

A Highly Efficient Synthetic Method for the Preparation of 3,4-Dimethylbenzaldehyde from *o*-Xylene in Aqueous Media

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In this study, 3,4-dimethylbenzaldehyde was obtained in 82.3% total yield by oxidation of 3,4-dimethylbenzyl chloride with NaNO₃/AcOH catalyzed by PEG-600 in aqueous media. The starting material 3,4-dimethylbenzyl chloride was prepared by chloromethylation of *o*-xylene in CTAB micellar catalytic system. Compared with other synthetic methods, this method not only enhanced the yield, but also afforded an efficient work-up procedure. The structures of the products were confirmed by Elemental analysis, ¹H NMR and ¹³C NMR or compared with authentic samples.

Keywords: 3,4-Dimethylbenzaldehyde, Micellar catalysis, Phase transfer catalysis, Chloromethylation, Oxidation

INTRODUCTION

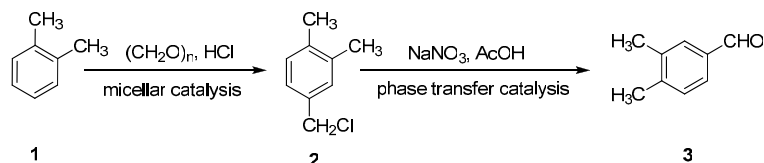
3,4-Dimethylbenzaldehyde (3,4-DBAL) is an important intermediate in the synthesis of a variety of fine or special chemicals such as pharmaceuticals, agrochemicals, dyes, flavors, fragrances, polymers, *etc.* [1-3]. Moreover, it is known as a key intermediate in the synthesis of bis-3,4-dimethyldibenzylidene sorbitol (3,4-DMDBS), which is a well-known nucleation transparent agent of polyolefin and the primary clarifying agent throughout the polyolefin market [4-7].

Generally, 3,4-dimethylbenzaldehyde is prepared by the Gatterman-Koch reaction *via* a direct carbonylation of *o*-xylene by the use of carbon monoxide and hydrogen chloride in the presence of AlCl₃ and Cu₂Cl₂ [8]. The reaction was subsequently expanded to include other catalysts such as HF-BF₃ [9-11], SbF₅-HF [12-14], HFO₃S-NbF₅ [15], CF₃SO₃H-NbBr₅ [16], *etc.* [17]. However, this procedure is invariably associated with certain limitations such as low yield, poor selectivity, long reaction time, environmental hazards,

special apparatus and drastic reaction conditions. Another procedure starting from 1,2,4-trimethylbenzene *via* an indirect selective electro-oxidation with metal complexes (*e.g.* Mn⁴⁺/Mn³⁺, Ce⁴⁺/Ce³⁺) as redox mediator system has also been reported [18-20], which, however, requires high reaction temperature, special equipment and troublesome work-up procedures. Consequently, there is a great need for an efficient and improved procedure for the synthesis of 3,4-dimethylbenzaldehyde.

Micellar catalysis is an effective means to accelerate organic reactions between oil phase and water phase reactants. In micellar catalysis system, lipophilic reactants are solubilized in the surfactant micelles, and the swelling micelles disperse in water phase containing hydrophilic reactants, so that the reaction interface area between oil phase reactants and water phase reactants is enlarged greatly. The interface magnifying effect as well as electrostatic interaction and concentrating effect result in dramatic increases of reaction rates [21,22]. In addition, micellar catalysis can make reaction conditions gentle, can effectively inhibit side reactions to occur, and can enhance the efficiency of organic

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Scheme 1. Two-step synthesis of 3,4-dimethylbenzaldehyde

synthesis. In our previous paper, we successfully applied surfactant micelles for the chloromethylation of 2-bromoethylbenzene and found that cetyltrimethylammonium bromide (CTAB) was the most active surfactant [23]. Phase transfer catalysis (PTC) is another versatile synthetic technique that has been widely applied to intensify otherwise slow heterogeneous reactions involving an organic substrate and an ionic reactant, either dissolved in water (liquid-liquid) or present in solid state (liquid-solid) [24]. Because PTC can decrease the reaction activation energy, accelerate reaction speed, make conditions convenient and inhibit side reaction to occur, it has been applied in various organic syntheses [25-27].

