Study Notes On Dieckmann Reaction

DIECKMANN REACTION

(An Intramolecular Claisen Reaction)

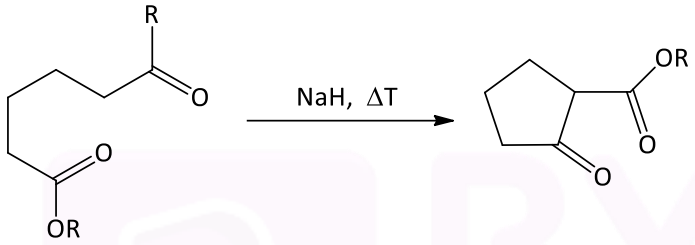
It is an intramolecular condensation of diester. In this reaction, diester undergoes intramolecular condensation in presence of base to yield β-ketoesters.

It is similar to intermolecular reaction, Claisen condensation. So, it is usually considered that the intramolecular Claisen condensation in dibasic acid esters is known as Dieckmann reaction.

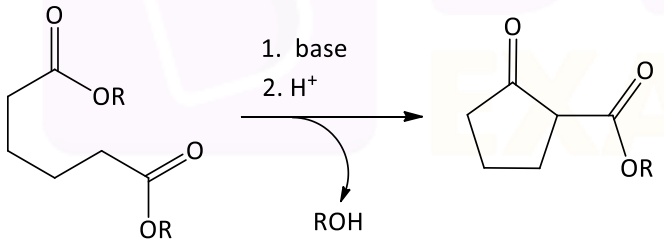
The Base catalyzed intramolecular cyclization of the dicarboxylic acid ester to yield β-keto-ester is Dieckmann condensation reaction whose general reaction is as follows-

This reaction usually occurs when a 5 or 6-membered ring could be formed.

General Reaction-



Or,

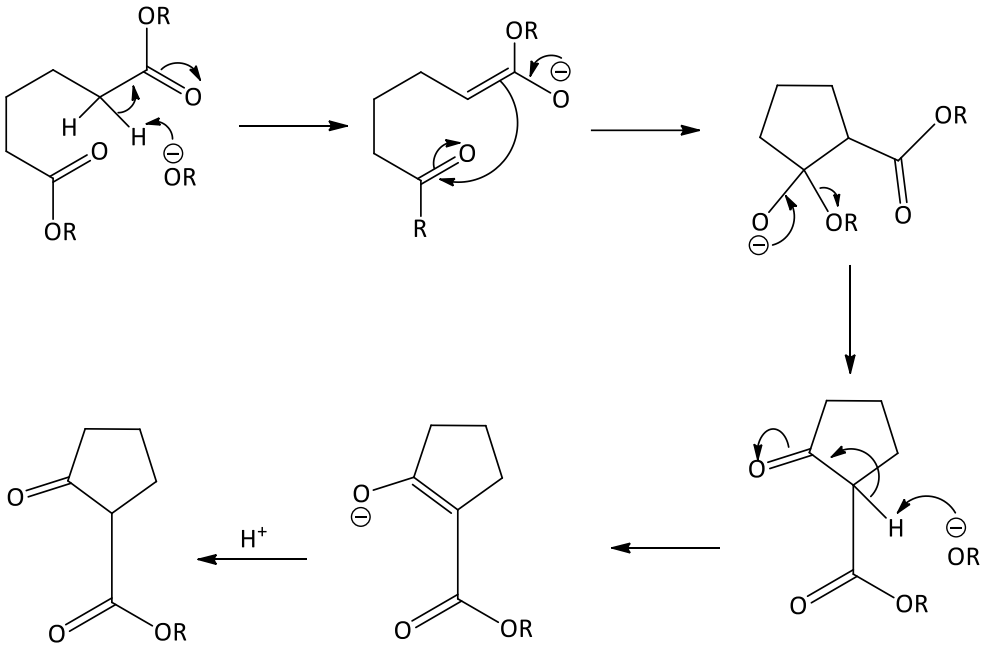


Note:

- The reaction best proceeds with dibasic acid esters having 6, 7 or 8 carbon atoms which give stable rings with s, 6, or 7 carbons. Yields for rings of 9 to 12 carbons are very low. High-dilution technique is used for the formation of large-size rings.

