KNO₃/ACE: A COST-EFFECTIVE MATERIAL FOR SYNTHESIS OF (2*E*,4*E*)-1,5-DIPHENYLPENTA-2,4-DIEN-1-ONE AND (*E*)-3-PHENYL-5-STYRYL-1*H*-PYRAZOLE

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ABSTRACT

Potassium nitrate impregnated on activated chicken eggshell (KNO₃/ACE) was successfully prepared, and then it was characterized by means of IR, XRD, FESEM and EDAX spectroscopy. The KNO₃/ACE showed high activity for the synthesis of chalcone compound, (2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-one (**3**) from the reaction between acetophenone (**1**) and cinnamaldehyde (**2**). The highest yield of compound **3** was achieved up to 93% after reaction at 60°C for 2 h in the presence of 15 wt% catalyst. Then, compound **3** was further treated with hydrazine hydrate (**4**) to produce (*E*)-3-phenyl-5-styryl-1*H*-pyrazole (**5**) up to 97% yield using the same optimized condition as in chalcone synthesis.

Keywords: KNO₃, ACE, Solid Catalyst, Chalcone, Pyrazole.

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INTRODUCTION

Pyrazole is a prominent heterocyclic nucleus containing five-membered ring with two adjacent nitrogen atoms.¹ Pyrazole and its derivatives have shown a wide spectrum of biological performance, including analgesic, antipyretic, sedative, anti-inflammatory and anticancer activities.²⁻⁴ Moreover, some pyrazole-containing compounds possessed anticonvulsant and antiviral effects.^{5,6} By considering their biological significance, the synthesis of pyrazole derivatives is of special interest for synthetic chemists.

On the other hand, the demand for a cost-effective and active catalyst in various organic transformation is still highly necessitated, and it is shifted from homogeneous to the heterogeneous system.⁷ Activated chicken eggshell(ACE) constitutes one of the highly applicable CaO-based catalysts in synthetic organic chemistry. Aldol condensation, transesterification in biodiesel production, and Schiff base formation have been reported to be catalyzed using ACE.⁸⁻¹²

In the previous study, some salts and bases, such as KCl, KNO₃ and KOH were impregnated on CaO-based catalyst to improve their catalytic activity.¹³⁻¹⁵ Hu et al. prepared KNO₃/CaO via dry impregnation method and applied it for glycerol carbonate synthesis.¹⁵ By successive work in making this catalyst, herein, we report preparation of KNO₃ impregnated on CaO-based material from chicken eggshell waste. Then, KNO₃/activated chicken eggshell, denoted as KNO₃/ACE, was utilized as a catalyst for chalcone and pyrazole synthesis (Fig.-1).

Fig.-1: Synthesis of a Pyrazole Derivative

EXPERIMENTAL

Materials

Eggshells waste was collected from an industrial household in Depok, Indonesia. All chemicals used were purchased from commercial suppliers. IR spectra were recorded on Shimadzu Prestige-21 spectrophotometer, while XRD patterns were taken on a PanalyticalX'Pert Pro MPD X-ray diffractometer with Cu-K α (0.154 nm) radiation. Catalyst morphology was observed on FESEM FEI Inspect F50 scanning electron microscope tandem EDAX spectroscopy. GC-MS spectra were gained from Agilent 6890 with instrument control parameters as follows: front inlet, split mode, initial temp. 290°C, pressure 9.21 psi, split ratio 200:1, split flow 198.1 mL/min, total flow 202.1 mL/min, gas saver on, saver flow 20.0 mL/min, gas type helium, capillary column model No. Agilent 19091S-433, HP-5MS 0.25 mm * 30 m * 0.25 μ m, max temp. 350°C, nominal diameter 250.0 μ m, constant flow, initial flow 1.0 mL/min, average velocity 37 cm/sec, outlet MSD, outlet pressure vacuum, thermal AUX 2 use: MSD transfer line heater, MS quad 150°C max 200°C, MS source 250°C max 300°C.

Preparation of KNO₃/ACE

ACE was prepared based on literature.⁷ Chicken eggshells waste was crushed into rough powder, then it was washed sequentially with water and acetone to remove inorganic and organic impurities. After that, it was dried in an oven at 120°C for 2 h. Dried eggshells waste was calcined at 900°C for 4 h to produce ACE as white solid. KNO₃/ACE was prepared underreported work with modification.¹⁵ Briefly, 10.0 g of the ACE was dried at 100°C for 3 h to eliminate absorbed water. It was then mixed with KNO₃ solution (3 g in 25 mL) in a glass flask and stirred for 15 min. The mixture was left overnight and then dried at 100°C for 4 h to evaporate residual water. It was ground and then calcined at 700°C for 5 h under air environment. Finally, the obtained catalyst was used in chalcone and pyrazole synthesis.

Synthesis of (*E*)-3-phenyl-5-styryl-1*H*-pyrazole

Synthesis of Chalcone

In a 10 mL round bottom flask, acetophenone,**1** (2.0 mmol), cinnamaldehyde,**2** (3.0 mmol) and ethanol (2.0 mL) were stirred in the presence of KNO₃/ACE catalyst for certain reaction time. The amount of catalyst and temperature were varied to afford optimized conditions. After that, hot ethanol was added into the reaction mixture, then it was filtered. The filtrate was cooled to get the solid crude product. Pure chalcone, (*2E*, *4E*)-1,5-diphenylpenta-2,4-dien-1-one (**3**) was isolated after recrystallization from hot ethanol. Spectral data of compound **3** is as follows: IR (KBr, 1/cm): 3060-3030 (C-H sp²), 1650 (C=O), 1600-1580 (C=C), 1460-1490 (phenyl ring). GC (min): 13.67. MS (m/z): 234 ([M]⁺), 215, 191, 157, 128, 105, 77, 51.

