What are active Methylene Groups?

Active Methylene Compounds The class of compounds which contain a methylene group (-CH₂-) directly bonded to two electron withdrawing groups such as -COCH₃, -COOC₂H₅, -CN, are called Active Methylene Compounds. This is so because the -CH₂- group in them is acidic and reactive. Ethyl acetoacetate (Acetoacetic ester) and Diethyl malonate (Malonic ester) belong to this class. Active Methylene Groups Active Methylene Groups Ethyl acetoacetate Diethyl malonate

(Malonic ester)

How will you obtain from Malonic Acid?

(Acetoacetic ester)

- Saturated Acids
- Ketone
- Unsaturated Acid
- Cyclic Acid
- Saturated Hydrocarbon

Saturated Acids

For preparing Saturated Acids from Malonic Ester, the required alkyl groups introduced into sodio-malonic ester. The substituted ester is then refluxed with potassium hydroxide solution, acidified with hydrochloric acid, and the precipitated acid dried and then heated just above its melting point. Alternatively, the potassium salt may be refluxed with sulphuric acid.

i.
$$\begin{aligned} &\mathbf{n} - \textit{Valeric acid} \\ &\mathbf{CH}_3 \cdot \mathbf{CH}_2 \cdot \mathbf{CH}_2 \cdot \boxed{\mathbf{CH}_2 \cdot \mathbf{CO}_2\mathbf{H}} \end{aligned}$$

$$&\mathbf{CH}_2(\mathbf{CO}_2\mathbf{C}_2\mathbf{H}_5)_2 \xrightarrow{\mathbf{C}_2\mathbf{H}_5\mathbf{ONa}} \mathbf{[CH}(\mathbf{CO}_2\mathbf{C}_2\mathbf{H}_5)_2]^-\mathbf{Na}^+ \xrightarrow{\mathbf{C}_3\mathbf{H}_7\mathbf{Br}} \mathbf{C}_3\mathbf{H}_7 \cdot (\mathbf{CO}_2\mathbf{C}_2\mathbf{H}_5)_2 \xrightarrow{\mathbf{KOH}} \mathbf{C}_3\mathbf{H}_7 \cdot \mathbf{CH}(\mathbf{CO}_2\mathbf{K})_2 \xrightarrow{\mathbf{HCl}} \mathbf{C}_3\mathbf{H}_7 \cdot \mathbf{CH}(\mathbf{CO}_2\mathbf{H})_2 \xrightarrow{\mathbf{150} - 200^\circ} \mathbf{CH}_3 \cdot \mathbf{CH}_2 \cdot \mathbf{CH}_2 \cdot \mathbf{CH} \cdot \mathbf{CO}_2\mathbf{H}$$

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Ketone:

Ketones can be formed by the reaction of Acyl Chloride (R" COCI) with Malonic Ester.

$$R \cdot \mathrm{CH}(\mathrm{CO}_2 R')_2 \xrightarrow[\text{(i)} R'' \cdot \mathrm{COCl}]{} R'' \cdot \mathrm{CO} \cdot \mathrm{CR}(\mathrm{CO}_2 R')_2 \xrightarrow{\mathrm{CH}_3 \cdot \mathrm{CO}_2 \mathrm{H}} R'' \cdot \mathrm{CO} \cdot \mathrm{CH}_2 R$$

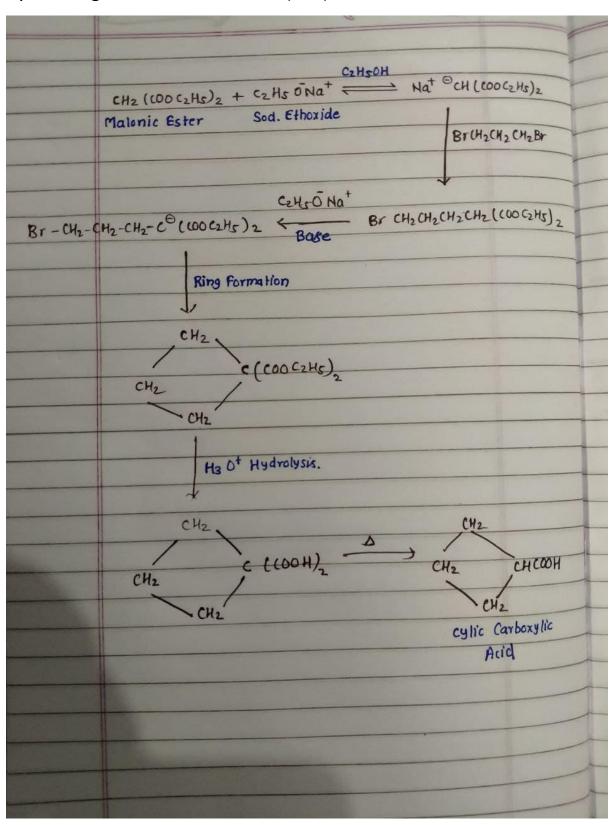
Unsaturated Acids:

 Diethyl malonate on condensation with benzaldehyde gives condensed product which on further hydrolysis followed by decarboxylation gives α, β-unsaturated acid (cinnamic acid).

$$\begin{array}{c} \text{COOC}_2\text{H}_5 \\ \text{C}_6\text{H}_5^-\text{CHO} + \text{H}_2\text{C} \\ \text{benzaldehyde} \\ \text{COOC}_2\text{H}_5 \\ \text{dimethyl malonate} \\ \\ \hline \text{HCI}/\text{H}_2\text{O} \\ \text{Hydrolysis} \\ \end{array} \\ \begin{array}{c} \text{COOC}_2\text{H}_5 \\ \text{COOH} \\ \hline \end{array}$$

Cyclic Acid:

By treating Malonic Acid with $Br(CH_2)_3Br$.



Saturated Hydrocarbon:

