Benzoin Condensation by Organocatalysis, and Consideration of Its Usage for Waste Management

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Abstract

The present study adopted organocatalysis for benzoin condensation. Benzaldehyde, 3-Ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide, and triethylamine were used as reagents. Benzoin condensation was occurred successfully by confirmation of hydrogen and carbon by nuclear magnetic resonance (NMR) spectroscopy and thin layer chromatography. Considerations for waste management and further study have been suggested in the discussion.

** **Keywords:** waste management, organocatalysis, benzoin condensation*

1. Introduction

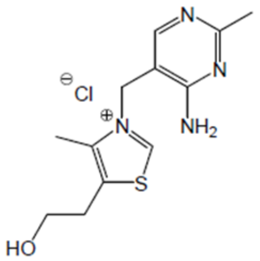
Municipal solid waste (MSW) indicates composite wastes in civic area (United Nations Environment Programme, 2005, p. 1). The solid waste originates from inhabitants' lifestyle as well as nature of the region, and urban wastes consist of mainly organic and inorganic components (United Nations Environment Programme, 2005, p. 1). This type of solid wastes can be classified as putrescibles, paper, metals, glass, plastics, rubber, leather, textiles, ceramics, dust, stones (United Nations Environment Programme, 2005, p. 1-2), and it affect environment and health in negative aspects by both direct and indirect ways (Giusti, 2009, p. 2230-2231). For instance, incineration of wastes emits a lot of pollutants such as dioxins, polycyclic aromatic hydrocarbons and heavy metals, which can bring many kinds of diseases like lymphoma and cancer (Giusti, 2009, p. 2233-2234). In order to reduce the production of such toxic substance, chemists have been trying to find out other kinds of materials, rather than metals, main origins of environmental pollution. One of the solutions is using organocatalysis. This research has dealt with a case of bioorganic catalyst, and has reviewed the possibility of its usage for waste management.

2. Theoretical Background

Organocatalysis

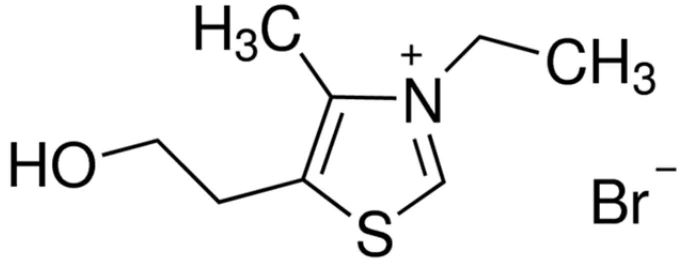
Typically speaking, scientists in chemistry mainly used enzymes or transition metals as catalysis for asymmetric catalysis. Despite of their efficiency for catalysis, many kinds of transition metals such as chromium, nickel, cobalt, zinc, and titanium are detrimental for environment and human's health. According to Benjamin List (2007), modern asymmetric catalysis focuses upon three ways: biocatalysis, metal catalysis, and organocatalysis (List, 2007, p. 5413). The organocatalysis has been adopted by a number of scientists and engineers recently, and it is expected to bring benefits in "cost, time and energy" (MacMillan, 2008, p. 305).

The organic molecule was used as starting material or generated substance in the past, however, this came into the spotlight in these days after its usage as catalysis has been identified (Yang, 2010, p. 19). In addition, the organocatalysis also showed its playing role in the field of asymmetric catalysis, whose main catalysis were enzymes and transition metals (Yang, 2010, p. 19). Considering these benefits and possibility, the field of organocatalysis is becoming a leading part of chemistry and alternative method for green chemistry. A characteristic that organocatalysis minimize the components that may pollute environment and convert them into other ones will be emphasized more and more in near future. With this expectation, the present study adopts one example of organocatalysis, named "3-Ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide", which is derived from thiamine (Vitamin B_1), for an experiment of benzoin condensation.



