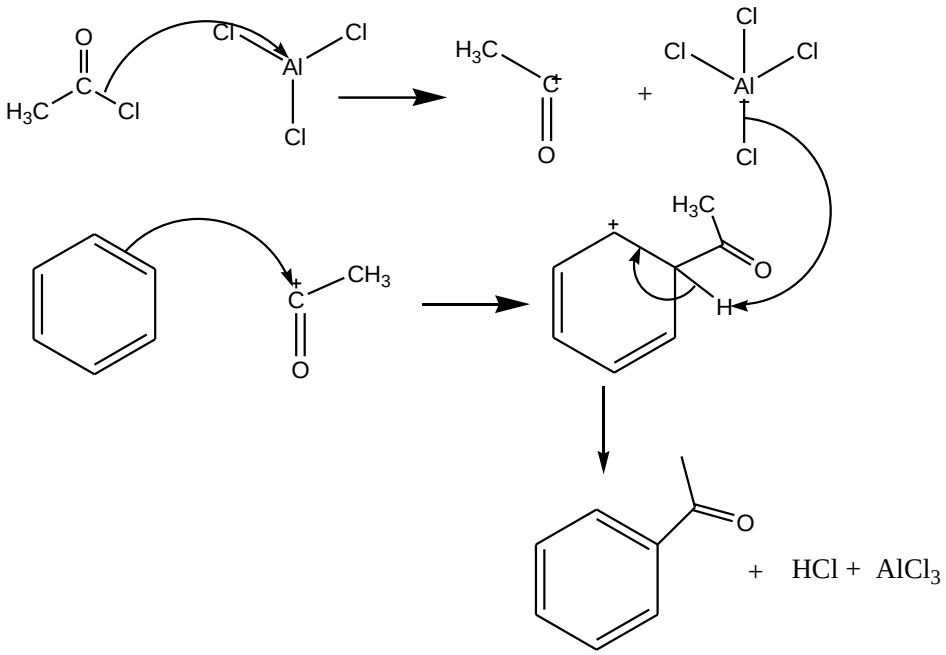
Question 5c (i)

Reagents

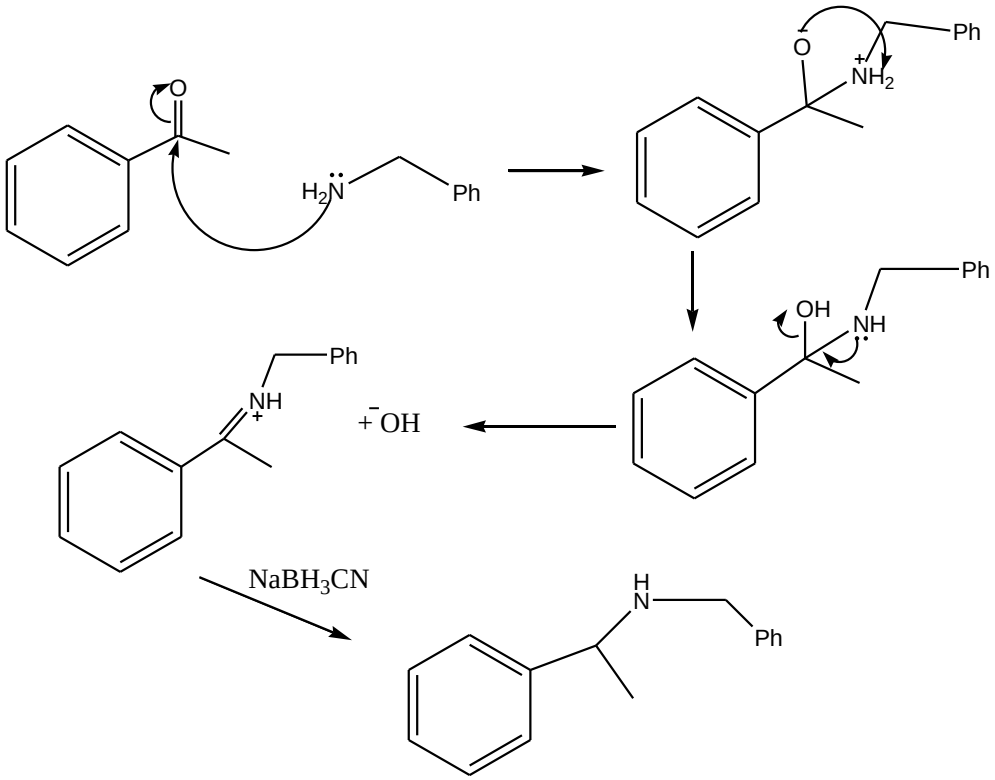
- Lewis acid (AlCl3)
- Acetyl chloride ($CH_3COCl$)