The objectives of the present work are to report an improved and economic procedure for the synthesis of 3,4-dimethylbenzaldehyde by oxidation of 3,4-dimethylbenzyl chloride with $\text{NaNO}_3/\text{AcOH}$ catalyzed by PEG-600 in aqueous media under PTC conditions. The starting material 3,4-dimethylbenzyl chloride was prepared by chloromethylation of *o*-xylene in CTAB micellar catalytic system (Scheme 1).

EXPERIMENTAL

Materials and Apparatus

Cetyltrimethylammonium bromide (CTAB), tetraethylammonium bromide (TEAB), tetrabutylammonium bromide (TBAB), tetradecyltrimethylammonium bromide (TTAB), dodecyltrimethylammonium bromide (DTAB), nonylphenol polyoxyethylene ether (NP-10), sodium dodecyl sulfonates (SDS) and (polyethylene glycol 600) PEG-600 all purchased from Aldrich Chemical Co., were of analytical grade and used without further purification. Other reagents purchased from Chinese companies were all of analytical or chemical grades. Distilled water was used for all the reactions. NMR spectra were recorded on a Bruker 400-MHz spectrometer using CDCl_3 as the solvent with tetramethylsilane (TMS) as an internal standard. High performance liquid chromatography

(HPLC) experiments were performed on a liquid chromatograph (Dionex Softron GmbH, USA), consisting of a pump (P680) and an ultraviolet-visible light detector (UVD) system (170U). The experiments were performed on Diacore C18 column, \varnothing 4.6 \times 150 mm. Elemental analyses were performed on a Vario EL III instrument (Elementar Analytensysteme GmbH, Germany).

Preparation of 3,4-Dimethylbenzyl Chloride (2)

A mixture of *o*-xylene (**1**, 10.6 g, 0.1 mol), CTAB (0.8 g, 2.3 mmol), 20% H_2SO_4 (60 ml) and AcOH (30 ml) was stirred in 250 ml round flask for 2 h at room temperature in order to solubilize *o*-xylene fully in the surfactant micelle solution. Then paraformaldehyde (3.15 g, 0.105 mol) was added and anhydrous hydrogen chloride gas was bubbled into the flask at the flow rate of 60 ml min^{-1} . The mixture was stirred for 4 additional hours at 45 $^\circ\text{C}$ and then cooled to room temperature. The reaction progress was monitored by TLC and HPLC. The residue obtained was extracted with methylene chloride (3 \times 20 ml). The combined organic phase was washed to neutral with 20% NaHCO_3 solution (3 \times 20 ml) and water (3 \times 20 ml), then dried over anhydrous Na_2SO_4 . The solvent was evaporated and then purified by column chromatography over silica gel (eluent:hexane/methylene chloride = 4.5/1) to give pure 3,4-dimethylbenzyl chloride (**2**, a colorless liquid, 13.8 g, yield 89.7%). ^1H NMR (400 MHz, CDCl_3): 2.29 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 4.56 (s, 2H, CH_2), 7.04-7.13 (m, 3H, Ar-H). ^{13}C NMR (100 MHz, CDCl_3): 21.9, 22.5, 46.8, 126.1, 129.7, 130.5, 135.8, 137.1, 137.5. Anal. Calcd. For $\text{C}_9\text{H}_{11}\text{Cl}$: C, 69.86%; H, 7.18%; Cl, 22.96%. Found: C, 69.90%; H, 7.17%; Cl, 22.93%.

Preparation of 3,4-Dimethylbenzaldehyde (3)

A mixture of 3,4-dimethylbenzyl chloride (15.4 g, 0.1 mol), PEG-600 (0.73 g, 1.2 mmol) and AcOH 10 ml was stirred in 250 ml round flask. Then a solution of NaNO_3 (9.35 g, 0.11

