Synthesis of Schiff Base Compound from Vanillin and *p*-Toluidine by Solvent Free-Mechanochemical Method

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ABSTRACT

Synthesis processes by solvent free or known as greeen method are widely used and developed compared to conventional method based on solution. This research has successfully synthesized Schiff base compound 2-methoxy-4-((*p*-tolylimino)methyl)phenol from vanillin dan *p*-toluidineby solvent free-mechanochemical method. Each of reactans with molar ratio 1:1 was grinded using mortar and pastle with variation of time grinding while 10, 15, dan 20 minutesand characterized the moleculer structure by spectrophotometric technique. Synthesis process was produce excellent result with high yield and purities. Synthesis products are pale yellow solid and slightly soluble in water. UV-Vis spectrum have optimum absorption on 329 and 285 nm,while FTIR spectra shows that each of product have charateristic bond C=N on 1585,532 - 1590,203 cm^{-1}. Analysis using GC-MS shows target compound has molecular ion on m/z 241 that indicated weight of Schiff base compound.

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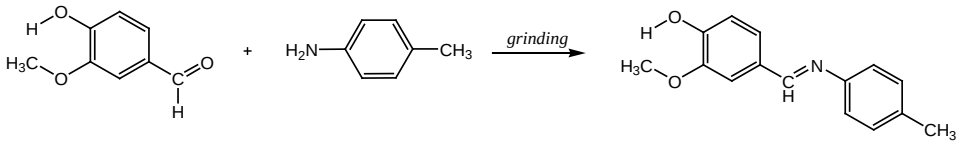
I. INTRODUCTION

Schiff base is an imine compound with characteristic bonding which is obtained through addition-elimination reaction of primary amine (R-NH_2) and carbonyl compound (aldehyde/ketone) that using acid catalyst [1-3]or without catalyst[4-7].Schiff base compound has pharmacological activities as antioxidant [8], anticancer [9], antitumor, antiinflamation, insektisida, antibacterial, and antituberculosis [2]. Schiff base compound also act as a ligan for complex compound that applied as sensor , catalyst, and corrosion inhibitor [10-11]

Schiff base compound can be synthesized conventionally by reflux of primary amine and aldehyde/ketonein volatile solvent and acid catalyst[12-13]. Generally, synthesis by conventional methods requires a long time, volatile solvent, toxic acid catalyst, and need high energy, so this method are not classified as environmentally friendly method. In addition, the uses of excess acid catalyst may cause a reversible reaction (imine hydrolisis) andamine protonation,so reducedthe ability of amine as a nucleophile [3, 14, 15]. Eventually, the yields of product is decrease.

Currently, green method that most developed are solvent free-mechanochemical method. That method are more effective because not involved other compound except the reactans, so reduce the total impurities in product. The other advantages of this method are syntesis technique that more simple and less energy. Some research on synthesis Schiff base compound by solvent free-mechanochemical method has been applied from variety of aromatic primary amine and aldehyde/ketone compound and giving excellent result [4, 7, 8, 16, 17].

In this research, we have successfully synthesized Schiff base compound from vanillin and *p*-toluidine by solvent free-mechanochemical method pass trough way on Figure 1. The reaction was designed by absence of acid catalyst and solvent and this reaction give effective result.



vanilin *p*-toluidin 2-metoksi-4-((*p*-tolilimino)metil)fenol

Figure 1. Scheme of solvent free mechanochemical synthesis of Schiff base

2. RESEARCH METHOD

Vanillin *p.a* (1.1g, 7.5 mmol) and *p*-toluidine *p.a* (0.8 g, 7.5 mmol) was grinded by mortar and pastle at room temperature. Time grinding was variated on 10, 15, and 20 minutes. The products was washed by cold water, without purification. The progress of reaction was monitored by TLC method and chloroform.Product's melting point was determined by MPA and the the solubility was tested by water and base solution (NaOH 2M). Characterization of products was used UV-Vis (Varian Cary), FTIR spectrophotometer (Varian FT 1000) and GC-MS (Varian CP-3800 SATURN 2200)[15-17].

3. RESULTS AND ANALYSIS

3.1Synthesis of Schiff base compound 2-methoxy-4-((*p*-tolylimino)methyl)phenol

Experimentally convertion of vanillin and *p*-toluidine into Schiff base compound 2-methoxy-4-((*p*-tolylimino)methyl)phenol by solvent-free mechanochemical method was produced pale yellow solid. Each of product have similiar physical characteristic that showed on Table 1. The products slightly soluble in water and the solubility was increased with addition of base solution (sodium hydroxide). It is caused reaction between Schiff base compound and sodium hydroxide solution produced salt that completely soluble in water.