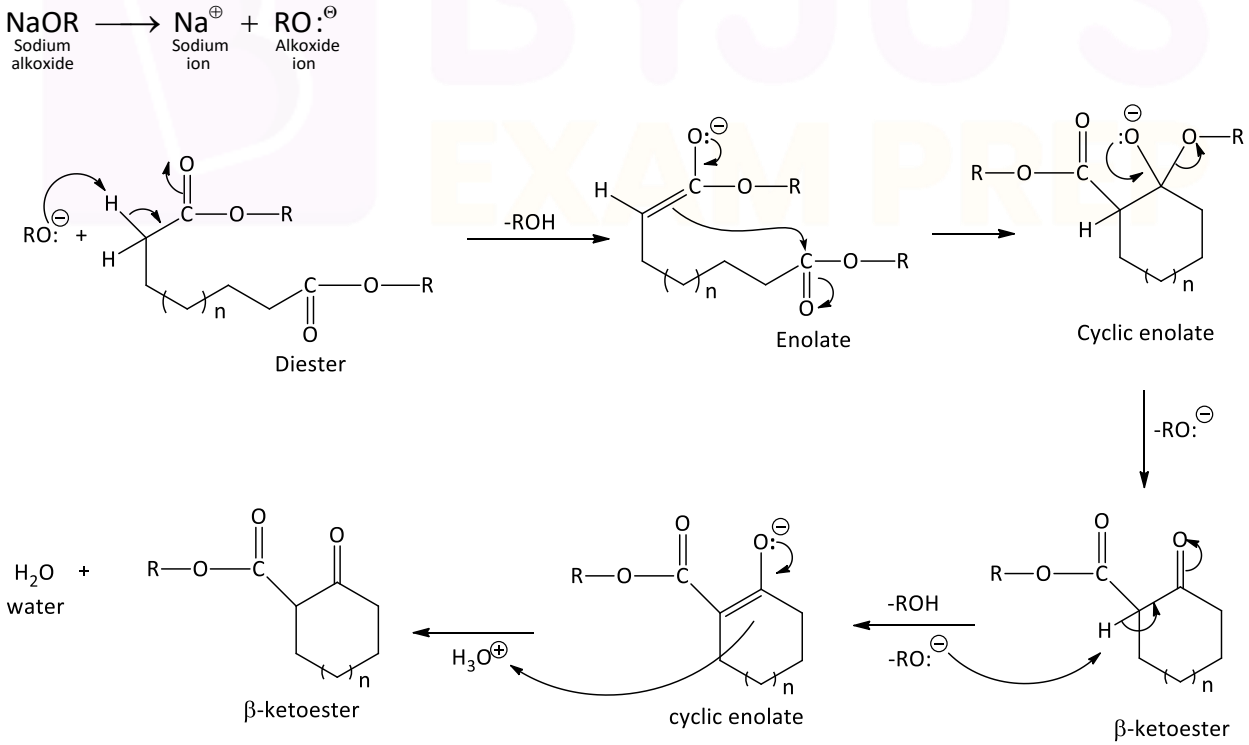
Reaction Mechanism-

A strong base removes the alpha proton resulting in an enolate. The enolate then attacks the carbonyl carbon of another ester molecule, resulting in a cyclic β-ketoester and regenerating the conjugate base. The base then deprotonates the cyclic compounds, and an acid workup is required to produce the final cyclic β-ketoester.



