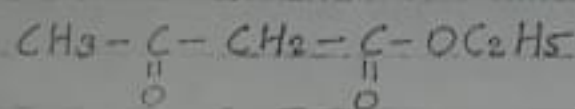


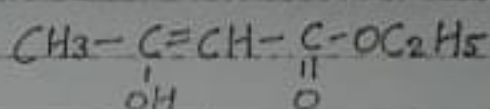
68 Establish the structure of Aceto acetic ester

Aceto acetic ester is also called Ethyl acetoacetate
Shows Keto-Enol Tautomerism.

By the elemental analysis and molecular weight determination, its molecular formula is $C_6H_{10}O_3$.



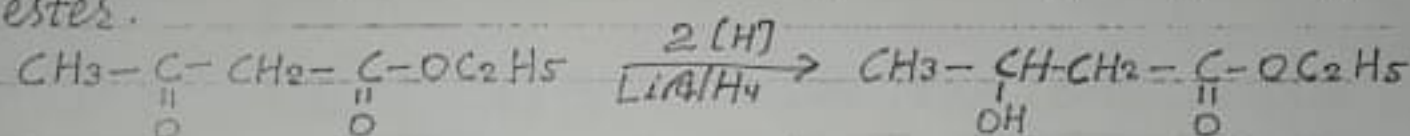
Keto Form



Enol Form

Evidence in favour of Keto Form $\left(\begin{array}{c} CH_2 \\ \mid \\ -C=O \end{array} \right)$:

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 hydrazyl amine and phenyl hydrazine.
3. When acetoacetic ester is reduced in presence of $LiAlH_4$ in pyridine solution to give β -hydroxy butyric ester.



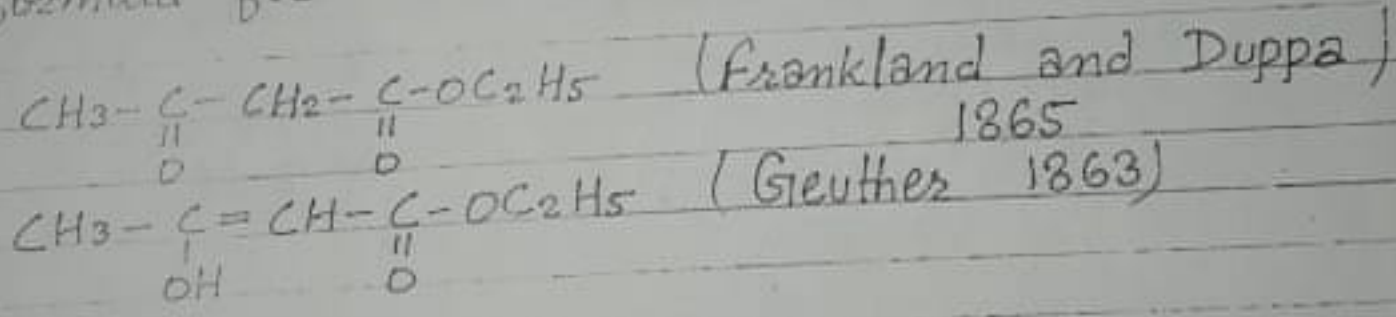
Above reaction indicates that keto group present in β -position of the ester.

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

Evidence in favour of Enol Form $\left(\begin{array}{c} -C-OH \\ \parallel \\ CH \end{array} \right)$:

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 derivatives. It means clear that alcoholic or phenolic group present in acetoacetic ester.
- 3. Acetoacetic ester is not aromatic compound. So, -OH group must be alcoholic.
- 4. When acetoacetic ester reacts with FeCl₃ solution to give a violet colour. Violet colour indicates that -C(OH)=CH group is present.
- 5. When acetoacetic ester reacts with ammonia and amines to form β-amino and β-alkyl amino acetic ester. Which is indicating that -OH gr. is linked to the β-carbon atom. Thus further supported by the reaction with PCl₅ to give β-chloro crotonic ester. Geuther (1863) had prepared this ester by reaction of Na of ethyl acetate. Frankland and Duppa also prepared the ester by a similar method in 1865 and they suggested two different formula for the same compound.



Geuther, Frankland and Duppa have enough reason to be believed that only their formula was correct. This controversy continued 1911. Later on Knorr settled it by ~~isomer~~ isolating both form of compounds are correct.

Knorr cooled a solution of ordinary acetoacetic 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 did not give any colour with FeCl₃ due to presence of Keto group.

For isolating the Enol form he suspended the sodium 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. (17)

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.