Thiamine (Vitamin B_1), a coenzyme

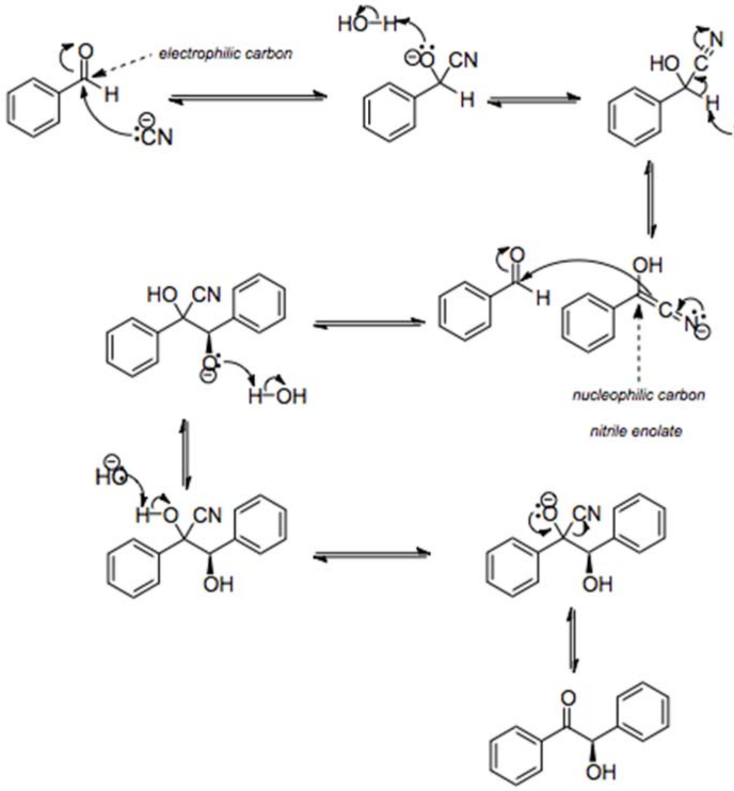
< Figure 1: Thiamine (Vitamin B_1) >

Category	Intermediates
Molecular Formula	$C_8H_{14}NOS \cdot Br$
Molecular Weight	252.17
Molecular Structure	

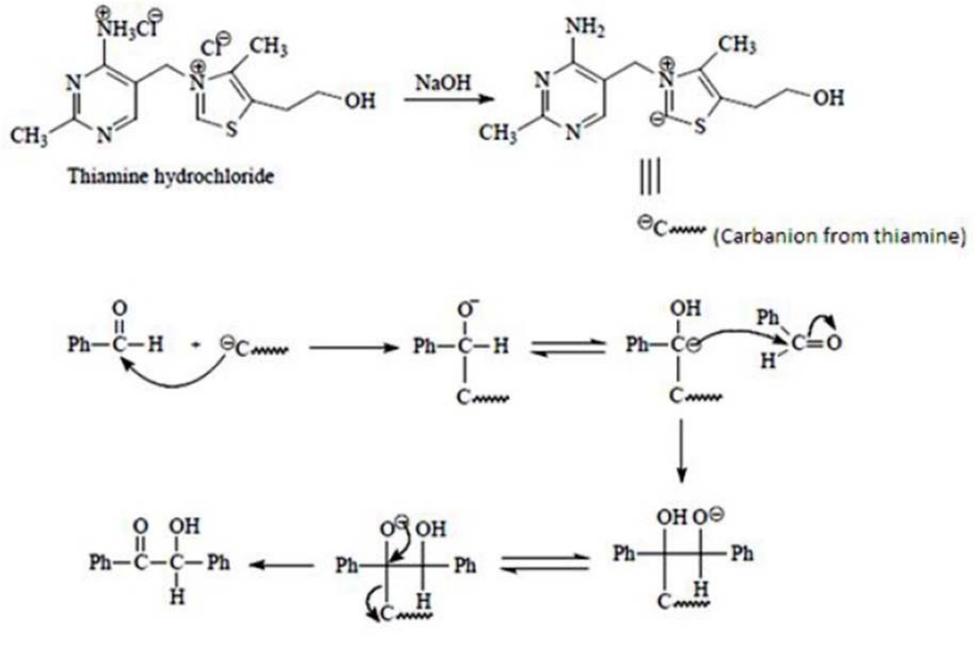
< Figure 2: 3-Ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide >

