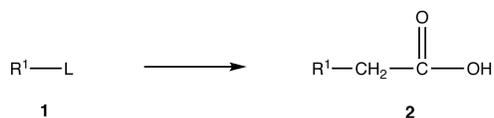


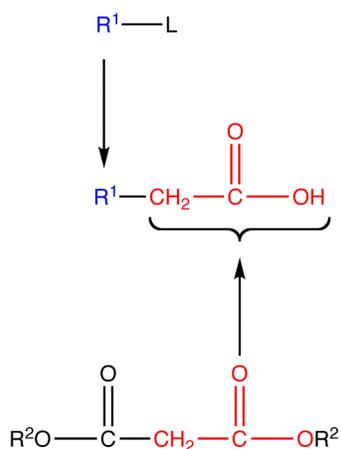
21.10: Malonic Ester Synthesis

Malonic ester is a reagent specifically used in a reaction which converts alkyl halides to carboxylic acids called the Malonic Ester Synthesis. 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.



- R^1 = alkyl group
- 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.



- R^2 = alkyl, aryl

Mechanism

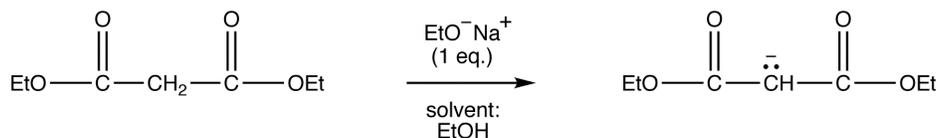
Malonic ester synthesis consists of four consecutive reactions that can be carried out in the same pot.

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

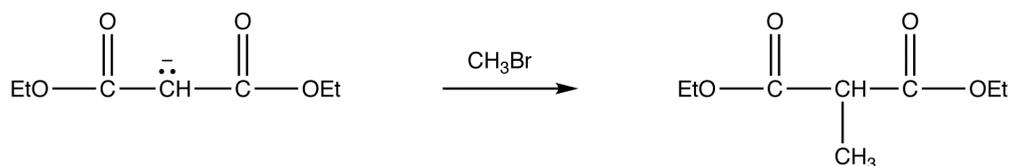
eg:



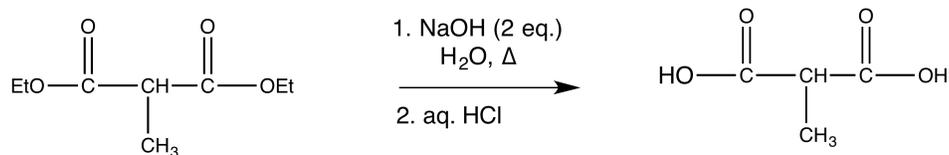
reaction 1:



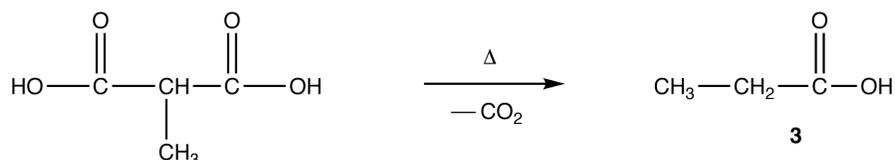
reaction 2:



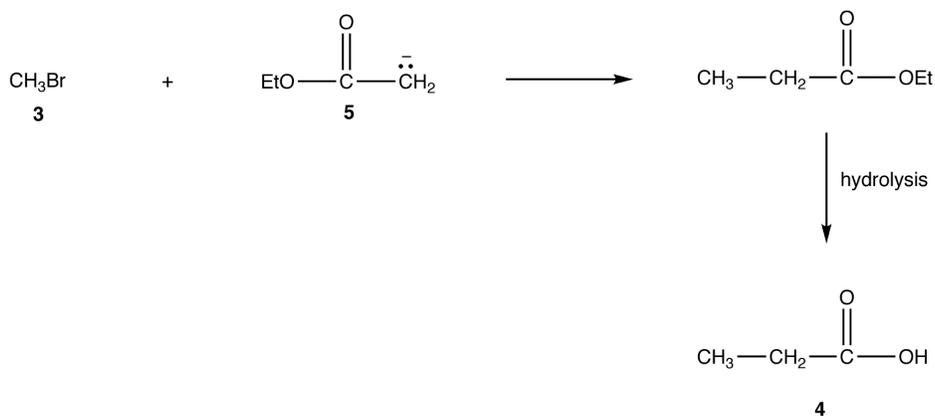
reaction 3:



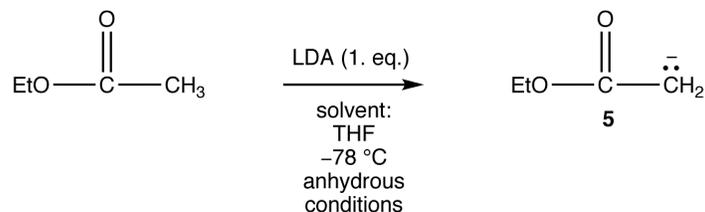
reaction 4:



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.

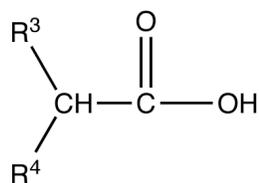


However, the generation of **5** from ethyl acetate quantitatively in high yield is not an easy task because the reaction requires a very strong base, such as LDA, and must be carried out at very low temperature under strictly anhydrous conditions.



Malonic ester synthesis provides a more convenient alternative to convert **3** to **4**.

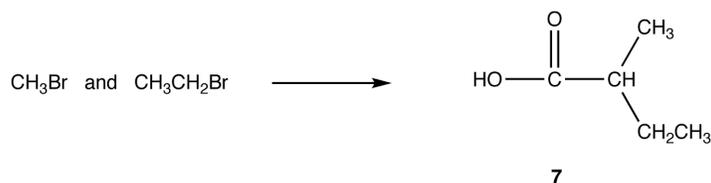
Malonic ester synthesis can be adapted to synthesize compounds that have the general structural formula **6**.



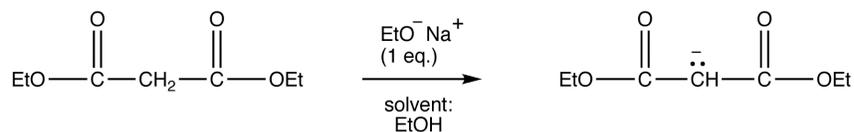
6

$\text{R}^3, \text{R}^4 =$ identical or different alkyl groups

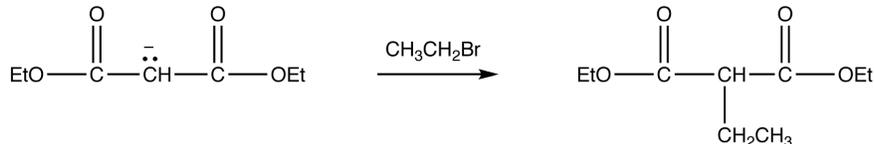
eg:



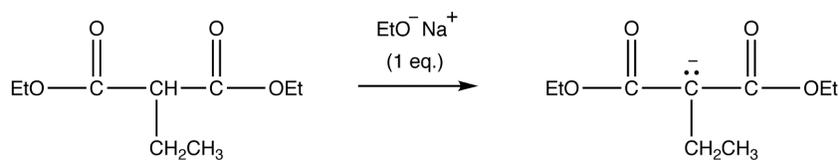
reaction 1:



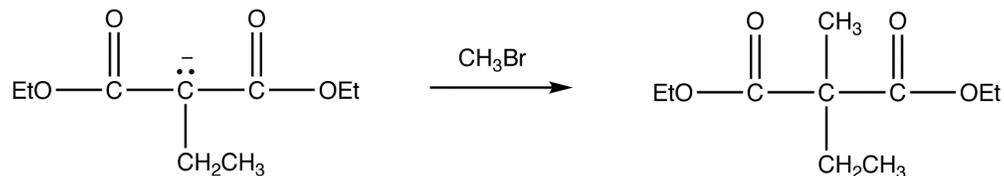
reaction 2:



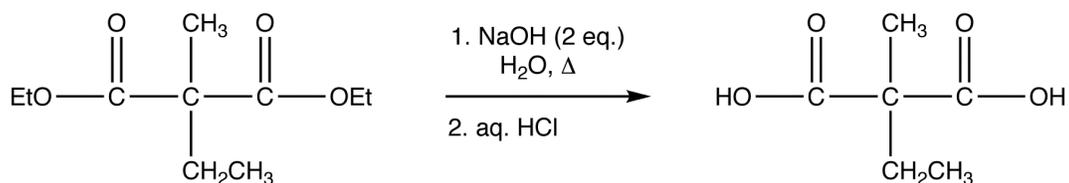
reaction 1 (repeat):



