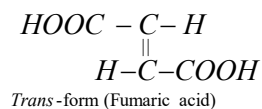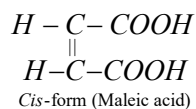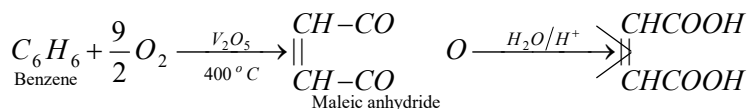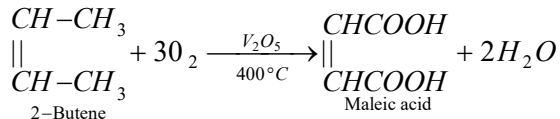# Unsaturated Dicarboxylic Acids.

The molecular formula of the simplest unsaturated dicarboxylic acid is $HOOC.CH = CH.COOH$ this formula, however represents two chemical compounds, maleic acid and fumaric acid, which are geometrical isomers.
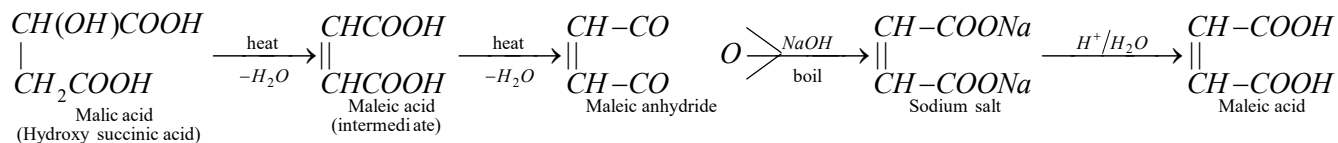
$$H - C - COOH$$
$$\overset{||}{H - C - COOH}$$
Cis-form (Maleic acid)

$$HOOC - C - H$$
$$\overset{||}{H - C - COOH}$$
Trans-form (Fumaric acid)

## (1) Methods of Preparation of Maleic Acid

### (i) By catalytic oxidation of 2-butene or benzene

$$\underset{2-Butene}{\overset{CH-CH_3}{\underset{CH-CH_3}{||}}} + 3O_2 \xrightarrow[400°C]{V_2O_5} \underset{Maleic\ acid}{\overset{CHCOOH}{\underset{CHCOOH}{||}}} + 2H_2O$$

$$\underset{Benzene}{C_6H_6} + \frac{9}{2}O_2 \xrightarrow[400°C]{V_2O_5} \underset{Maleic\ anhydride}{\overset{CH-CO}{\underset{CH-CO}{||}}} O \xrightarrow{H_2O/H^+} \overset{CHCOOH}{\underset{CHCOOH}{||}}$$

### (ii) From malic acid:

$$\underset{\substack{Malic\ acid \\ (Hydroxy\ succinic\ acid)}}{\overset{CH(OH)COOH}{\underset{CH_2COOH}{|}}} \xrightarrow[-H_2O]{heat} \underset{\substack{Maleic\ acid \\ (intermediate)}}{\overset{CHCOOH}{\underset{CHCOOH}{||}}} \xrightarrow[-H_2O]{heat} \underset{Maleic\ anhydride}{\overset{CH-CO}{\underset{CH-CO}{||}}} O \xrightarrow[boil]{NaOH} \underset{Sodium\ salt}{\overset{CH-COONa}{\underset{CH-COONa}{||}}} \xrightarrow{H^+/H_2O} \underset{Maleic\ acid}{\overset{CH-COOH}{\underset{CH-COOH}{||}}}$$

## (2) Methods of Preparation of Fumaric Acid

**(i) From maleic acid:**

$$\underset{\text{Maleic acid}}{\begin{array}{l} H-C-COOH \\ \parallel \\ H-C-COOH \end{array}} \xrightarrow[\text{boil}]{HCl} \begin{array}{l} HOOC-C-H \\ \parallel \\ H-C-COOH \end{array}$$
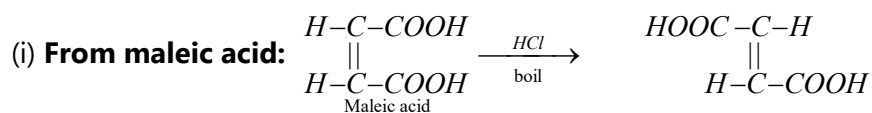
**(ii) By oxidation of furfural with sodium chlorate**

$$\begin{array}{l} HC \\ \parallel \\ HC \end{array} \begin{array}{l} CH \\ \parallel \\ C-CHO \end{array} O + 4[O] \xrightarrow{NaClO_3} \begin{array}{l} HOOC-C-H \\ \parallel \\ H-C-COOH \end{array} + CO_2$$
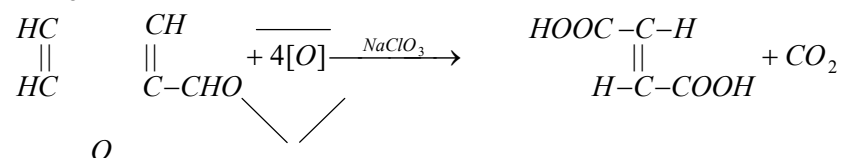
**(iii) By heating malic acid at about 150°C for long time**

$$\underset{\text{Malic acid}}{\begin{array}{l} CH(OH)COOH \\ | \\ CH_2COOH \end{array}} \xrightarrow[150\,°C,\ -H_2O]{\text{heat}} \begin{array}{l} HOOC-C-H \\ \parallel \\ H-C-COOH \end{array}$$
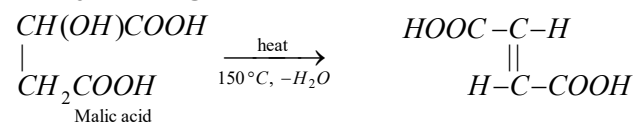
**(iv) By heating bromosuccinic acid with alcoholic potash:** By heating bromosuccinic acid with alcoholic potash.

$$\begin{array}{l} CH_2COOH \\ | \\ CH.(Br)COOH \end{array} \xrightarrow{\text{Alc.}KOH} \begin{array}{l} HOOC-C-H \\ \parallel \\ H-C-COOH \end{array} + KBr + H_2O$$
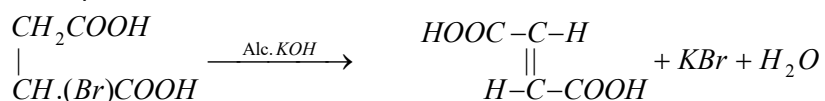
**(4) Physical Properties**

(i) Both are colourless crystalline solids. Both are soluble in water.
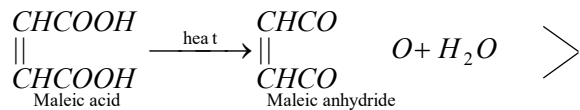
(ii) The melting point of maleic acid (130.5°C) is lower than the melting point of fumaric acid (287°C).

**(5) Chemical Properties**

Chemically, both the acids give the reactions of alkenes and dibasic acids except that the maleic acid on heating forms an anhydride while fumaric acid does not give anhydride.

$$\underset{\text{Maleic acid}}{\underset{\underset{CHCOOH}{\|}}{CHCOOH}} \xrightarrow{\text{heat}} \underset{\text{Maleic anhydride}}{\underset{\underset{CHCO}{\|}}{CHCO}} O + H_2O$$

Both form succinic acid on reduction with sodium amalgam. They undergo addition reactions with bromine, hydrobromic acid, water, etc. and form salts, esters and acid chlorides as usual. With alkaline $KMnO_4$ solution, they get oxidised to tartaric acid.

$$\underset{\substack{\text{Tartaric acid}\\ \text{(Meso)}}}{\underset{COOH}{\underset{|}{\underset{H-C-OH}{\underset{|}{\underset{H-C-OH}{\underset{|}{COOH}}}}}}} \xleftarrow[\text{(Syn-addition)}]{\text{Alk.}KMnO_4} \underset{\substack{\text{Maleic acid}\\ \text{(Cis)}}}{\underset{H-C-COOH}{\underset{\|}{H-C-COOH}}} \xrightarrow[\text{(anti-addition)}]{Br_2\,\text{water}} \underset{\text{(Racemic mixture)}}{\underset{COOH}{\underset{|}{\underset{H-C-Br}{\underset{|}{\underset{Br-C-H}{\underset{|}{COOH}}}}}}}$$

$$\underset{\substack{\text{Tartaric acid}\\ \text{(Racemic mixture)}}}{\underset{COOH}{\underset{|}{\underset{H-C-OH}{\underset{|}{\underset{HO-C-H}{\underset{|}{COOH}}}}}}} \xleftarrow[\text{(Syn-addition)}]{\text{Alk.}KMnO_4} \underset{\text{Fumaric acid (Trans)}}{\underset{H-C-COOH}{\underset{\|}{HOOC-C-H}}} \xrightarrow[\text{(anti-addition)}]{Br_2\,\text{water}} \underset{\text{((Meso)}}{\underset{COOH}{\underset{|}{\underset{H-C-Br}{\underset{|}{\underset{H-C-Br}{\underset{|}{COOH}}}}}}}$$