Benzoin Condensation

The benzoin condensation, also known as condensation reaction, indicates a combination of two aromatic aldehydes, which forms a larger molecule. We can achieve benzoin when we give a heat to two aromatic aldehydes with potassium cyaniade. During this procedure, the reaction of condensation is occurred, and the produced benzoin is asymmetric. Benzoin condensation can be reacted with thiazolium functions or thiazolium ions (Thanuja, 2014).



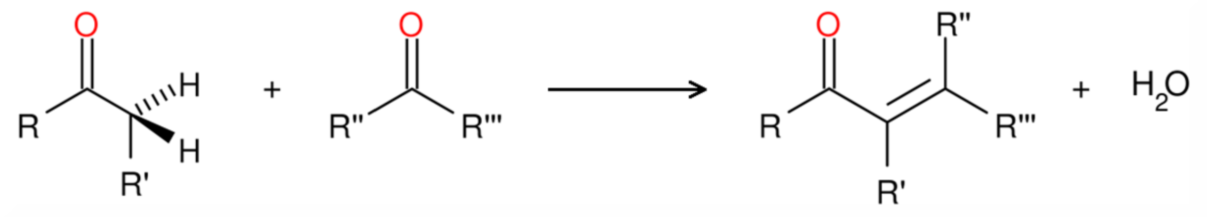
< Figure 3: Benzoin mechanism using cyanide as a catalyst >



< Figure 4: Benzoin mechanism using Thiamine hydrochloride as a catalyst >

Aldol Condensation

This is a reaction to produce aldol CH3CH(OH)CH2CHO by base upon two molecules of acetaldehyde. It easily eliminate water molecule and produce CH3CH = CHCHO. During the reaction, the molecules of enol or enolate ion reacts with a carbonyl compound, and β-hydroxyaldehyde or β-hydroxyketone is formed. Aldol condensation is applied for organic synthesis to form carbon-carbon bonds



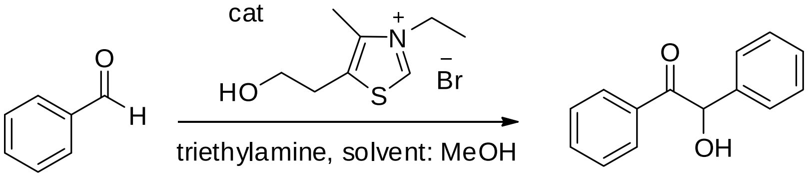
< Figure 5: Overview of Aldol Condensation >

Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectroscopy is invented for studying the structure of organic compounds. Its target is nuclei in a magnetic field such as $^{1}H, ^{13}C$ etc. ^{1}H NMR is mainly used for confirming compounds or analyzing various organic compounds as hydrogen exists in most organic molecules. When the outer magnetic field does not exist, each nuclei's magnetic moment orients randomly. However, when the nuclei locates in outer magnetic field, the magnetic moment is identical with or opposite against the direction of outer magnetic field. The identical case is called α-spin state, which indicates low energy one, and the opposite case is known as β-spin state, which means high energy one. As we expose RF energy, as much as the energy gap between α and β-spin states, to the nuclei in α-spin state, the nuclei converts into β-spin states, and emits signs as much as the gap energy. NMR recognizes this signal and shows the oscillation of the gap energy. At this process, we can figure out the number of hydrogen in the compounds by analysis of spectrum. With the same principle, we can analyze the number of kinds of carbons with using ^{13}C NMR.

