Malonic ester synthesis is a synthetic procedure used to convert a compound that has the general structural formula 1 into a carboxylic acid that has the general structural formula 2.

\[
\begin{align*}
\text{R}^1 \text{-L} & \rightarrow \text{R}^1 \text{-CH}_2 \text{-C}\text{-OH} \\
1 & \quad 2
\end{align*}
\]

- \( \text{R}^1 \) = alkyl group
- \( \text{L} \) = leaving group

The group \( \text{CH}_2\text{CO}_2\text{H} \) in 2 is contributed by a malonic ester, hence the term malonic ester synthesis.

\[
\begin{align*}
\text{R}^1 \text{-L} & \rightarrow \text{R}^1 \text{-CH}_2 \text{-C}\text{-OH} \\
\text{R}^2\text{O} \quad \text{CH}_2 \quad \text{C}\text{-OR}^2
\end{align*}
\]

- \( \text{R}^2 \) = alkyl, aryl

Malonic ester synthesis consists of four consecutive reactions that can be carried out in the same pot.

- reaction 1: acid-base reaction
- reaction 2: nucleophilic substitution
- reaction 3: ester hydrolysis (using saponification)
- reaction 4: decarboxylation

eg:
A more direct method to convert 3 into 4 is the reaction of 3 with the enolate ion (5) of ethyl acetate followed by hydrolysis of the resultant ester.

However, the generation of 5 from ethyl acetate quantitatively in high yield is not an easy task because the reaction requires a very strong base, such as LDA, and must be carried out at very low temperature under strictly anhydrous conditions.
Malonic ester synthesis provides a more convenient alternative to convert 3 to 4. Malonic ester synthesis can be adapted to synthesize compounds that have the general structural formula 6.

- $R^3, R^4 =$ identical or different alkyl groups

e.g.:

reaction 1:

reaction 2:

reaction 1 (repeat):

reaction 2 (repeat):
reaction 3:

\[
\begin{align*}
\text{CH}_3\text{CH}_3 & \quad \text{CH}_3\text{CH}_3 \\ \text{CH}_3\text{O} & \quad \text{CH}_3\text{O} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH}_3 & \quad \text{CH}_3\text{CH}_3 \\ \text{CH}_3\text{O} & \quad \text{CH}_3\text{O} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{Br} & \quad \rightarrow \\
\text{CH}_3\text{CH}_3 & \quad \text{CH}_3\text{CH}_3 \\
\text{CH}_3\text{O} & \quad \text{CH}_3\text{O} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

reaction 4:

\[
\begin{align*}
\text{CH}_3\text{CH}_3 & \quad \text{CH}_3\text{CH}_3 \\ \text{CH}_3\text{O} & \quad \text{CH}_3\text{O} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{O}, 5 & \quad \rightarrow \\
\text{CH}_3\text{CH}_3 & \quad \text{CH}_3\text{CH}_3 \\
\text{CH}_3\text{O} & \quad \text{CH}_3\text{O} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

\[
\begin{align*}
2 \text{ eq. HCl} & \quad \rightarrow \\
\text{CH}_3\text{CH}_3 & \quad \text{CH}_3\text{CH}_3 \\
\text{CH}_3\text{O} & \quad \text{CH}_3\text{O} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

see also [acetoacetic ester synthesis](#)

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**Contributors**

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