

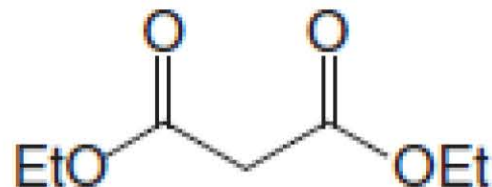
The Malonic Ester Synthesis: Synthesis of Substituted Acetic Acids

Malonic ester synthesis



The synthesis of *mono-* and *disubstituted acetic acids*

The most commonly used malonic ester is diethyl malonate

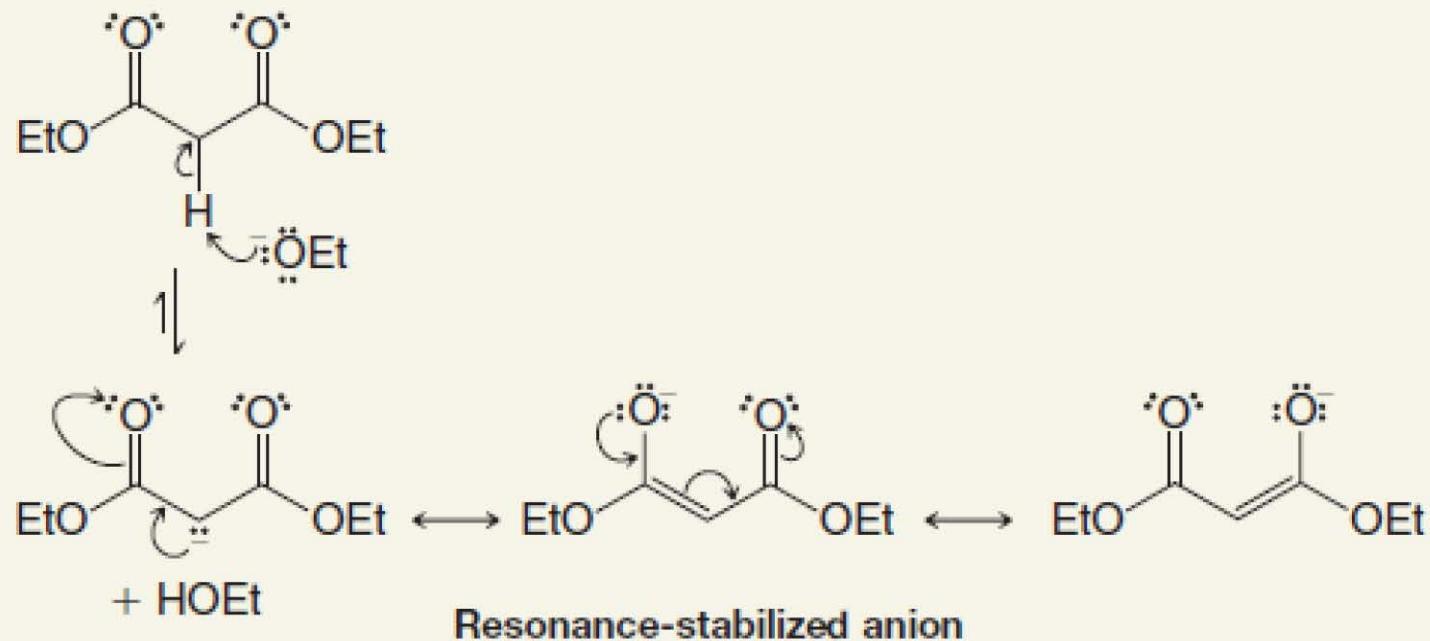


Diethyl malonate (a β -dicarboxylic acid ester)