Mechanism of transformation of A to B



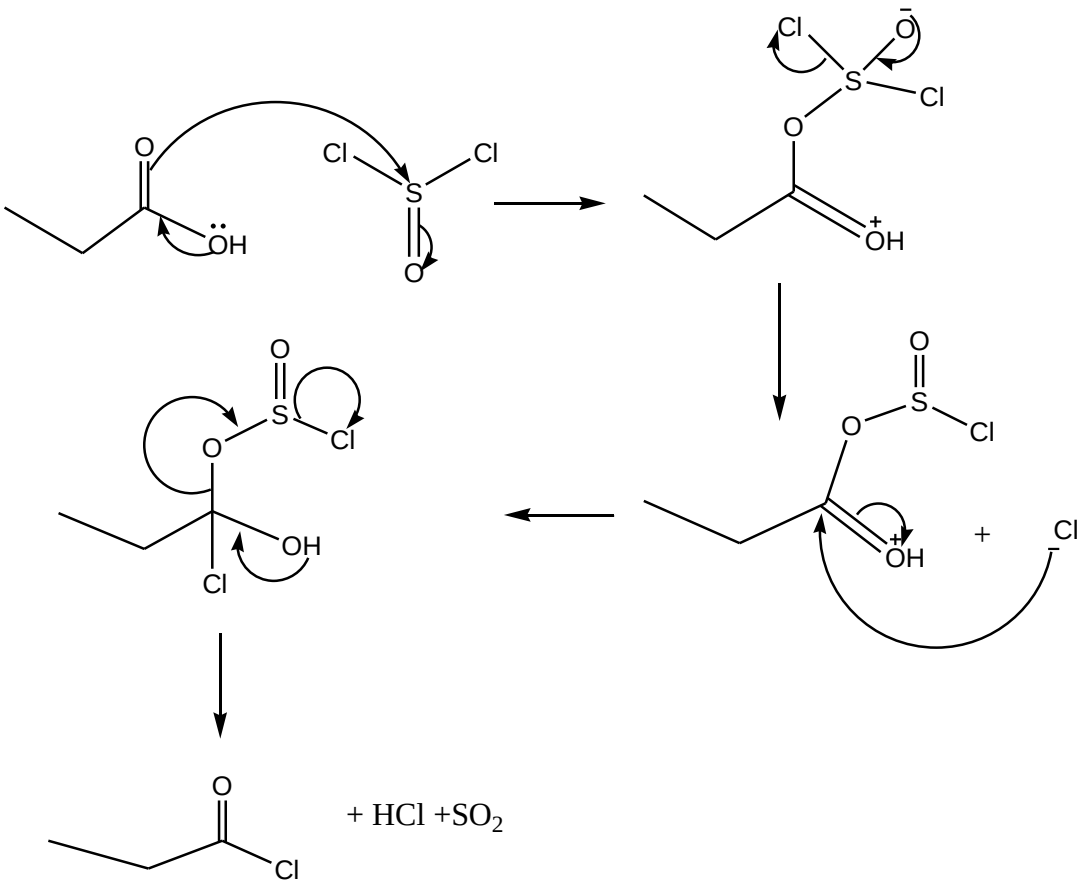

Question 5c (ii)