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mol) in H₂O (10 ml) was added dropwise while the mixture was being heated at reflux. The reaction progress was monitored by TLC and HPLC. The reaction was completed in 3 h, and then cooled to room temperature. The organic product was extracted with methylene chloride (3×30 ml). The combined organic phase was washed to neutral with 10% NaHCO₃ solution (3×20 ml) and water (3×20 ml), then dried over anhydrous Na₂SO₄. The solvent was removed and the residue was distilled under vacuum to give pure 3,4-dimethylbenzaldehyde (**3**, a colorless liquid, 12.3 g, 92%). b.p.: 83 °C/5 mmHg (lit. [20] b.p.: 233-235 °C). ¹H NMR (400 MHz, CDCl₃): 2.32 (s, 3H, CH₃), 2.34 (s, 3H, CH₃), 7.38-7.53 (m, 3H, Ar-H), 9.91 (s, H, -CHO). ¹³C NMR (100 MHz, CDCl₃): 17.9, 18.7, 127.2, 129.7, 130.2, 134.1, 136.9, 143.5, 194.2. Anal. Calcd. For C₉H₁₀O: C, 80.54%, H, 7.51%, O, 11.94%. Found: C, 80.56%, H, 7.51%, O, 11.92%.

RESULTS AND DISCUSSION

In a preliminary study, the chloromethylation was carried out in oil-water biphasic system in the presence and absence of CTAB. As shown in Fig. 1, in the absence of surfactant (CTAB), the chloromethylation reaction proceeded very slowly, the yield was less than 20% after 7 h, and the conversion was only 73%. Reaction performed with CTAB (its critical micelle concentration, CMC, in pure water at 25 °C is 9.20×10^{-4} M [28]) at a concentration of 2.57×10^{-2} M (18 CMC) proceeded very rapidly, the yield reached 89.7% in a shorter time (4 h), and the conversion increased to 94%. After that, the conversion and the yield leveled off.

Figure 2 shows the effects of CTAB concentration on the chloromethylation. When CTAB concentration was below CMC, the yield after 4 h was only 25.4%, the conversion was about 78%, and hardly varied with surfactant concentration. However, the yield and the conversion increased with an increase in the surfactant concentration higher than CMC, and leveled off after the surfactant concentration reached 18CMC. The experimental facts distinctly display the high efficiency of micellar catalysis system. When no surfactant is used or surfactant concentration is below CMC, the reaction system is a suspension (under stirring) with two phases, and the reaction rate is very slow. However, when surfactant interface between oil phase and water phase is very small, so

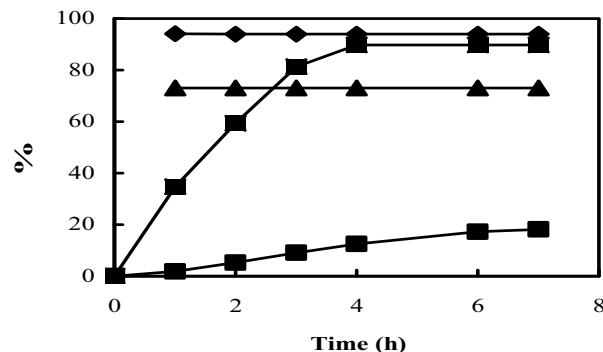


Fig. 1. Plot of the chloromethylation degree of *o*-xylene vs. time in presence and in absence of CTAB: (■) yield, no CTAB; (■) yield, CTAB; (▲) conversion, no CTAB; (◆) conversion, CTAB.

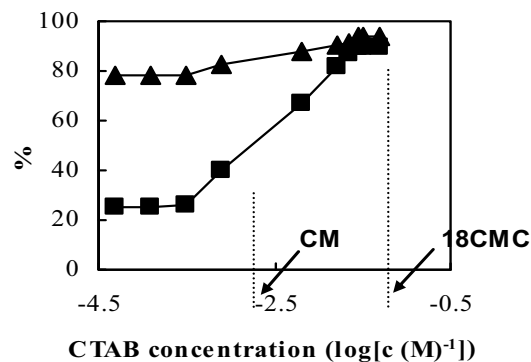


Fig. 2. Influences of concentration of CTAB on the chloromethylation: (▲) conversion, (■) yield.

micelles were formed, *o*-xylene was solubilized into the micelles, the interface area of oil phase/water phase was magnified suddenly and the rate of chloromethylation reaction occurring at the interface was accelerated abruptly, so the conversion showed a break point at CMC. Above CMC, the number of micelles increased with the increasing surfactant concentration, so the rate of chloromethylation reaction speeded up and a higher conversion was obtained. Further increase of the surfactant concentration induced micelles to expand, which in turn caused slow increase of oil/water interfacial area. Therefore, at high CTAB concentration, the rate of increase gradually slowed down and the conversion of

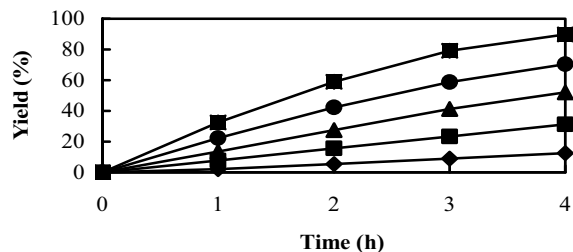


Fig. 3. Influences of different types of surfactants on the chloromethylation: (◆) no surfactant, (■) SDS, (▲) NP-10, (●) TTAB, (■) CTAB.