3. Process of Experiment

Synthesis of Benzoin



Reagent	benzaldehyde	3-Ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide	triethylamine

Mw	106.2g/mol	252.17g/mol	101.19g/mol
Wt/mol	0.2㎖	0.05g	0.06㎖
Mole	2 mmol	0.2 mmol	0.4 mmol
Eq.	1	0.1	0.2
d.	1.044g/㎖	-	0.7255g/㎖

< Figure 6: Reagent Information >

Cautions

- Dress appropriately for the laboratory period. Bare feet, shoes, shorts and halter or tank tops are not allowed in the laboratory. Long hair and loose clothing should be tied back.
- Personal items, including, but not limited to, book bags and books should be put in the area of the lab room designated for that purpose.
- Do not work alone in the laboratory.
- Before start our experiments, Safety glasses or goggles and lab coat must be worn at all times in laboratory.
- Never smoke, eat, drink, or apply cosmetics in the laboratory.

Apparatus and Machines

* **Tools:** 20, 250㎖ round-bottom flask, 20㎖ vial, 3㎖ syringe, small needles, separatory funnel, Pasteur pipette, filter flask, and thin layer chromatography (TLC).

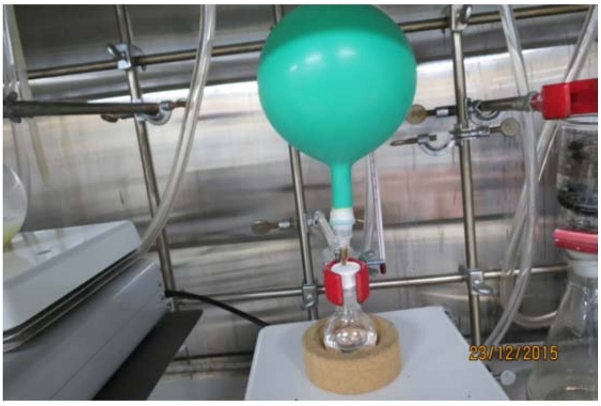
* **Machine of Structure Determination**: Nuclear magnetic resonance (NMR) spectroscopy at the Department of Energy Science at Sungkyunkwan of University

< **Figure 7: NMR Spectroscopy at Dept. of Energy Science, Sungkyunkwan University** >

Procedure of Benzoin Condensation (Method)

A solution of the benzaldehyde (2 mmol) in methanol (3㎖) was added to 3-Ethyl-5-(2-hydroxyethyl)-4-methylthiazoliumbromide (*ca*. 0.2mmol), followed by degassed triethylamine, and the mixture stirred at room temperature. After 16 hours, the solution was then diluted with dichloromethane (20㎖), washed with water (10㎖) repeating two times, dried (Na_2SO_4) and evaporated under reduced pressure. The crude was purified by column chromatography 9:1 (hexane/EtOAc) to obtain the desired product as white solid.

(1) Put the reactants and solvent in the 20㎖ round-bottom flask by charging Ar gas at room temperature and stirred using magnetic bar.



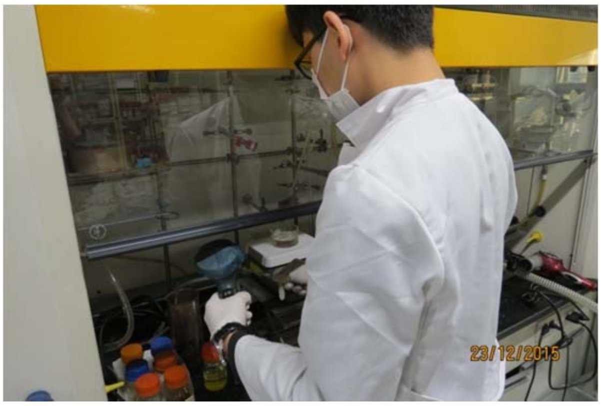
(2) Confirm a change of reaction through TLC. It was seen another spot, not spot of benzaldehyde.