Mechanism of transformation of B to C



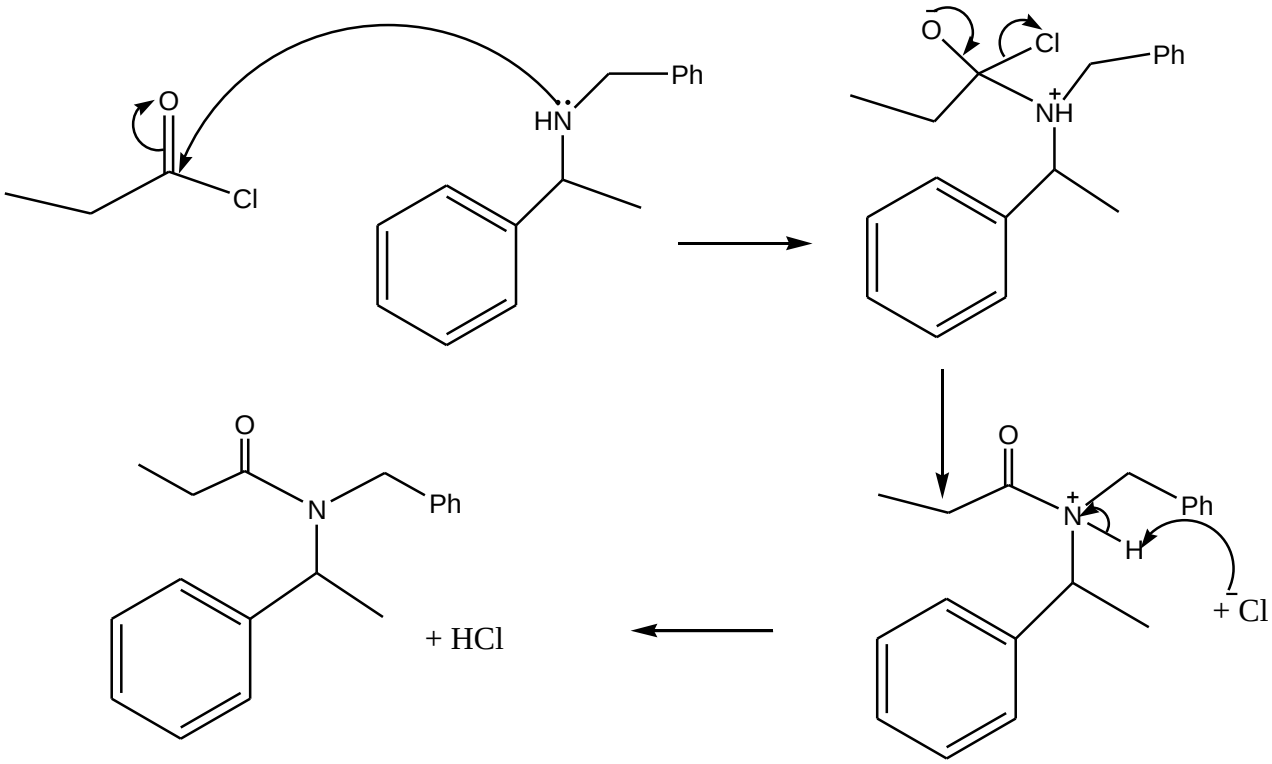
Question 5c (iii)

Mechanism for the conversion of D to E



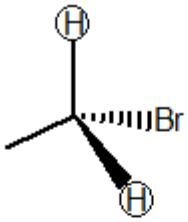

Question 5c (iv)

Mechanism of reaction between C and E to give F

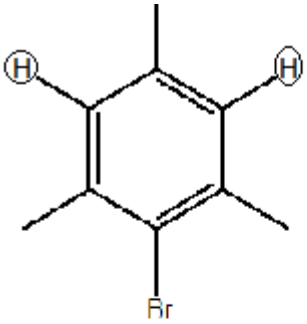


5. Answer (a), (b) and (c).

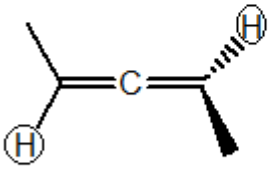
a. Topism is a form of analysis that compares atoms or groups of atoms in relation to their environment. For the following molecules, indicate whether the shaded atoms or groups are homotopic, enantiotopic, diasteriotopic or constitutionally heterotropic.