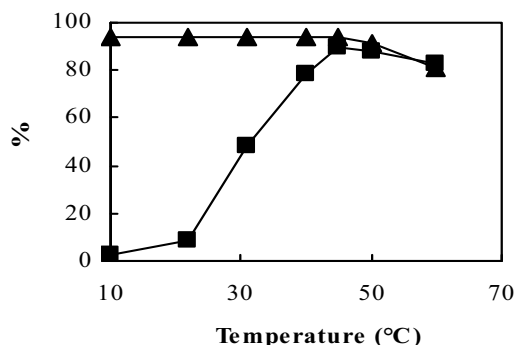


Fig. 4. Influences of temperature on the chloromethylation: (▲) conversion, (■) yield.

o-xylene did not change significantly. Besides CTAB, we also tried to use other types of surfactants such as SDS, NP-10 and TTAB as catalysts in the reaction. As shown in Fig. 3, it was observed that the yield was highest for the CTAB system, higher for the TTAB, lower for the NP-10 and much lower for the SDS. The different catalytic abilities of surfactants could be attributed to their different solubilization abilities. CTAB, TTAB, NP-10 and SDS have various CMC, the lower CMC leads to more micelles at the same concentration causing more *o*-xylene to be solubilized into micelles and greater encounter probability between *o*-xylene and reactive species. Thus, the observed rate and yield of the reaction is CTAB > TTAB > NP-10 > SDS.

Figure 4 shows the effects of reaction temperature on the chloromethylation. The catalytic activity increased with the

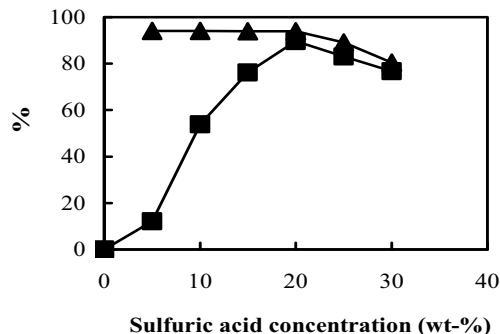


Fig. 5. Influences of concentration of sulfuric acid on the chloromethylation: (▲) conversion, (■) yield.

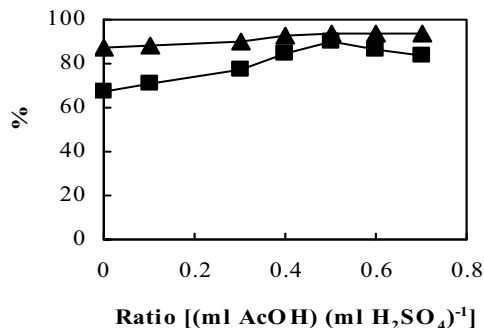


Fig. 6. Influences of volume ratio of acetic acid and sulfuric acid on the chloromethylation: (▲) conversion, (■) yield.

temperature to 45 °C; however, the yield decreased with further increase of the temperature. The yield reached maximum at 45 °C under which the conversion could be kept at the highest. These findings show that a moderate temperature such as 45 °C enhances the chloromethylation.