a: Benzaldehyde

b: the mixture

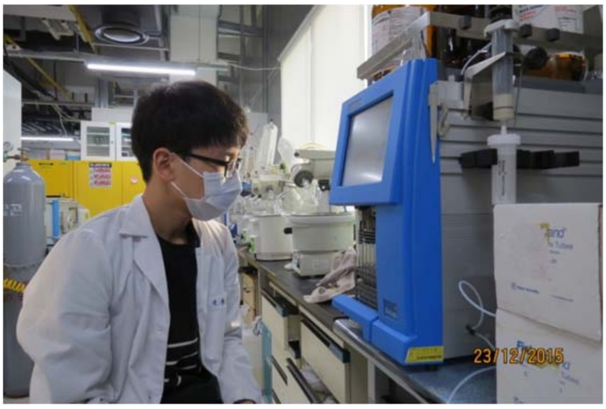
TLC condition is 4:1 (hexande/EtOAc)

(3) Confirm the presence or absence of hydroxy group (-OH) in Benzoin. Therefore, put TLC of this experiment in color fixing agent named for ceric ammonium molybdate (CAM) and heated by a heat gun.

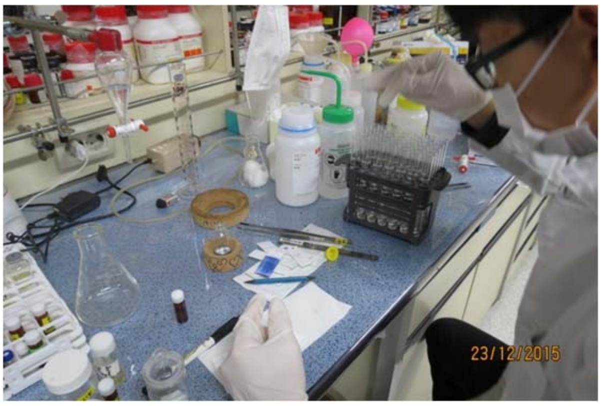


(4) After work-up, evaporate solvent through evaporator.

(5) Separation through medium phase liquid chromatography (MPLC)



(6) Check TLC isolated compound in solvent and collected clean-spot.

