Ćwiczenia nr 3- CHEMIA ORGANICZNA - semestr letni - Aldehydy i Ketony, Reakcje Kondensacji

1. Podaj produkt kondensacji aldolowej:

(a)
$$2$$

H

H

H

NaOH

H₂O

(b) H

H

H

NaOH

H₂O

(c) O

H

H

NaOH

H₂O

(d) O

H

H

NaOH

H₂O

(e) O

H

NaOH

H₂O

2. Przeprowadź następujące syntezy używając dowolnych reagentów:

3. Podaj produkt kondensacji Claisena

- a) benzoesan etylu + octan etylu
- b) octan etylu + mrówczan etylu
- c) propionian etylu + szczawian dietylu

4. Podać mechanizm cyklizacji:

a) kondensacji aldolowej

b) kondensacji Dieckmana

5. Synteza struktur wykorzystując reakcje kondensacji

The Aldol Addition

$$H\ddot{\mathbb{O}}$$
: $H \iff \begin{bmatrix} \ddot{\mathbb{O}} \\ \ddot{\mathbb{O}} \end{bmatrix} + H\ddot{\mathbb{O}}$

Enolate anion

In this step the base (a hydroxide ion) removes a proton from the α carbon of one molecule of acetaldehyde to give a resonance-stabilized enolate.

Step 2 Addition of the enolate

The enolate then acts as a nucleophile and attacks the carbonyl carbon of a second molecule of acetaldehyde, producing an alkoxide anion.

The alkoxide anion now removes a proton from a molecule of water to form the aldol.

The Aldol Cyclization

Other enolate anions

This enolate leads to the main product via an intramolecular aldol reaction. The alkoxide anion removes a proton from water.

Base-promoted dehydration leads to a product with conjugated double bonds.



A MECHANISM FOR THE REACTION

The Claisen Condensation

Step 1

An alkoxide base removes an α proton from the ester, generating a nucleophilic enolate ion. (The alkoxide base used to form the enolate should have the same alkyl group as the ester, e.g., ethoxide for an ethyl ester; otherwise transesterification may occur.) Although the α protons of an ester are not as acidic as those of aldehydes and ketones, the resulting enolate is stabilized by resonance in a similar way.

Step 2

Nucleophilic addition

Tetrahedral intermediate and elimination

The enolate attacks the carbonyl carbon of another ester molecule, forming a tetrahedral intermediate. The tetrahedral intermediate expels an alkoxide ion, resulting in substitution of the alkoxide by the group derived from the enolate. The net result is nucleophilic addition—elimination at the ester carbonyl group. The overall equilibrium for the process is unfavorable thus far, however, but it is drawn toward the final product by removal of the acidic α hydrogen from the new β -dicarbonyl system.

A MECHANISM FOR THE REACTION

The Dieckmann Condensation

Ethoxide ion removes an α hydrogen.

The enolate ion attacks the carbonyl group at the other end of the chain.

An ethoxide ion is expelled.

The ethoxide ion removes the acidic hydrogen located between two carbonyl groups. This favorable equilibrium drives the reaction.

Addition of aqueous acid rapidly protonates the anion, giving the final product.