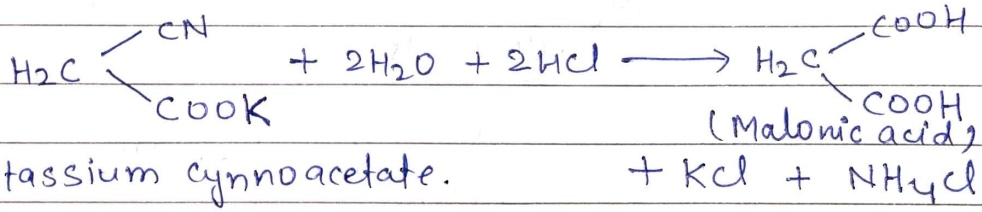
Dr. Manoj Kumar
Associate Professor
Department of Chemistry
Raja Singh College, Siwan

Malonic Ester

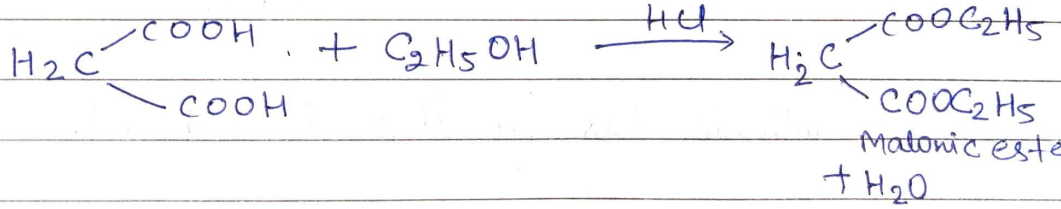
Malonic ester is a reagent specifically used in a reaction which converts alkyl halides to carboxylic acids called malonic ester synthesis. Diethyle malonate is also called malonic ester, which is diethyl ester of malonic acid. It has molecular formula $C_7H_{12}O_4$ or $CH_2(COOC_2H_5)_2$.

- It occurs naturally in grapes and strawberries.
- It is a colourless, pleasant smelling liquid with boiling points 199.2°C
- It is sparingly soluble in water, free soluble in alcohol and ether.

Method of preparation :→ It is prepared very conveniently by boiling sodium or potassium cyanoacetate with alcohol and concentrated HCl.

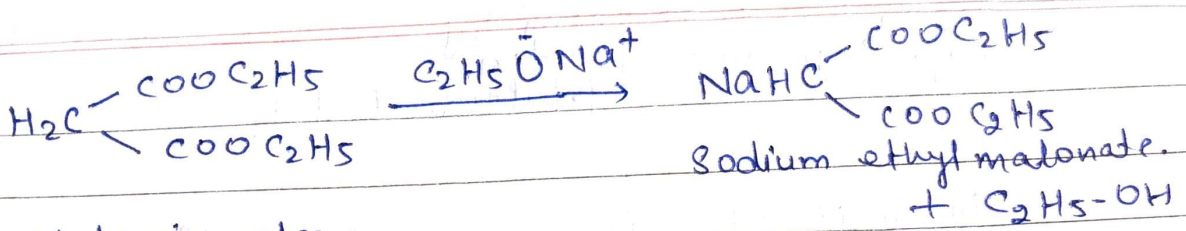


Potassium cynnoacetate.