This can also be understood as-

Dieckmann Condensation Mechanism-

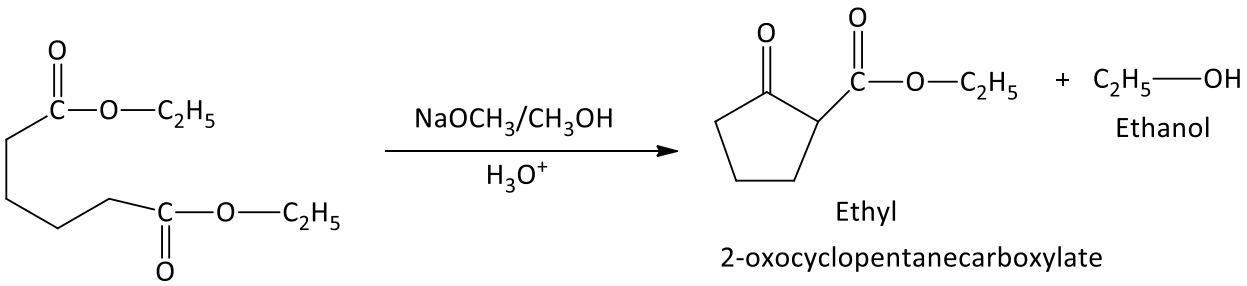


Dieckmann Condensation Mechanism

Note:

Due to the steric stability of five- and six-membered rings, these structures will preferentially be formed. 1,6 diesters will form five-membered cyclic β-keto esters, while 1,7 diesters will form six-membered β-keto esters.

Examples-



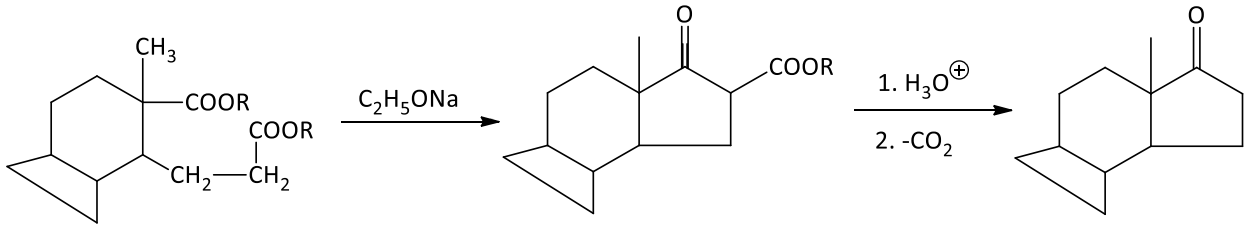
Diethyl adipate

Application of Dieckmann Condensation-

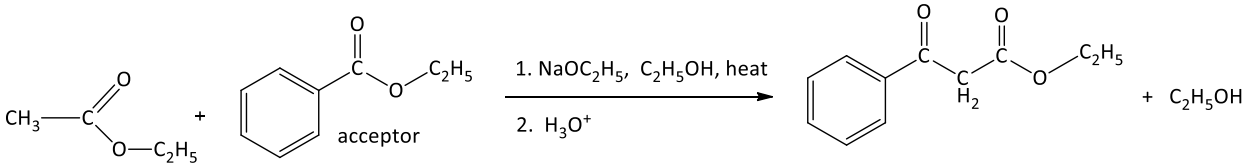
Dieckmann condensation is used in the preparation of cyclic indole. There has been a report of preparing five-membered pyrroles through this condensation method.

The reaction affords a useful route for the synthesis of cyclopentanone and cyclohexanone derivatives. Some examples are given for illustration.

1.The reaction has been used to build up five- or six-membered rings in the synthesis of various natural products. The general process is given below.



2. Synthesis of steroid-



BYJU'S EXAM PREP

CSIR NET Chemical Science 2022

A Foundation Course

Complete Prep of Chemical Science for June 2022 Aspirants

Why take this course?

- 450+ Hrs Live Classes & Doubt Sessions for complete conceptual clarity
- 3000+ Practice Questions covering all levels of difficulty
- 20+ Unit Wise Study Modules & Mind Maps
- 50+ Full Mock Tests, Chapter Wise Mock Tests, PYQs Mock Tests