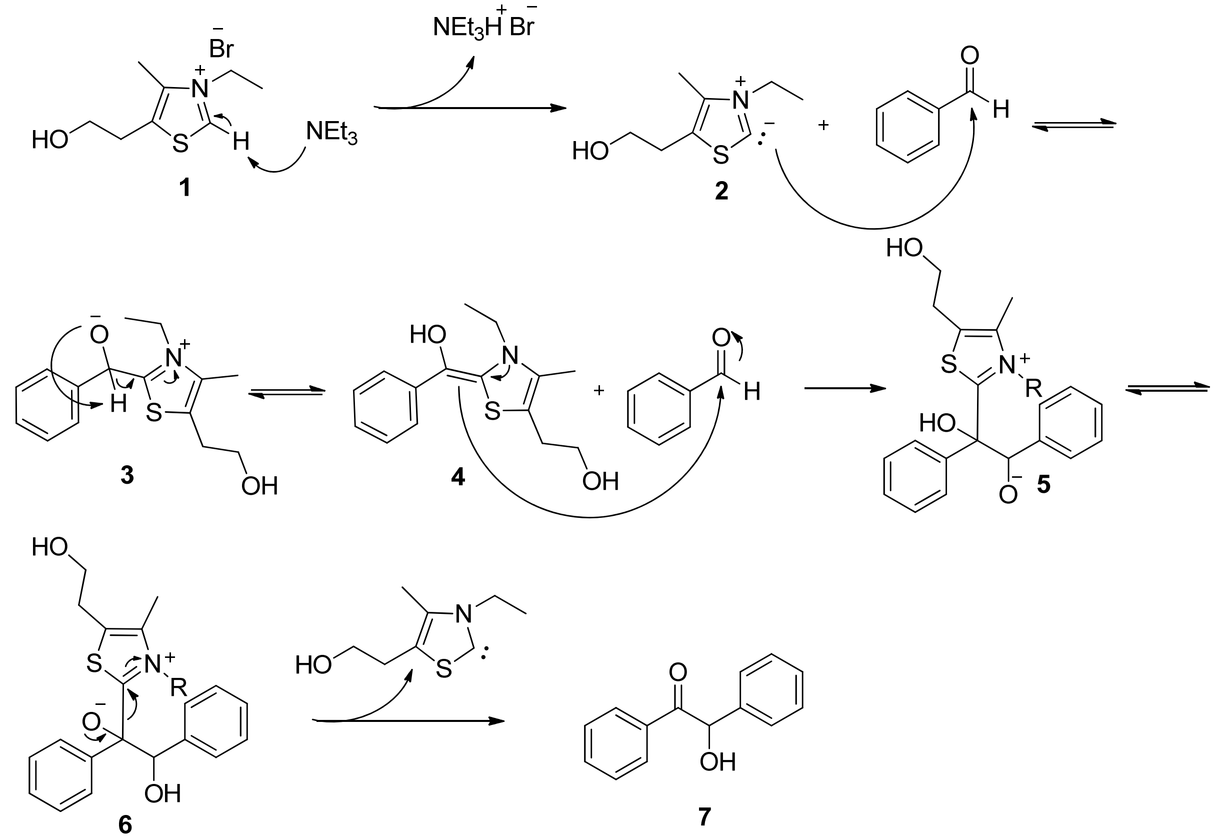


(7) Dissolve product of this experiment in $CDCl_3$ NMR solvent to make NMR sampling.

(8) After check of the NMR peak, achieve product of Benzoin.