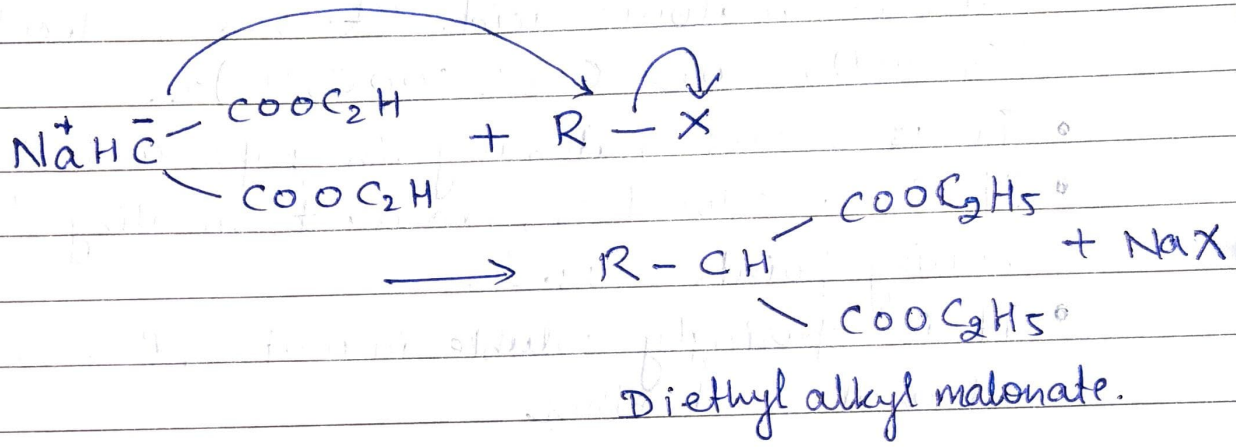
Chemical properties —

① Salt formation :→ Diethyl malonate (malonic ester) react with a strong base like Sodium ethoxide (C_2H_5ONa) to form salt of Sodium.



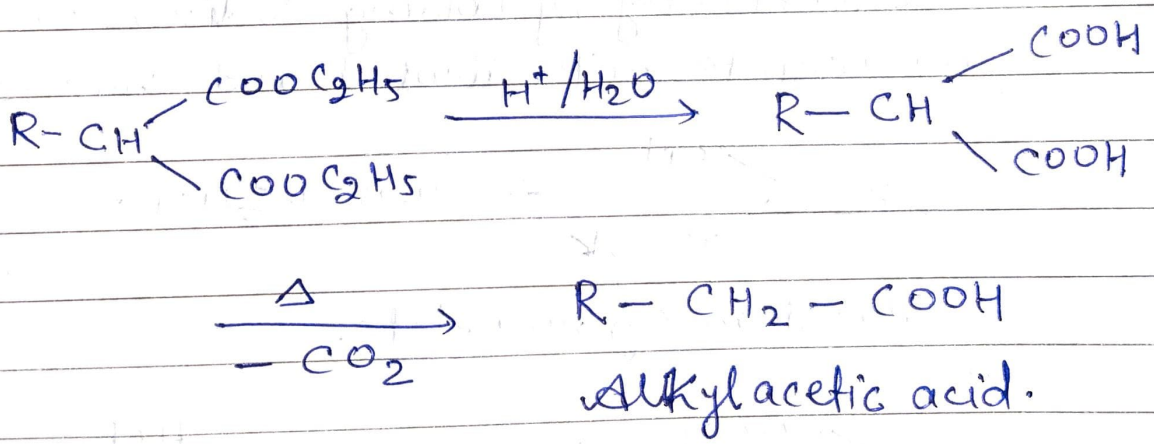
Malonic ester.

② Alkylation :→ Diethy malonate anion is nucleophilic and react with halid to give diethyl alkylmalonate.



Diethyl alkyl malonate.

③ Hydrolysis and Decarboxylation

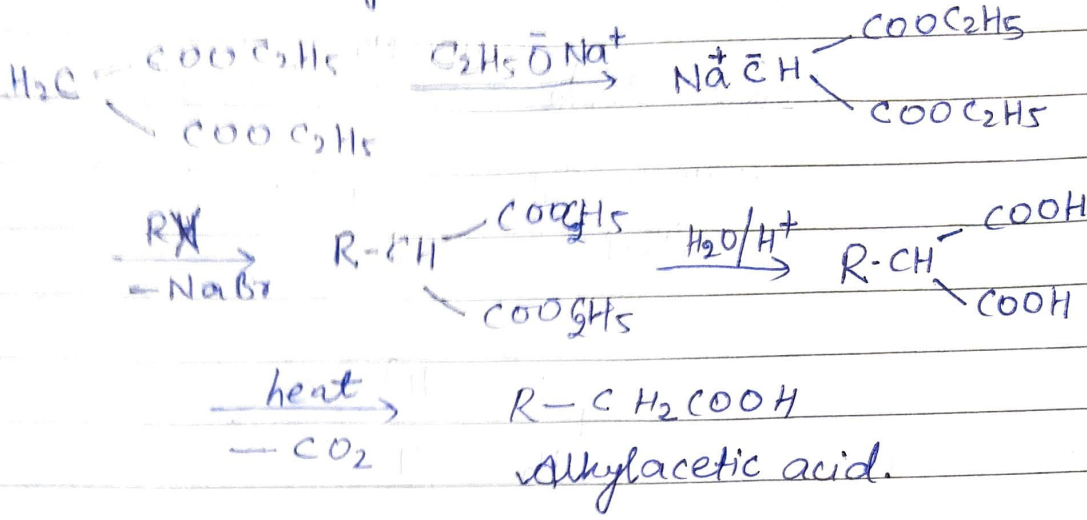


Alkylacetic acid.

