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.

\[ \text{R}^1 - \text{L} \rightarrow \text{R}^1\text{CH}_2\text{C} = \text{OH} \]

- \( \text{R}^1 = \) 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.

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

- \( \text{R}^2 = \) 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

eg:

reaction 1:

reaction 2:

reaction 1 (repeat):

reaction 2 (repeat):
reaction 3:

reaction 4:

see also acetoacetic ester synthesis

Contributors

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