4. Result

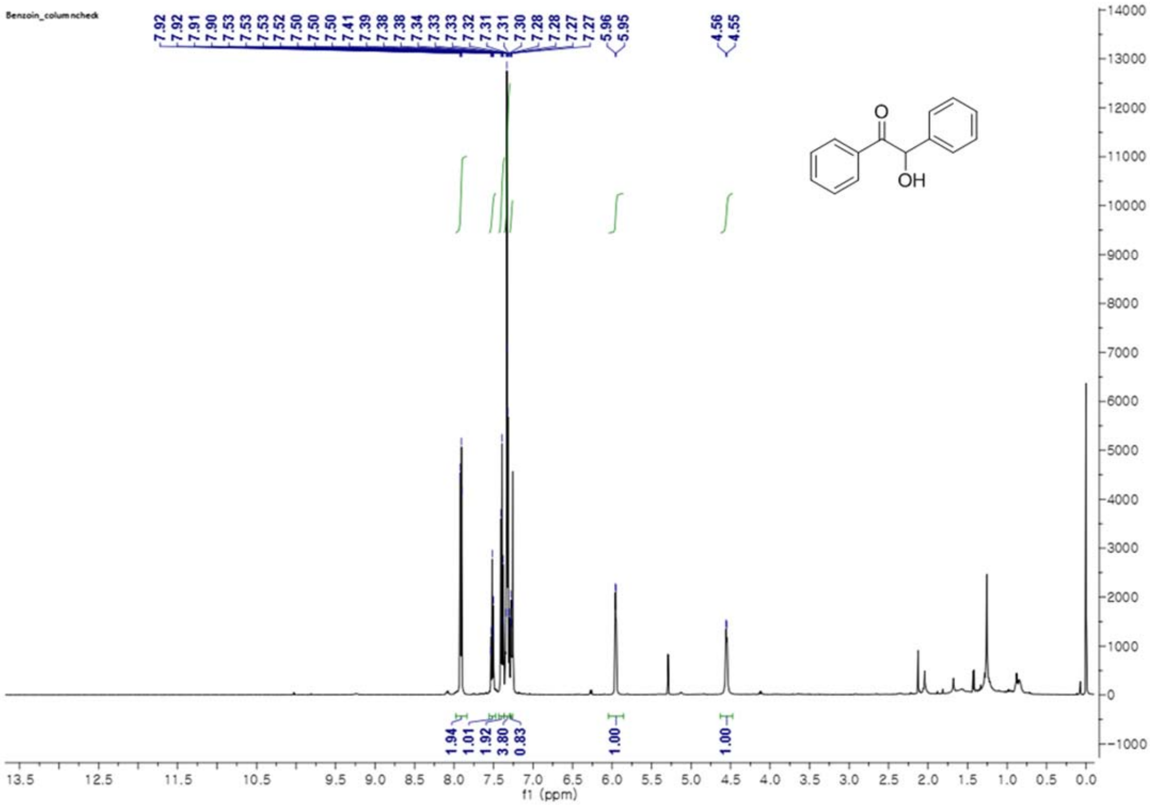
(1) Mechanism of Reaction



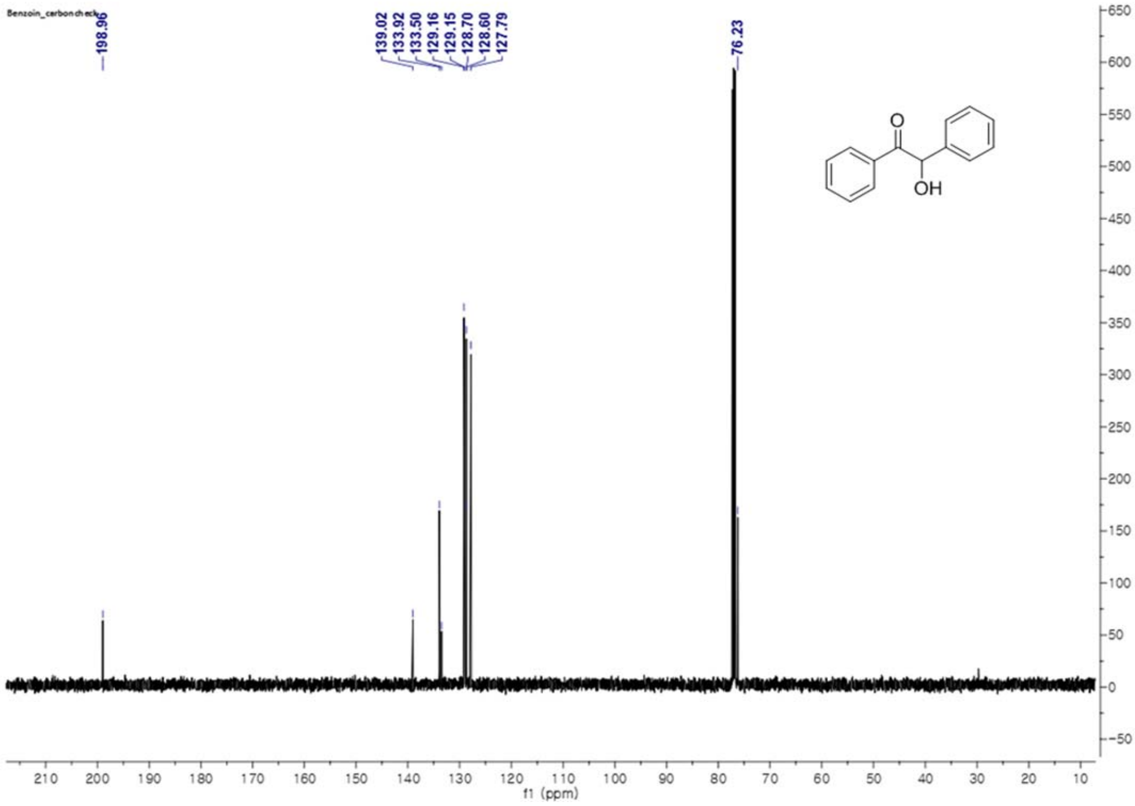
< Figure 8: Steps of Reaction >

The thiazolium salts were converted into ylide by deprotonation, followed by nucleophilic addition to benzaldehyde. The electron withdrawing thiazolium ring then allows deprotonation of adduct 3 and resulting enamine 4 attacks the second benzaldehyde molecule. Release of product 7 from adduct 6 regenerates the ylide and complete catalytic cycle.