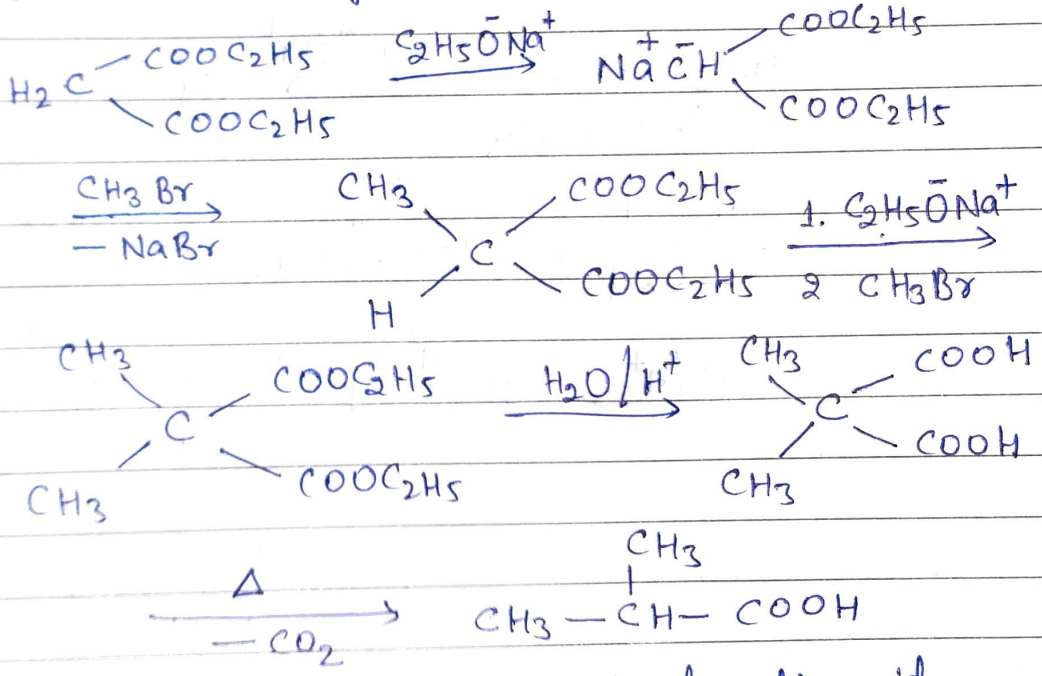
Synthesis Uses for different Compound.

⇒ Malonic esters are used for synthesis of various compound such as Carboxylic acid, Keto acid, α-amino acid and barbituric acid etc.

① Synthesis of Alkylacetic acid

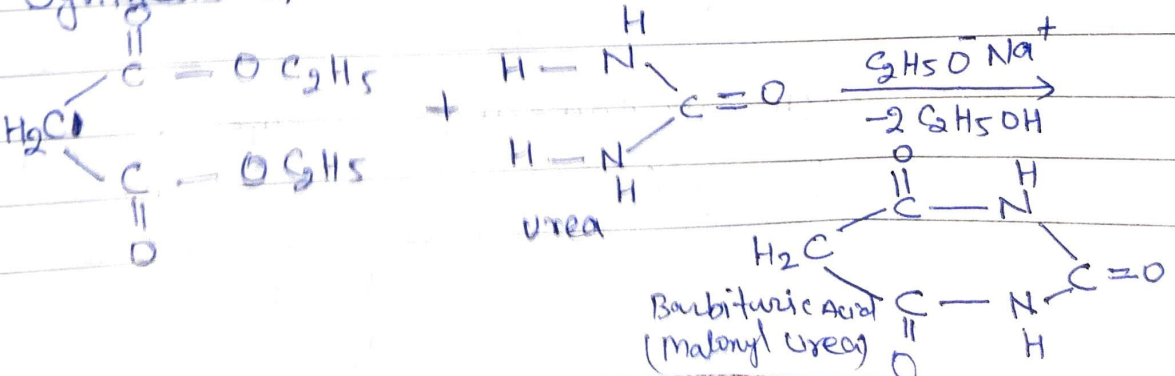


② Synthesis of Dialkylacetic Acids.