Table 1.Physical character of product

Parameter	P.10	P.15	P.20
Physical form	Solid	Solid	Solid
Colour	Pale yellow	Pale yellow	Pale yellow
(%) yield	95.1315	95.5570	96.0820
Melting Point (°C)	118-121	117-119	118-120
Solubility	Slightly soluble	Slightly soluble	Slightly soluble
Rf	0.50	0.48	0.45

P.10 : time variation 10 min
P.15 : time variation 15 min
P.20 : time variation 20 min

The results of monitoring with TLC method showed that target compound has yellow spot when obseved without UV lights and dark colour with UV light 254 nm. This spot are certainly have a difference with spot of reactans that colourless when observed without UV lamp.

3.2 Characterization of Product

3.2.1 UV-Vis Analysis

The optimum absorption of spectrum of Schiff base 2-methoxy-4-((*p*-tolylimino)methyl)phenol was measured at 329 and 285 nm.

3.2.2 FTIR Analysis

FTIR spectra of product synthesis was showed on Figure 2. All three of products has characteristic strong absorption of imine functional group (C=N) on 1585.532-1590.203 cm^{-1}. This spectra were really different compared with FTIR spectra of vanillin and *p*-toluidine. Vanillin has strong absorption C=O carbonilon 1665,841 cm^{-1}, while on product's spectra weren't identified. *p*-Toluidine spectra have characteristic strong amine absorption (-NH_2)on 3470 and 3388 cm^{-1} that weren't identified on product's spectra.

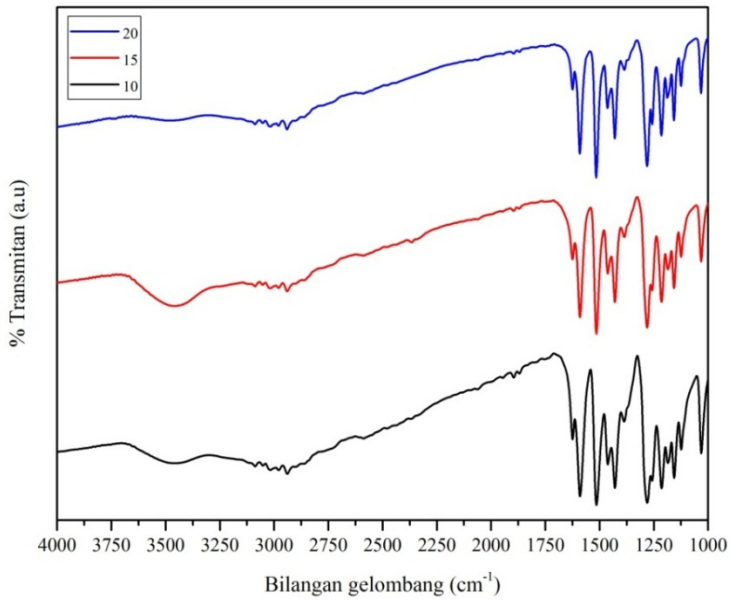


Figure 2. FTIR spectra of products with time grinding variation (a) 10 min, (b) 15 min, (c) 20 min

Table 2. Functional group of Schiff base products

Functional Group	**Wavenumber (cm^{-1})**		
	P.10	**P.15**	**P.20**
-OH stretch	3463.9	3462.3	3472.3
C_{sp2}-H stretch aromatic	3086.9	3087.5	3087.4
C_{sp3}-H stretch aliphatic	2939.2	2939.4	2940.2
-HC=N- stretch	1589.9	1590.2	1590.7
CH_3 deformation	1461.9	1462.3	1463.4
	1429.0	1429.2	1429.7
C-O-C asimetric	1280.5	1280.6	1281.0
C-O-C asimetric	1031.0	1031.6	1032.2
-CH_2 bend	1155.9	1156.5	1156.1
	1123.6	1124.1	1124.4

3.2.3 GC-MS Analysis

Analysis result using GC-MS showed that product synthesis has % purity until 93.7679%. Other component in product synthesis are residue of reactans in small amount. Target compound has molecular ion with m/z 241 that indicating the weight of Schiff base compound . The base peak as the most stable ion was detected with m/z 240.

4. CONCLUSION

The mechanochemical synthesis of Schiff base compound is effective and giving excellent conversion to the product based on the yield and purity. This method are more less pollution and less energy also easy to applied. Furthermore, we can make trial of isolate the Schiff base product to increase the purity.

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