(2) NMR Data



< Figure 9: ^{1}H NMR (500 MHz, $CDCl_3$) >



< Figure 10: ^{13}C NMR (125 MHz, $CDCl_3$) >

We can check the number of proton in benzoin with ^1H NMR. The numbers above indicates which ppm peak is located, and below part shows the general number (twelve) of proton by integration of other peaks. Specifically, the peak can be found between 6 ppm to 8 ppm for benzene. Because electronegativity of O at OH radical is strong, proton at OH radical and proton of carbon with OH radical are shown between 4 ppm to 6 ppm. Peaks in less than 2 ppm are solvent ones, which are not significant for this experiment. At ^{13}C NMR, we can check the number of carbon. As intensity increases, it indicates that the number of carbon is two or more than this, not one.

5. Discussion

Umpolung (Polarity Inversion)

The present study has examined contribution of organocatalysis for benzoin condensation. The catalyst, 3-Ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide, was applied to benzaldehyde. The benzoin condensation was successful by confirming proton and carbon in benzoin with NMR spectroscopy. The catalyst in this experiment is nucleophile. Generally, benzoin condensation tries to keep cyanide ion (CN^-) because electronegativity of N is bigger than that of C in CN. However, in this experiment, electrons were driven more to C, and carbon became nucleophile. This indicates that the base, triethylamine, did a deprotonation, and umpolung, polarity inversion occurred.

Chemical Approach for Environmental Friendly Plans on Waste Management

Scientists in chemistry, engineering and waste management have been struggling to find out alternative ways for dealing with MSW. Kyoseva and Dombalov (2013) introduced "catalytic thermal-tribo-chemical treatment" for utilizing MSW for co-environmental aspect, Noreña, Aguilar, Torres, Gutiérrez, and Mugica (2012) have discussed "plastic waste catalytic cracking materials" with chemical catalysts, and Lam, Lee and Mohamed (2010) reviewed biodiesel in terms of heterogeneous acid and enzyme catalyze. These cases have a common point in that they use enzymes or catalysts for utilizing waste. Even though typical approaches with metals have potential as environmental friendly methods, we also need to examine possibility of organocatalyst as well for its contribution for this issue, considering its better aspects in time, expense and energy efficiency. For example, the experiment in this paper discovered role of organocatalysis upon benzoin condensation, which can be later tested in further details for macromolecules. Considering that most materials of waste are made up of macromolecules, the function of organocatalyst, which is regarded as better catalyst than transition metal one, is valuable enough to be tested in MSW management.

6. Reference

United Nations Environment Programme (2005). Solid Waste Management (ISBN: 92-807-2676-5).

Giusti, L. (2009). A review of waste management practices and their impact on human health. *Waste management*, *29*(8), 2227-2239.

List, B. (2007). Introduction: Organocatalysis. *Chemical Reviews*, *107*(12), 5413-5415. DOI: 10.1021/cr078412e

MacMillan, D. W. (2008). The advent and development of organocatalysis. *Nature*, 455(7211), 304-308. DOI:10.1038/nature07367

Yang, J. W. (2010). Chiral Brønsted Acid Organocatalysis. *Chem World*, *50*(1), 19-24.

Thanuja, B. (2014). Synthesis, characterization by spectra, single crystal XRD and study of the dielectric, ultrasonic, thermal, biological and opto electronic properties of benzoins and its derivatives. http://hdl.handle.net/10603/18252

Kyoseva, V., & Dombalov, I. (2014). Chemical Conversion of Municipal Solid Wastes into Raw Materials and Energy Resources. *Journal of Chemical Technology and Metallurgy*, *49*(2), 179-184.

Noreña, L., Aguilar, J., Torres, M., Gutiérrez, M., & Mugica, V. (2012). *Materials and Methods for the Chemical Catalytic Cracking of Plastic Waste*. INTECH Open Access Publisher.

Lam, M. K., Lee, K. T., & Mohamed, A. R. (2010). Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: a review. *Biotechnology Advances*, *28*(4), 500-518.

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