

23.9: INTRAMOLECULAR CLAISEN CONDENSATIONS - THE DIECKMANN CYCLIZATION

OBJECTIVES

After completing this section, you should be able to

1. write an equation to illustrate an internal Claisen condensation, that is, a Dieckmann cyclization.
2. identify the product formed when a 1,6- or 1,7-diester undergoes an internal Claisen condensation.
3. identify the diester needed to prepare a given cyclic β -keto ester by an internal Claisen condensation.
4. identify the structural features present in a diester that lead to the formation of more than one product in an internal Claisen condensation.

KEY TERMS

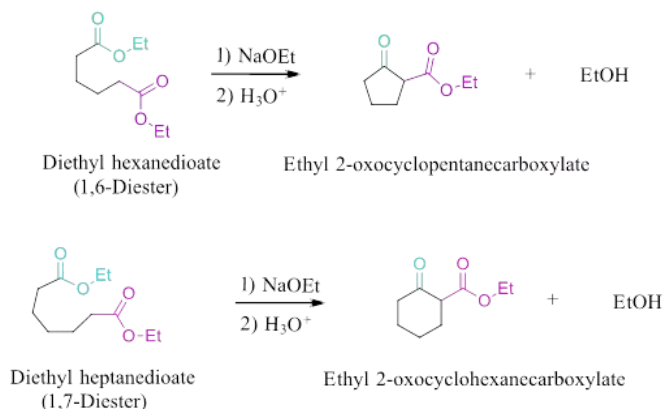
- Dieckmann cyclization

STUDY NOTES

Essentially no new material is introduced in this section; Dieckmann cyclizations are intramolecular Claisen condensations. These reactions occur for 1,6- and 1,7-diesters, as these substances result in the formation of compounds containing five- and six-membered rings, respectively. You may recall that the formation of such ring systems is favoured because they are relatively free of strain.

THE DIECKMANN CYCLIZATION

Diesters can undergo an intramolecular reaction, called the Dieckmann condensation, to produce cyclic β -keto esters. This reaction works best with 1,6-diesters, which produce five-membered rings, and 1,7-diesters which produce six membered rings.

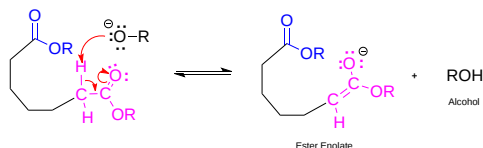


Examples of the Dieckmann Cyclization reaction.

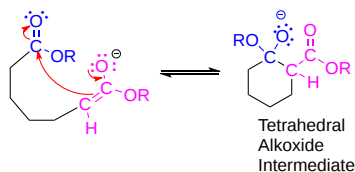
MECHANISM

The mechanism of the Dieckmann condensation is the same as a Claisen condensation. An alkoxide base removes an α -hydrogen from one of the esters to form an ester enolate. The enolate then adds to the carbonyl carbon of the other ester to form a tetrahedral alkoxide intermediate. The alkoxide reforms the carbonyl bond which causes the elimination of the $-OR$ leaving group and forms a cyclic β -keto ester. The high acidity of the β -keto ester allows it to be deprotonated by the reactions base to form a second enolate. Like the Claisen condensation, this deprotonation step drives the equilibrium towards the products and is required for the reaction to occur. A full equivalent of base is necessary during this reaction.

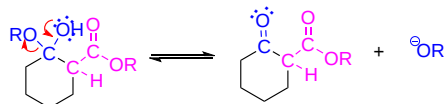
STEP 1: ENOLATE FORMATION



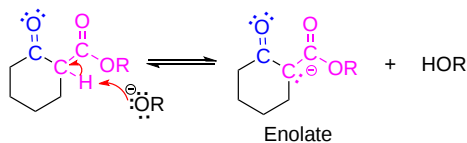
STEP 2: NUCLEOPHILIC ATTACK



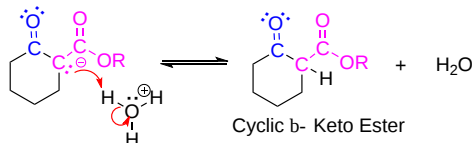
STEP 3: REMOVAL OF LEAVING GROUP



STEP 4: DEPROTONATION

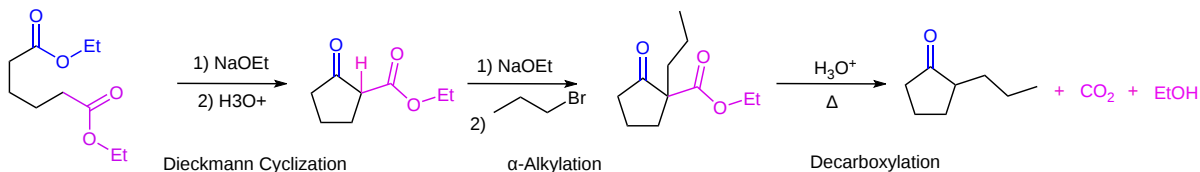


STEP 5: PROTONATION



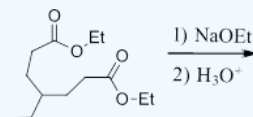
FURTHER REACTIONS OF THE DIECKMANN CYCLIZATION PRODUCT

The cyclic beta-keto ester product of a Dieckmann cyclization can be modified by reaction similar to those used in the acetoacetic ester synthesis (Section 22-7). The acidic alpha-hydrogens of the beta-keto ester allow it to easily be deprotonated and alkylated in an alpha-substitution reaction. Having a carbonyl group in the beta position allows the ester to be removed through decarboxylation. The combination of these three reactions (1) Dieckmann cyclization, (2) alpha alkylation, and (3) decarboxylation provides an efficient method for preparing 2-substituted cyclopentanones and cyclohexanones.

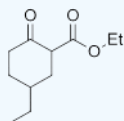


? EXERCISE 23.9.1

Draw the expected product for the following reaction:

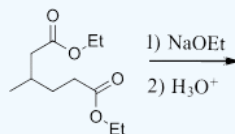


Answer

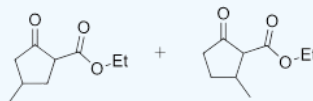


? EXERCISE 23.9.2

The Dieckmann cyclization of the following molecule is expected to give a mixture of two cyclized products. Draw the structure of the two products and briefly explain why a mixture is formed.



Answers



Each has the ability to act as a Claisen donor and a Claisen acceptor. The reaction should produce a roughly 50/50 mixture where each ester acts as a Claisen acceptor.

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