6. Establish the structure of Aceto acetic ester

Aceto acetic ester is also called Ethyl acetoacetate shows Keto-Enol Tautomerism.
By the elemental analysis and molecular weight determination, its molecular formula is $C_6H_{10}O_3$.

$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5$ $\qquad$ $CH_3-\overset{\overset{OH}{|}}{C}=CH-\overset{\overset{O}{\|}}{C}-OC_2H_5$

Keto form $\qquad$ Enol form

Evidence in favour of Keto form $\left(\begin{matrix}CH_2\\|\\-C=O\end{matrix}\right)$:

1. It reacts with HCN and $NaHSO_3$ to give an addition product just like ketonic group.
2. Like other carbonyl groups compounds it forms condensation product with hydroxyl amine and phenyl hydrazine.
3. When acetoacetic ester is reduced in presence of $LiAlH_4$ in pyridine solution to give β-hydroxy butyric ester.

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightarrow[LiAlH_4]{2[H]} CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5$$

Above reaction indicates that keto group present in β-position of the ester.

4. On boiling with dilute caustic potash (Ketonic hydrolysis) it forms acetone, CO_2 and C_2H_5OH.

Evidence in favour of Enol form $\left(\begin{matrix}-C-OH\\\|\\CH\end{matrix}\right)$:

1. When ethanolic bromine solution (Br_2-water) is added to the ester, the reddish brown colour of bromine disappears (colourless). This reaction reveals that olefinic linkage present in aceto acetic ester.

2. It reacts with sodium to form sodio desivatives. It means clear that alcoholic or phenolic group present in aceto acetic ester.
3. Aceto acetic ester is not aromatic compound. So. -OH group must be alcoholic.
4. When aceto acetic ester reacts with $FeCl_3$ solution to give a violet colour. Violet colour indicates that $-\underset{\underset{OH}{|}}{C}=CH$ group is present.
5. When aceto acetic ester reacts with ammonia and amines to form β-amino and β-alkyl amino acetic ester. Which is indicating that -OH gr. is linkeel to the β-carbon atom. Thus further supported by the reaction with PCl_5 to give β-chloro crotonic ester.

Geuther (1863) had prepared this ester by reaction of Na of ethyl acetate. Frankland and Duppa also prepareel the ester by a similar method in 1865 and they suggested two different formula for the same compound.

$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-OC_2H_5$ (Frankland and Duppa) 1865

$CH_3-\underset{\underset{OH}{|}}{C}=CH-\underset{\underset{O}{\|}}{C}-OC_2H_5$ (Geuther 1863)

Geuther. Frankland and Duppa have enough reg to beleived that only their formula was correct. This controversy continued 1911. Later on Knorr setted its by ~~isomer~~ isolating both form of compounds are correct.

Knorr cooled a solution of ordinary aceto acetic ester in a light petrol or ether to -78 and obtained long needle shaped crystal of Keto form (mp - 39°C). This form of an ester didnot give any colour with $FeCl_3$ due to presence of Ke group.

For isolating the Enol form he suspended the Sodio derivatives in light petrol at -78°C and treated with suspended ester with just enough HCl to decompose the Na salts. NaCl was filtered off and solvent evaporated at -78°C. A colourless oily liquid was obtained which gave the colour of $FeCl_3$ and discharge the colour of ethanolic bromine.

The above phenomenon indicates that obtained ester is the enolic form.

Keto-Enol Tautomerism of Ester

To explain the dual nature of compound it was assumed that two forms of ester i.e., Keto and Enol form existed in a dynamic equilibrium. These two forms were called tautomers of each other. The phenomenon is called Keto-Enol Tautomerism. The term tautomerism was given by Laar in 1885.

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-OC_2H_5 \rightleftharpoons CH_3-\underset{\underset{OH}{|}}{C}=CH-\underset{\underset{O}{\|}}{C}-OC_2H_5$$

Keto Form
92.5 %

Enol Form
7.5 %