The effects of the concentration of sulfuric acid at 45 °C are shown in Fig. 5. No reaction occurred in the absence of sulfuric acid, and an increase in its concentration enhanced the catalysis. The yield reached maximum at the 20% sulfuric acid; however, it decreased with further increase of its concentration. Fig. 6 shows the effects of the volume ratio of AcOH to 20% H₂SO₄ at 45 °C. In the absence of acetic acid, the chloromethylation reaction proceeded poorly, only 67.7%

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Table 1. PEG-600 Catalyzed Oxidation of 3,4-Dimethylbenzyl Chloride with NaNO₃ in Aqueous Media^a

Entry	NaNO ₃ (mol)	PEG-600 (mmol)	AcOH (ml)	Time (h)	Yield (%) ^b
1	0.11	-	-	10	17
2	0.11	1.2	-	10	53
3	0.11	1.3	-	10	53
4	0.11	1.2	10	3	92
5	0.11	1.3	10	3	92
6	0.11	-	10	3	67
7	0.11	1.2	12	3	92
8	0.11	1.2	15	3	92

^aReaction conditions: 3,4-dimethylbenzyl chloride (0.1 mol), NaNO₃ (0.11 mol), H₂O (10 ml), reflux.

^bIsolated yield.

yield was obtained and the conversion decreased to 87%. An increase in the amount of acetic acid (*i.e.* increase in volume ratio) enhanced the catalysis, the yield reached maximum at 0.5 of the ratio. However, the yield decreased slowly with further increase in the amount of acetic acid although the conversion seemed to be stable. Such a pattern of behavior shown by acetic acid may be due to the enhancement of solubility to prompt the contact of paraformaldehyde with *o*-xylene *via* solvation. Nevertheless, further studies are required for an adequate clarification of the mechanism.

3,4-Dimethylbenzyl chloride was initially oxidized using sodium nitrate (NaNO₃) as oxidant in the presence of PEG-600 and AcOH at reflux and the yield was 92% (Table 1, entry 4) after 3 h. Other nitrates such as potassium nitrate (KNO₃), calcium nitrate (Ca(NO₃)₂) and sodium nitrite (NaNO₂), are also excellent oxidants for the oxidation of 3,4-dimethylbenzyl chloride with yields over 85% under the same reaction conditions. However, the yield was decreased in the order: NaNO₃ > KNO₃ > NaNO₂ > Ca(NO₃)₂. Thus, based on the results obtained, the best oxidant was NaNO₃. Typical results are shown in Fig. 7.

The oxidation of 3,4-dimethylbenzyl chloride (**2**) was then carried out by vigorously stirring the two-phase system (**2** and 10 ml H₂O) at reflux temperature with NaNO₃ (0.11 mol). The yield was only 17% (Table 1, entry 1) after 10 h. Using PEG-600 (1.2 mmol) as phase-transfer catalyst, under the same conditions, **3** was obtained in a higher yield 53% (Table 1, entry 2). The colors of the reaction mixture varied from

colorless to yellow and a red-brown gas was observed as the reaction proceeded. After the addition of AcOH 10 ml to the catalytic system, the yield increased to 92% (Table 1, entry 4) within 3 h, which shows that AcOH can promote the oxidation reaction to some extent. Further addition of the amount of AcOH, under the same conditions, did not enhance the yield significantly (Table 1, entries 7 and 8). The results are shown in Table 1.

Phase-transfer catalyst and AcOH must coexist in this oxidation system (Table 1, entries 3-8). The yield was raised to 92% in a shorter period (3 h) if both PEG-600 and AcOH were present in the reaction system (Table 1, entry 4). The PEG-600 was also crucial for achieving high yields because the yield decreased to 67% in the absence of PEG-600 (Table 1, entry 6) but increased to 90% in its presence. Using 1.3 mmol of PEG-600, under the same conditions, did not enhance the yield significantly (Table 1, entries 3 and 5). Therefore, the optimal reaction conditions were observed in entry 4 in Table 1. Besides PEG-600, we also used cetyltrimethylammonium bromide (CTAB), tetraethylammonium bromide (TEAB), tetrabutylammonium bromide (TBAB), dodecyltrimethylammonium bromide (DTAB) and sodium dodecyl sulfonates (SDS) as phase-transfer catalysts and the yields were merely 82%, 70%, 79%, 73% and 77%, respectively (Table 2). Therefore, the best phase transfer catalyst was PEG-600.