Synthesis of Pyrazole

In a 10 mL round bottom flask, compound **3** (1.7 mmol), hydrazine hydrate **4** (2.3 mmol) and ethanol (1.7 mL) were stirred in the presence of KNO₃/ACE catalyst. Variation of catalyst amount, time, and the temperature was performed to get optimized conditions. Hot ethanol was added into the reaction mixture, then it was filtered. The filtrate was cooled to get the solid crude product. Pure pyrazole, (*E*)-3-phenyl-5-styryl-1*H*-pyrazole (**5**) was obtained after recrystallization from hot ethanol. Spectral data of compound **5** is as follows: IR (KBr, 1/cm): 3360-3250 (N-H), 3050-3020 (C-H sp²), 1620-1600 (C=C), 1600-1520 (C=N), 1500-1430 (phenyl ring). GC (min): 15.891. MS (m/z): 246 [M]⁺, 245 ([M-H]⁺), 218, 189, 169, 142, 115, 77, 51.

RESULTS AND DISCUSSION

Catalyst Characterization

The first step in the execution of research purpose was the preparation of KNO₃/ACE. The catalyst was prepared by impregnation method of KNO₃ solution into ACE solid support. Fig.-2a shows the IR spectra of raw chicken eggshell, ACE, and KNO₃/ACE. In the IR spectrum of the chicken eggshell sample, a broad peak around 3500-3200 cm⁻¹ suggests the presence of -OH vibration from residual water in chicken eggshell.⁷ Peaks around 1380 cm⁻¹ and 825 cm⁻¹ indicate the existence of nitrate ions in KNO₃/ACE sample.¹⁵ The narrow band at 3650 cm⁻¹ is ascribed to the -OH stretching vibration. Meanwhile, appearing bands at 1450-1430 cm⁻¹ and 920 cm⁻¹ are associated with carbonate functionalities.¹⁶ These observation manifests that the catalyst surface was slightly hydroxylated and carbonated due to its contact with air

during analysis. EDAX spectrum reveals strong signals in the calcium, potassium, and oxygen regions and confirms the formation of KNO_3/ACE (Fig-2b).

Fig.-2: (a) IR Spectra, (b) EDAX Result, (c) XRD Pattern of ACE, (d) XRD Pattern of KNO_3/ACE , (e) SEM Image of ACE and (f) KNO_3/ACE

The crystalline nature of ACE and KNO_3/ACE samples was confirmed by X-ray diffraction analysis. XRD patterns of these samples are shown in Fig.-2(c) and 2(d). The peaks for ACE are subjected to mix phase of calcium oxide ($2\theta = 32.22^\circ, 37.40^\circ, 53.90^\circ, 64.25^\circ, 67.50^\circ, 79.10^\circ, 88.54^\circ$) and calcium hydroxide ($2\theta = 28.71^\circ, 34.10^\circ, 50.92^\circ, 54.23^\circ, 71.85^\circ$).¹⁷ After the impregnation process, KNO_3 characteristic ($2\theta = 29.45^\circ, 33.92^\circ, 46.65^\circ$) are found in KNO_3/ACE sample, indicating successful preparation of this material.¹⁵ The surface morphologies of the materials were observed using FESEM. Raw chicken eggshell has an irregular surface and heterogeneous particle size.¹⁶ After calcination, ACE has more homogeneous cubic structure and smaller particle size. After treatment with KNO_3 , the sample has a bigger particle size with cubic and irregular structures, conforms to XRD results.

Synthesis of (2E,4E)-1,5-diphenylpenta-2,4-dien-1-one (3) and (E)-3-phenyl-5-styryl-1H-pyrazole (5)

Aldol condensation reaction between acetophenone and cinnamaldehyde in the absence of KNO₃/ACE catalyst only gave 14% yield of compound **3** (Table-1 Entry 1). Meanwhile, the presence of 5 wt% and 15 wt% of the catalyst increases the desired product yield. As expected, this reaction works well since the addition of a base catalyst. It will deprotonate H- α in acetophenone to give nucleophile and then attack cinnamaldehyde. Incompletion of Aldol condensation reaction was observed when the reaction only conducted for 0.5 and 1 h (Table-1 Entry 6 and 7), with a yield of 31 and 49%, respectively. When the reaction time was prolonged up to 2 h, compound **3** was obtained in excellent yield (93%) at 60°C (Table-1 Entry 3). In the synthesis of compound **5**, a similar trend was observed to that Aldol condensation in producing compound **3**. Catalyst-free as well as short reaction time conditions (Table-1 Entry 1, 6, 7) in the reaction between compound **3** and hydrazine hydrate, **4** only produced pyrazole, **5** in low to medium yields. An excellent yield up to 97% were obtained within 2 h at 60°C in the presence of 15 wt% KNO₃/ACE catalyst.

Table-1: Optimization in the Synthesis of Compound 3 and 5

Entry	Catalyst (wt%)	T (°C)	Time (h)	Yield (%)	
				3	5
1	0	60	2	14	14
2	5	60	2	37	62
3	15	60	2	93	97
4	15	25	2	40	22
5	15	80	2	83	68
6	15	60	0.5	31	25
7	15	60	1	49	40

CONCLUSION

We have successfully prepared of KNO₃/ACE via impregnation method. It showed remarkable activity in the highly convenient synthesis of chalcone compound, (2E,4E)-1,5-diphenylpenta-2,4-dien-1-one (**3**) as well as pyrazole compound, (E)-3-phenyl-5-styryl-1H-pyrazole (**5**).

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