Solventless claisen-schmidt condensation of benzaldehydes

Backgrounds and Theory (A)Introduction of aldol condensation In an aldol condensation reaction, the ? -carbon of an aldehyde or ketone molecule reacts with another carbonyl carbon to form a ? -hydroxyl aldehyde or ? -hydroxyl ketone, followed by dehydration to give a conjugated enone if an ? -H is present. It is a very useful reaction for the synthesis of ? ,? -unsaturated carbonyl compounds. The aldehyde or ketone molecule is first converted to enol or enolate by acid or base catalyst respectively. In this experiment, the base-catalyzed method is used and the ? proton of the aldehyde or ketone molecule is removed by a strong base like hydroxides and alkoxides to form an enolate ion: Although hydroxide ion is not strong enough to convert all of the aldehyde or keton molecules to the corresponding enolates for both aldehydes and ketones (i. e. the equilibrium lies well to the left), there are usually enough enolate ions for the reaction to proceed at a reasonable rate. The enolate ion will then react with the carbonyl compound to form an intermediate anion, which is quickly protonated by water. When the ? hydroxyl aldehyde or ? -hydroxyl ketone is formed, it will be sometimes spontaneously dehydrated to give an ? ,? -unsaturated carbonyl compound since a C= C bond can be formed by this process and it is very stable due to the conjugation with the carbonyl group. Therefore if the dehydration is not spontaneous, it can also be easily induced by gentle heating. However, self condensation will occur, especially if both of the reactants are ketones, and a mixture of products will be formed. This is mainly due to the similar electrophilicity of the reactants.

For example, when 3-pentanone is reacted with cyclopentanone: A mixture of products will be formed as both the reactants can become enolate ion and

react with itself or another reactant. Also, more kinds of products will be formed after dehydration as different kinds of ? -proton is available. If the reactants are unsymmetrical, the reaction will become more regioselective. For example, if 2-methylpentan-3-one is reacted with reacted with cyclopentanone: The upper one will be the major product since ? -proton is available for the formation of conjugated double bond by dehydration.

The extra stability of the product shifts the equilibrium to its side. (B)Claisen-Schmidt Condensation – a Branch of Aldol Condensation Clasisen-Schmidt condensation is a branch of aldol condensation which eliminates most of the regioselectivity problems. In the reaction, an aromatic aldehyde is condensed with a ketone to form an ? ,? -unsaturated ketone. For example: Since an extra alkyl group (EDG) is present in ketone, it is less electrophilic than the aldehyde. Therefore only the ? -carbon of the ketone will attack the aldehyde, but not the other way round.

Also, there will not be any self condensation as only aldehyde will be attacked. The dehydration process of the above reaction is also regioselective as there is only one kind of ? -proton present in the compound. Therefore only one kind of product will be formed. In this experiment, the Clasisen-Schmidt condensation of benzaldehyde and p-methylacetophenone will be studied. (C)Traditional Method vs Solventless Method (Green Chemistry) Organic reactions usually require organic solvents as to provide a medium for the interactions of reactants and to moderate the temperature and reaction rate.

Nevertheless, the use of organic solvent needs a significant cost on materials required and also increases the burden to chemical waste treatment and

theenvironment. Green Chemistry is therefore developed in order to reduce material consumption and increase the efficiency of chemical production by minimizing the use of solvents. The Claisen-Schmidt condensation of benzaldehyde and acetophenone would have a very high atom economy (> 92%) with the reaction solvent eliminated. In this experiment, the efficiencies of the traditional and solventless methods will be compared.