Dimethylacetic acid
(2-Methylpropanoic acid).

③ Synthesis of Barbituric Acid



Date
Page

(4) Synthesis of Succinic Acid

$$CH_2(COOC_2H_5)_2 \xrightarrow{C_2H_5\bar{O}Na^+} Na^+\bar{C}H(COOC_2H_5)_2$$

$$\xrightarrow[-NaCl]{ClCH_2COOC_2H_5} \begin{array}{l} CH(COOC_2H_5)_2 \\ | \\ CH_2COOC_2H_5 \end{array} \xrightarrow{H_2O/H^+}$$

$$\begin{array}{l} CH(COOH)_2 \\ | \\ CH_2COOH \end{array} \xrightarrow[(-CO_2)]{\Delta} \begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array}$$

Succinic Acid.

(5) Synthesis of Keto Acid.

$$H_2C \begin{array}{l} -COOC_2H_5 \\ \backslash COOC_2H_5 \end{array} \xrightarrow{C_2H_5\bar{O}Na^+} Na^+\bar{C}H \begin{array}{l} COOC_2H_5 \\ COOC_2H_5 \end{array}$$

$$\xrightarrow[-NaCl]{CH_3\overset{O}{\overset{\|}{C}}Cl} CH_3-\overset{O}{\overset{\|}{C}}-CH \begin{array}{l} COOC_2H_5 \\ COOC_2H_5 \end{array}$$

$$\xrightarrow{H_2O/H^+} CH_3\overset{O}{\overset{\|}{C}}CH \begin{array}{l} COOH \\ COOH \end{array} \xrightarrow[-CO_2]{\Delta}$$

$$CH_3\overset{O}{\overset{\|}{C}}CH_2COOH$$

Acetoacetic acid.

(6) Synthesis of higher Normal Diacids.

$$\begin{array}{l} CH_2I \\ | \\ CH_2I \end{array} + \begin{array}{l} Na^+CH(COOC_2H_5)_2 \\ Na^+CH(COOC_2H_5)_2 \end{array} \xrightarrow[-2NaI]{}$$

$$\begin{array}{l} CH_2CH(COOC_2H_5)_2 \\ | \\ CH_2CH(COOC_2H_5)_2 \end{array} \xrightarrow{H_2O/H^+} \begin{array}{l} CH_2CH(COOH)_2 \\ | \\ CH_2CH(COOH)_2 \end{array}$$

$$\xrightarrow[-2CO_2]{\Delta} \begin{array}{l} CH_2CH_2COOH \\ | \\ CH_2CH_2COOH \end{array}$$

(Adipic acid)

(7) Synthesis of α, β-unsaturated Acid

$$CH_3CH=O + H_2C(COOC_2H_5)_2 \xrightarrow[-H_2O]{\text{Pyridine}}$$

$$CH_3CH=C(COOC_2H_5)_2 \xrightarrow{H_2O/H^+}$$

$$CH_3CH=C(COOH)_2 \xrightarrow[-CO_2]{\Delta}$$

$CH_3CH=CHCOOH$

Crotonic acid.

(8) Synthesis of α-Amino acids.

Glycine (a typical α-amino acid) can be obtained.

$$CH_2(COOC_2H_5)_2 \xrightarrow{C_2H_5\bar{O}Na^+} Na^+\bar{C}H(COOC_2H_5)_2$$

Sodium salt

$$\xrightarrow{CH_3I} CH_3-CH(COOC_2H_5)_2 \xrightarrow[-HBr]{Br_2}$$

$$CH_3-CBr(COOC_2H_5)_2 \xrightarrow{H_2O/H^+} CH_3-CBr(COOH)_2$$

$$\xrightarrow[-CO_2]{\Delta} CH_3-CHBr-COOH \xrightarrow{NH_3}$$

$CH_3-CH(NH_2)-COOH$

α-Amino acid

Glycine (Gly)