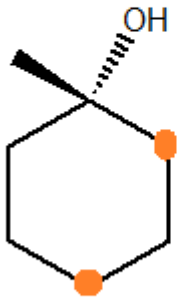

Enantiotopic




Homotopic



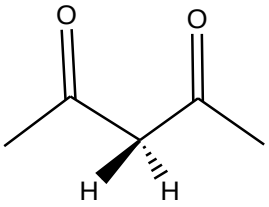

Diastereotopic




Constitutionally heterotopic

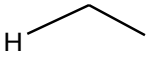
Homotopic

b). Rationalize the following series of solution p$K_a$ values for each carbon acid by considering the relevant ionization equilibrium.



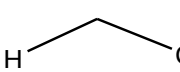

p$K_a$ = 9

The hydrogens in this molecule are very acidic because their bonding electrons are pulled upwards towards the two carbonyls that are adjacent on either sides to the bonding carbon. These hydrogens are therefore easily removed and therefore the molecule is significantly acidic as shown by the p$K_a$ value of 9.



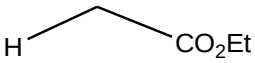

p$K_a$ = 10

The alpha protons to the electron withdrawing group are acidic because of the pull of bonding electrons towards the nitrogen. Since there is only one nitro group that is causing the pull of electrons, this molecule is slightly less acidic than the above molecule with p$K_a$ of 9, and therefore its p$K_a$ value is 10.



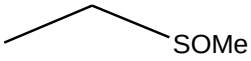

p$K_a$ = 19

The electronegative element in this molecule is sterically hindered by the substituent – methyl and it also donates electrons to the electron withdrawing group. Therefore, the pull of electrons on acidic protons is weakened and thus the molecule is less acidic.




p$K_a$ = 26

The ester group available in this molecule as an electron withdrawing group is not very strong to cause a significant pull of electrons. This molecule is thus basic as compared to the above other structures.



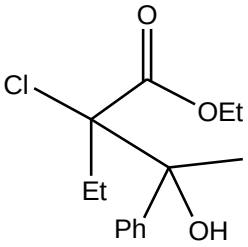

p$K_a$ = 35

This molecule is basic because –SOMe is not a good electron withdrawing group. The protons attached to this molecule are thus not acidic and hence the high p$K_a$ value of 35.

