in 80% aqueous acetone at  $25^\circ\text{C}$

n	0 (3 membered ring)	1 (4 membered ring)	2 (5 membered ring)	3 (6 membered ring)	4 (7 membered ring)
$\rho$	-5.15	-4.91	-3.82	-4.60	-3.87

a) Based on the measured  $\rho$  values, what is the most likely mechanism being followed in these reactions? Explain.

highly  $-\rho$  val  $\Rightarrow$

the charge is being delocalised  $\Rightarrow$   $\text{C}^+$  formation

$\frac{1}{2}$

$\Rightarrow \text{S}_{\text{N}}1$

b) In which of these five structures will the effect of the substituent Z be most predominant? Why?

least stable  $\text{C}^+$   $\Rightarrow$  first case with  $n=0$

As  $\text{C}^+$  becomes stable, Z effect reduces

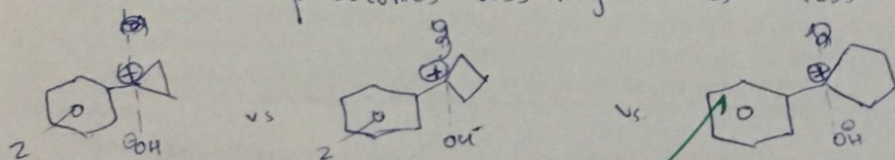
c) Explain the trend in the variation of the  $\rho$  values for the above series. That is, explain the initial fall in the magnitude of  $\rho$ , its rise and subsequent fall again!

[ Hint: What is the **bond angle** in each of the cyclic structures? What does the **magnitude** of  $\rho$  tell us? Are these related? ]

[ Hint: What is the difference in conformation of the different rings? ]

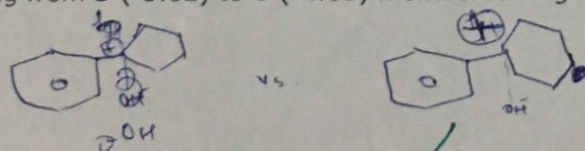
Change in  $\rho$  going from 3 (-5.15) to 4 (-4.91) to 5 (-3.82) membered rings is due to:

$\rho$  becomes less negative  $\Rightarrow$  less delocalisation of the charge / more  $\text{e}^-$  leaving ring in TS



The ~~decreasing~~ increasing bond angle of the rings puts greater strain on the benzene - (C-OR) bond  $\Rightarrow$  less eff. delocalisation

Change in  $\rho$  going from 5 (-3.82) to 6 (-4.60) membered ring is due to:



The two six membered rings have repulsion between the ortho-H & are non planar (different conformation) & hence more effective delocalisation of the charge occurs

Change in  $\rho$  going from 6 (-4.60) to 7 (-3.87) membered ring is due to:

Closer ~~prox~~ to planarity  $\Rightarrow$  again less effective delocalisation

[ 1.5, 1.5, 2, 2, 1 ]