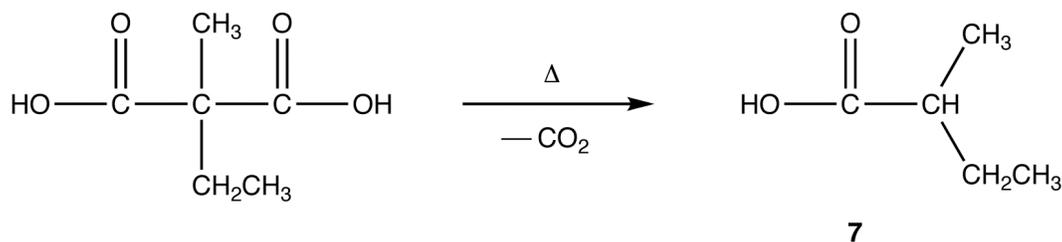
reaction 2 (repeat):



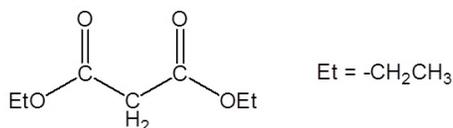
reaction 3:



reaction 4:

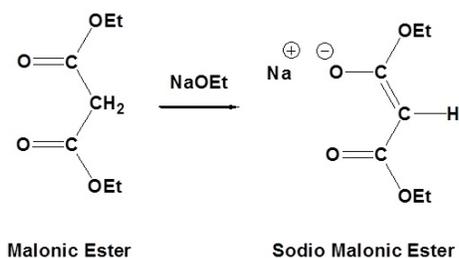


Malonic Ester Synthesis

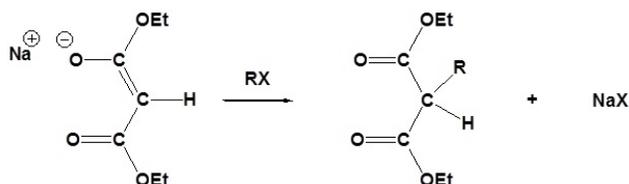


Malonic Ester

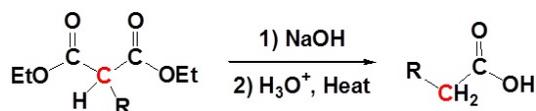
Due to the fact that Malonic ester's α hydrogens are adjacent to two carbonyls, they can be deprotonated by sodium ethoxide (NaOEt) to form Sodio Malonic Ester.



Because Sodio Malonic Ester is an enolate, it can then be alkylated with alkyl halides.

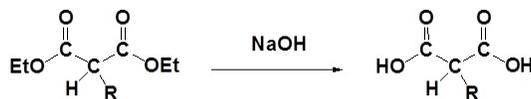


After alkylation the product can be converted to a dicarboxylic acid through saponification and subsequently one of the carboxylic acids can be removed through a decarboxylation step.

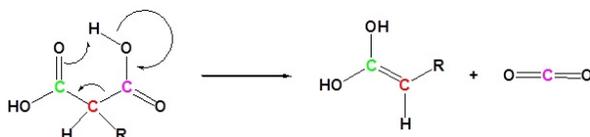


Mechanism

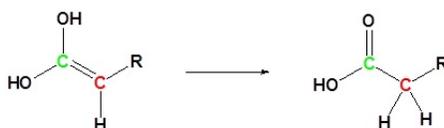
1) Saponification



2) Decarboxylation



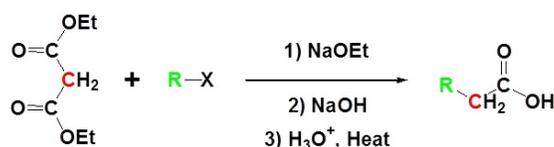
3) Tautomerization



All of the steps together form the Malonic ester synthesis.



Example



- Bernard E. Hoogenboom , Phillip J. Ihrig , Arne N. Langsjoen , Carol J. Linn and Stephen D. Mulder, The malonic ester synthesis in the undergraduate laboratory, *J. Chem. Educ.*, 1991, 68 (8), p 689

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