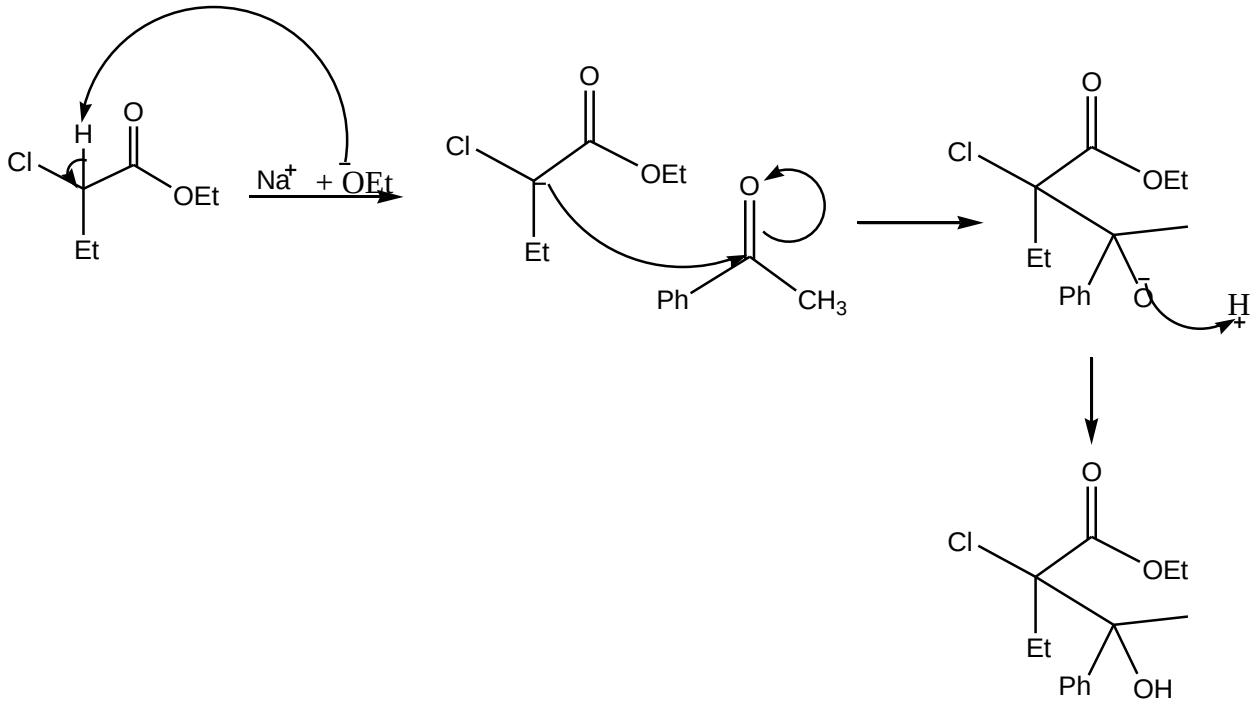
(5). Answer (a) and (b)

(a)- With respect to the following synthetic sequence:

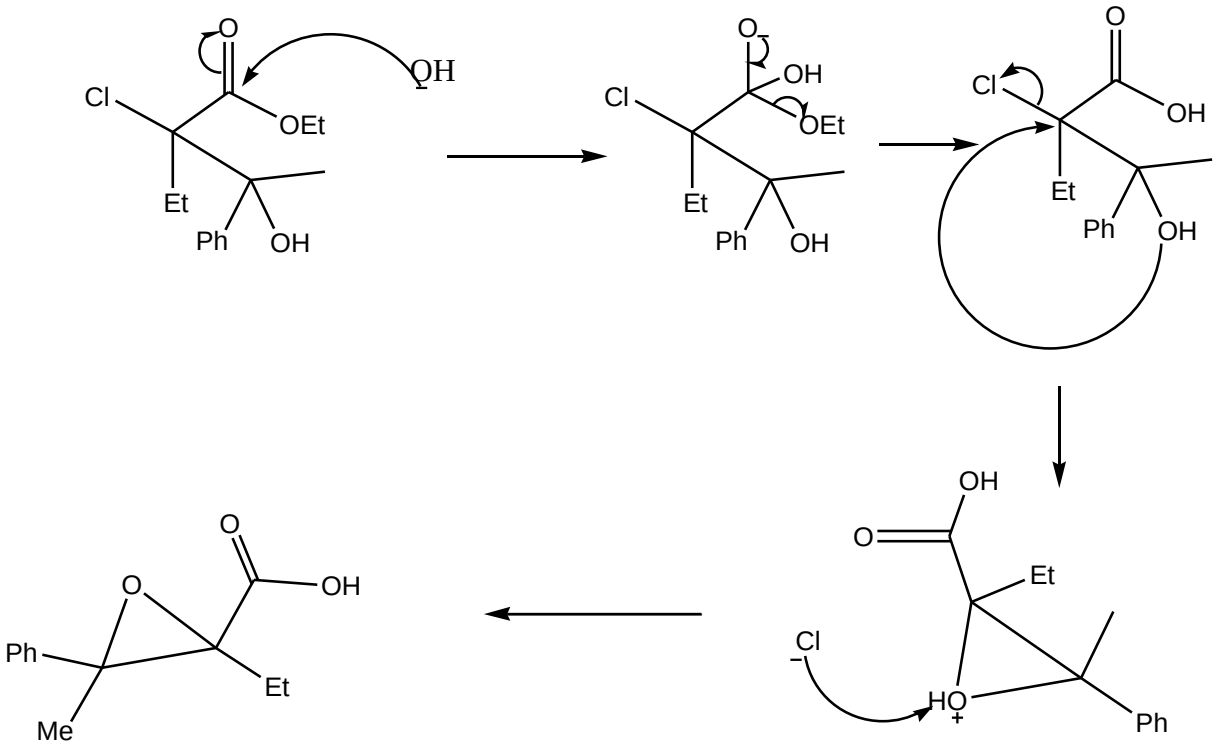
(i). Predict the structure of A



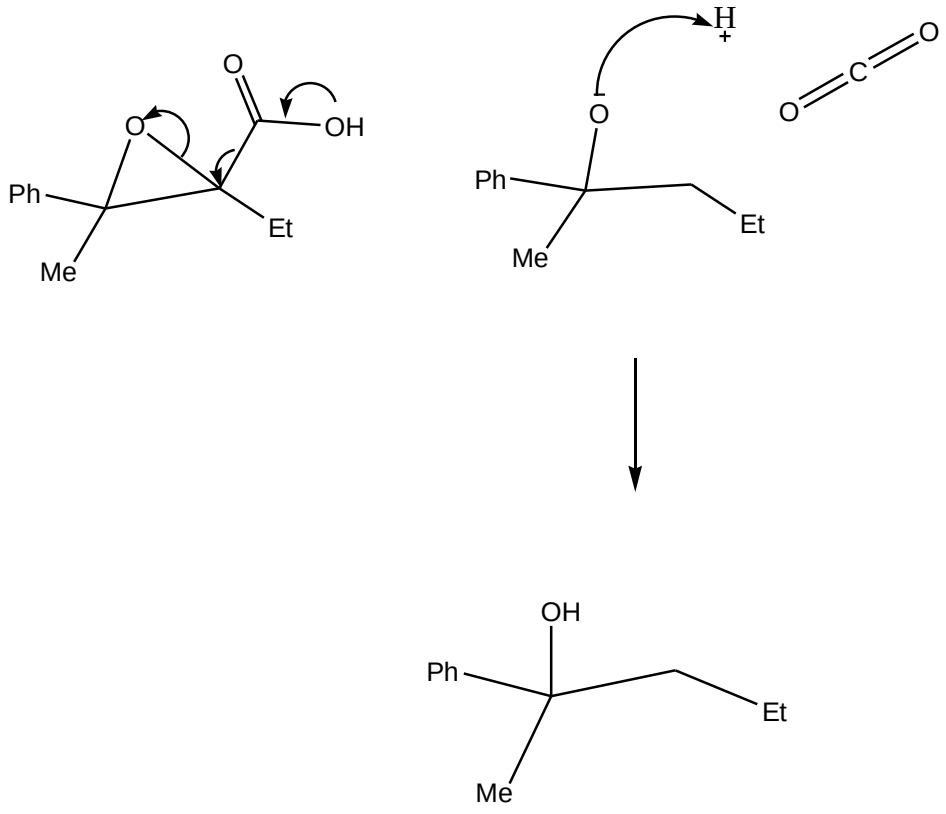

Mechanism of formation of structure A



(ii). Draw a mechanism for the transformation of A to B

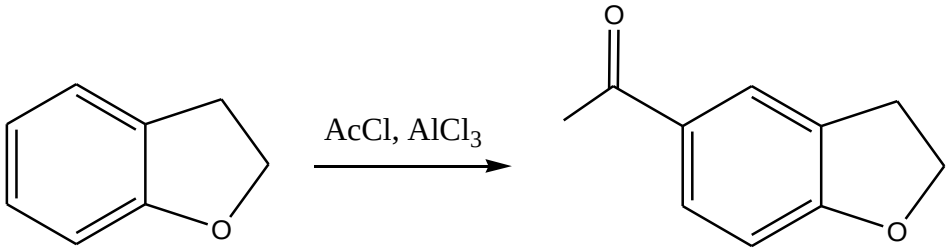



(iii). The mechanism for the decarboxylation of B to afford ketone C



b). Account for the following observations

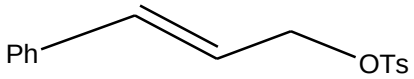
(i). Reaction of cyclic ether F with AcCl in the presence of AlCl3 afforded ketone G as the major product.




F G

Because the conditions are favourable, Friedel Craft's acylation ensues to afford major product G. Product G is preferred because of higher resonance stabilization. This position is further more stable because it is the furthest position from electron withdrawing group- Oxygen.

(ii). Stirring tosylate H in acetic acid gives a mixture of three isomeric esters, the ratio of which changes with reaction time and temperature.

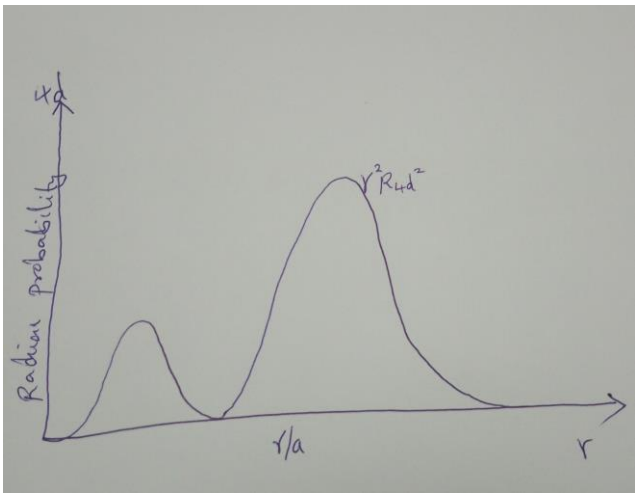



Introduction of tosylates is done to a molecule containing an –OH group that needs to be substituted with another group. Substitution of OH with a group containing tosylate is done since alcohol is not a very good leaving group. Tosylates are inert and does not have an acidic proton and are therefore introduced in synthesis to replace the acidic –OH of sulfonates and therefore making them ideal for acid base reactions. Acid base reaction between tosylate and acetic acid will therefore in the course of reaction, tosylate non-reactive and non-acidic group is removed first to form an intermediate product containing semi-acidic acidic protons. These protons can be abstracted to yield another intermediate (carbocation) and therefore the incoming group coordinates and forms the final product. The interconversion between the two intermediate products and the final product thus causes three isomeric esters whose ratio changes as reaction progresses to completion.

4. Answer (a), (b) and (c).

a). An atomic orbital is described by the quantum numbers $n$= 4, $l$=2

(i). 4d subshell




(iii). M$l$= -2, -1, 0, 1,2

c). Complete and balance the equations.