Figure 8 shows the effects of the amount of sodium nitrate on the oxidation. No reaction occurred in the absence of NaNO₃, and the increase in the amount of NaNO₃ (*i.e.* the

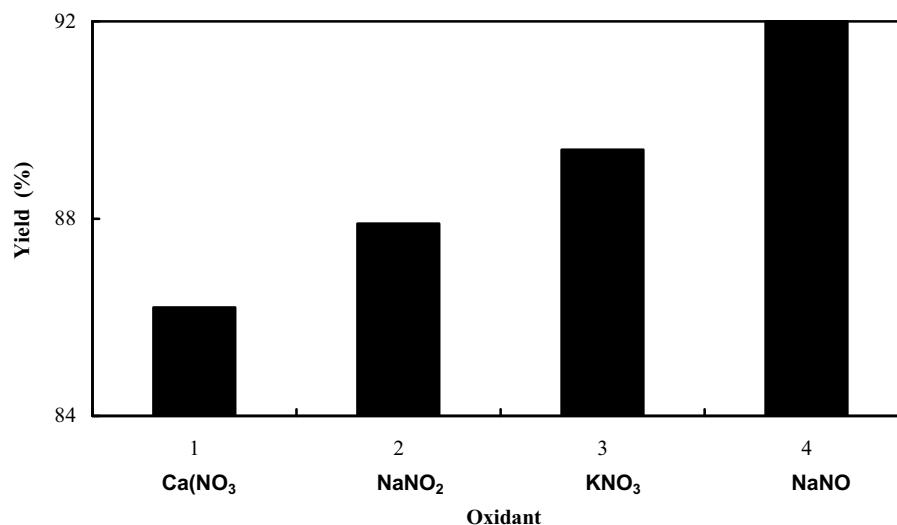


Fig. 7. Influences of type of nitrates on the oxidation.

Table 2. PTC Catalyzed Oxidation of 3,4-Dimethylbenzyl Chloride with NaNO₃/AcOH in Aqueous Media^a

Phase transfer catalyst	Time (h)	Yield (%) ^b
PEG-600	3	92
CTAB	5	82
TEAB	6	70
TBAB	4	79
DTAB	7	73
SDS	3	77

^aReaction conditions: 3,4-dimethylbenzyl chloride (0.1 mol), NaNO₃ (0.11 mol), PTC (1.2 mmol), AcOH (10 ml), H₂O (10 ml), reflux. ^bIsolated yield.

ratio of NaNO₃ to 2) enhanced the yield of the reaction and the yield reached maximum at 1.1 of the ratio. However, further addition of NaNO₃ resulted in the decrease of the yield, which is due to the formation of 3,4-dimethylbenzoic acid, which was confirmed by HPLC.

CONCLUSIONS

A facile and efficient procedure for the synthesis of

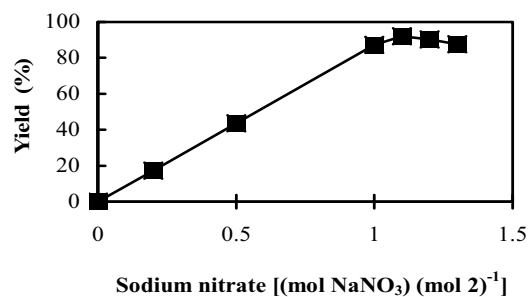


Fig. 8. Influences of amount of sodium nitrate on the oxidation.

3,4-dimethylbenzaldehyde was developed in this research, by CTAB micellar-catalyzed chloromethylation of *o*-xylene as the starting material and the subsequent oxidation with NaNO₃/AcOH catalyzed by PEG-600 in aqueous media.

One of the notable aspects of our work was that the CTAB micellar-catalyzed chloromethylation of *o*-xylene was carried out successfully. The conversion for 2 in the micellar solutions was remarkably improved to 94% which provided a striking contrast to other procedures catalyzed by Lewis acids, ionic liquids or rare-earth metal triflates whose conversion for 2 was usually 72~80% [29-34], which demonstrated a higher yield

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for the chloromethylation of *o*-xylene. Another noteworthy point in our study was that we managed to develop a novel and efficient procedure for the preparation of **3** from **2** *via* an oxidation with sodium nitrate and acetic acid catalyzed by PEG-600 in aqueous media under PTC conditions. Compared with other oxidation procedures [35-42], this procedure not only enhanced the yield, but also had the merits of being economical, convenient and eco-safe. The good yields obtained in all cases, makes this oxidation procedure very attractive.

In conclusion, we have developed an excellent procedure for the preparation of 3,4-dimethylbenzaldehyde in two steps in an 82.5% total yield. Judging from the conditions employed, this method has great prospects for industrial applications.

ACKNOWLEDGEMENTS

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