The Malonic Ester Synthesis

A MECHANISM FOR THE REACTION

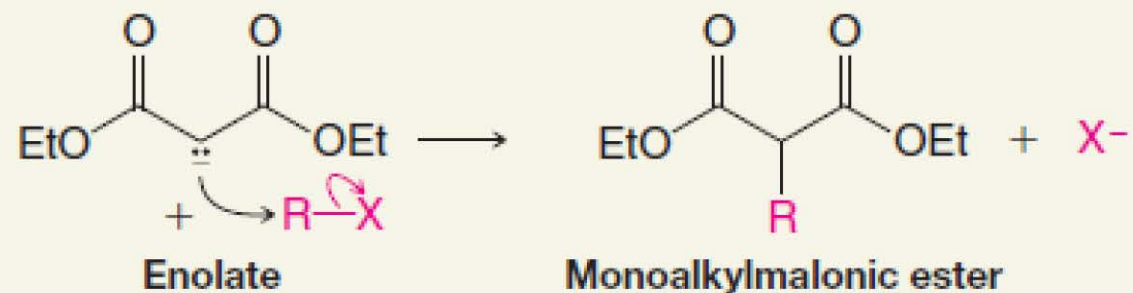
Step 1 Diethyl malonate, the starting compound, forms a relatively stable enolate:



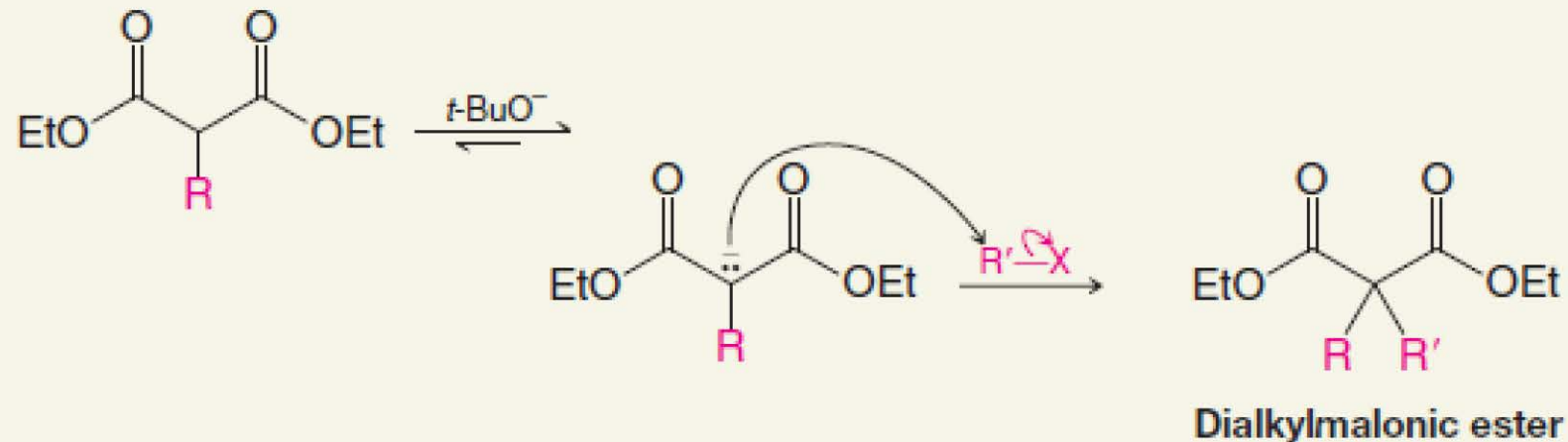
The Malonic Ester Synthesis

A MECHANISM FOR THE REACTION

Step 2 This enolate can be alkylated in an S_N2 reaction,



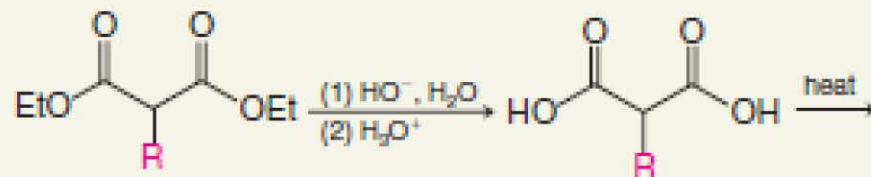
and the product can be alkylated again if our synthesis requires it:



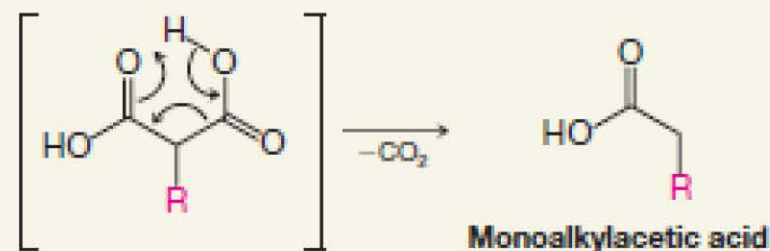
The Malonic Ester Synthesis

A MECHANISM FOR THE REACTION

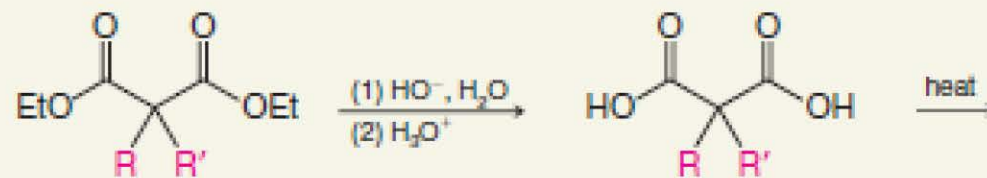
Step 3 The mono- or dialkylmalonic ester can then be hydrolyzed to a mono- or dialkylmalonic acid, and substituted malonic acids decarboxylate readily. Decarboxylation gives a mono- or disubstituted acetic acid:



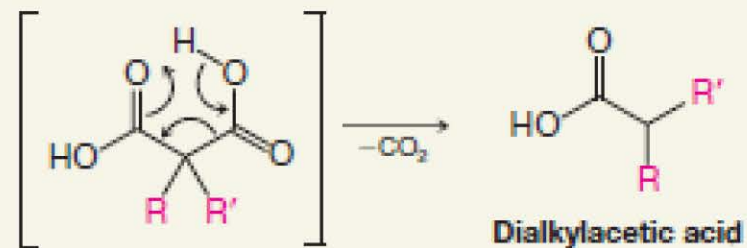
Monoalkylmalonic ester



or after dialkylation,



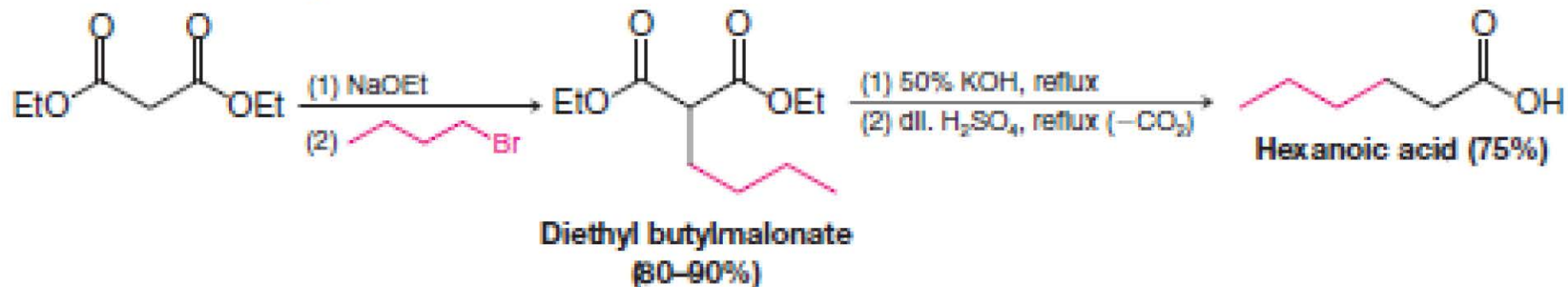
Dialkylmalonic ester



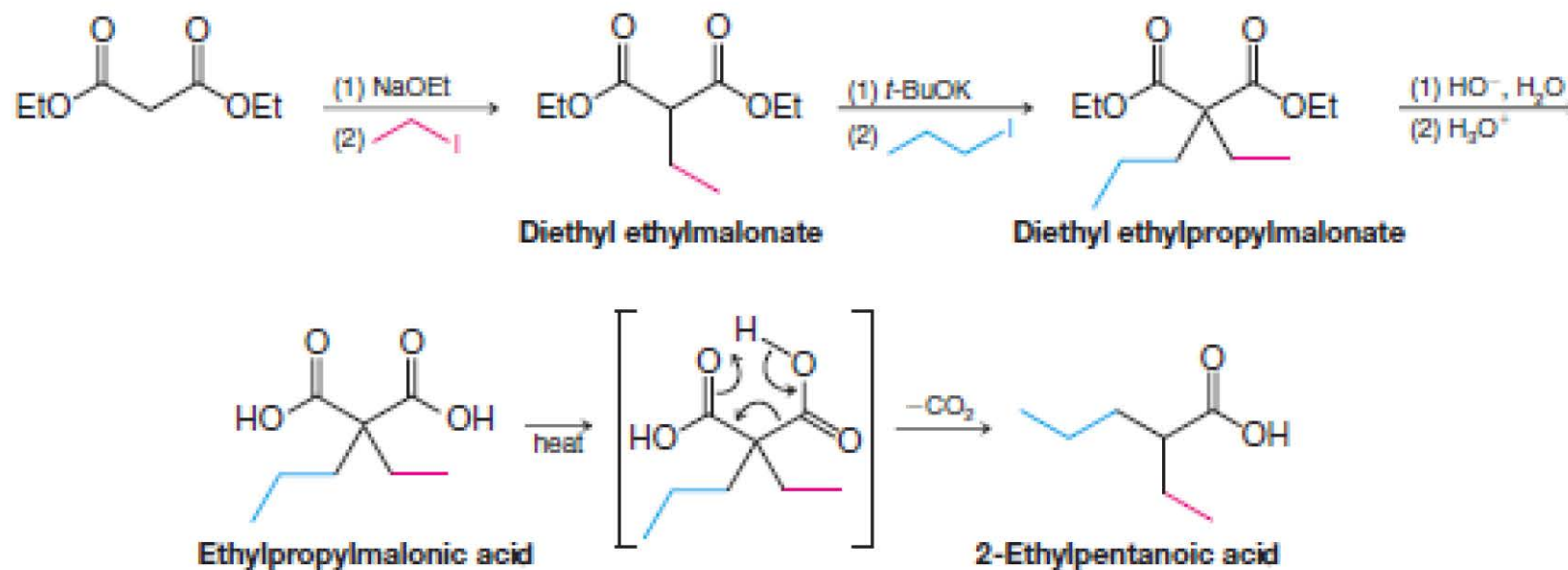
The Malonic Ester Synthesis

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A Malonic Ester Synthesis of Hexanoic Acid



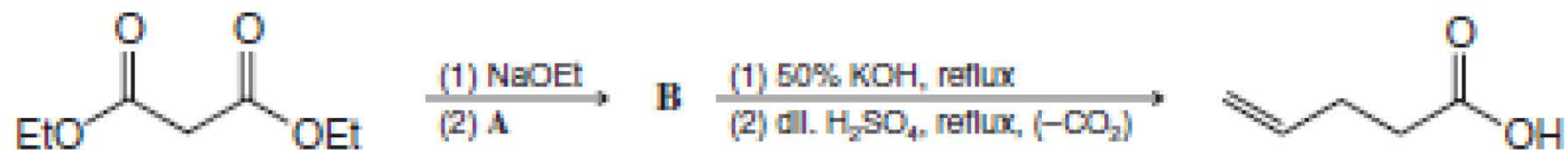
A Malonic Ester Synthesis of 2-Ethylpentanoic Acid



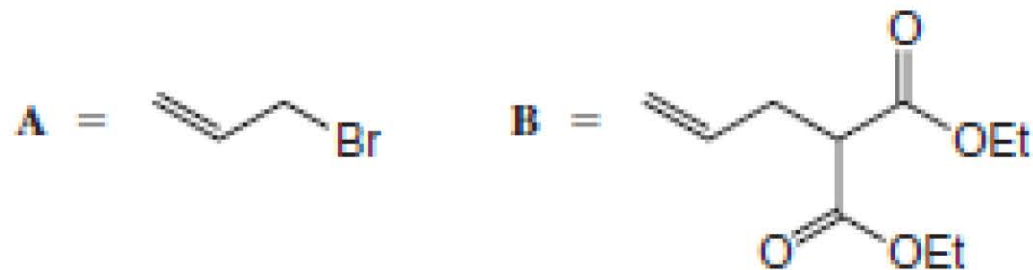
The Malonic Ester Synthesis

SOLVED PROBLEM

Provide structures for compounds **A** and **B** in the following synthesis.



ANSWER:



Practice Problem:

Outline all steps in a malonic ester synthesis of each of the following: (a) pentanoic acid, (b) 2-methylpentanoic acid, and (c) 4-methylpentanoic acid.