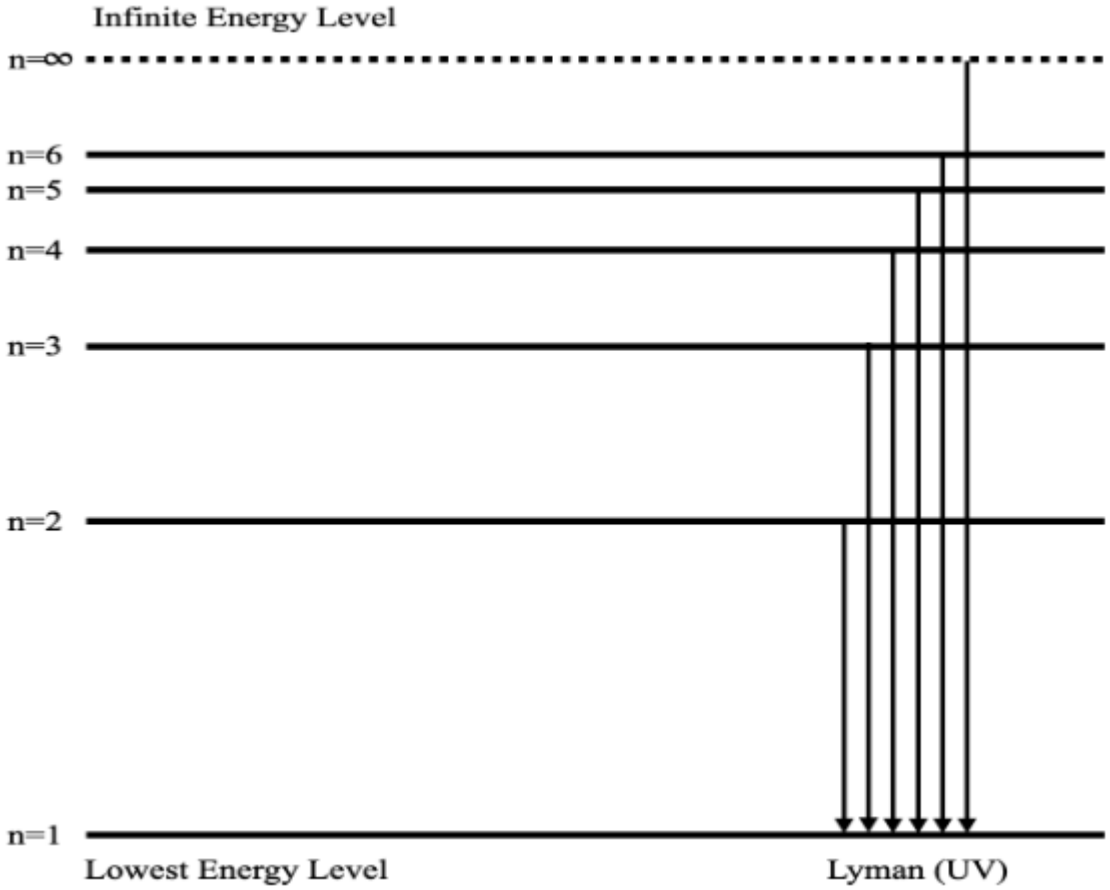
$2NO + N_2O_4 + 2OH^- \longrightarrow 4NO_2^- + H_2$

$2IO_3^- + 2TiOH + 6Cl^- + 16H^+ \longrightarrow 2TiCl_3 + I_2 + 8H_2O$

$Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \longrightarrow 3Sn^{4+} + 2Cr^{3+} + 7H_2O$

4b). Lines of the Lyman series in the emission spectrum of atomic hydrogen.

(i)



ii)

Second line, $n_1 = 1$ $n_2 = 3$

$$E = h\nu = \frac{hc}{\lambda} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \times hc$$

⇒ For the second line of lyman series;

$$E = 1.0974 \times 10^7 m^{-1} \left( \frac{1}{1^2} - \frac{1}{3^2} \right) \times 6.626 \times 10^{-34} \times 2.998 \times 10^8$$

$$= 1.938 \times 10^{-18} J$$

iii)

$$E = \frac{hc}{\lambda} \text{, } \lambda \text{ for } H_2 = 9.01 \times 10^{-8} M$$

$$E = \frac{6.63 \times 10^{-34} \times 2.99 \times 10^8}{9.01 \times 10^{-8}}$$

$$= 2.17 \times 10^{-18} \rightarrow \text{for 1 particle}$$

Then Energy for Avogadro's number of particles

$$= 2.17 \times 10^{-18} \times 6.023 \times 10^{23}$$

$$= 1.308 \times 10^6 \text{ Joules}$$

⇒ This is close to the first ionization energy of hydrogen molecule.