Improved Preparation of 3,3′,4,4′-tetramethyldiphenylethane by Self Coupling Reaciton in Aqueous Media

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In this article, 3,3′,4,4′-tetramethyldiphenylethane was obtained in 86.5% total yield by self coupling reaction of 3,4-dimethylbenzyl chloride catalyzed by Cu/Cu_2Cl_2/PEG-600 and promoted by iron in aqueous media and the starting material 3,4-dimethylbenzyl chloride was prepared by chloromethylation of o-xylene in CTAB micellar catalytic system. Compared to other synthetic methods, the improved method not only enhanced the yield, but also made the operating units easy workup. The mechanisms of the chloromethylation and the self coupling were proposed. The structures of the products were confirmed by Elemental analysis, ^{1}H NMR and ^{13}C NMR or compared with authentic samples.

Keywords: 3,3′,4,4′-tetramethyldiphenylethane; Micellar catalysis; Phase transfer catalysis; Chloromethylation; Self coupling reaciton.

INTRODUCTION

3,3′,4,4′-tetramethyldiphenylethane (TMDE) is an important intermediate in the synthesis of a variety of fine or special chemicals such as dyes, flavors, polymers, etc. Moreover, it is known as an important thermosensitive paper sensitizer and has been becoming the primary sensitizer throughout the market because of its excellent properties such as damp-resistant, oil-resistant, light-resistant, etc.[1-4]

Generally, 3,3′,4,4′-tetramethyldiphenylethane is prepared by Friedel-Crafts alkylation reaction between o-xylene and 1,2-dichloroethane.[5-8] However, this procedure is invariably associated with certain limitations such as low yield, poor selectivity, special anhydrous condition operation and the use of virulent 1,2-dichloroethane. Another procedure starting from o-xylene and acetaldehyde via a isomerization reaction has been reported recently,[9] which, however, requires high reaction temperature, expensive and special apparatus and troublesome work-up procedures. Consequently, there is a great desire to develop an efficient and improved procedure for the synthesis of 3,3′,4,4′-tetramethyldiphenylethane.

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.[10,11] In addition, micellar catalysis can make reaction conditions gentle, can effectively avoid side reactions to occur, and enhance the efficiency of organic synthesis. In our previous paper, we had successfully applied surfactant micelles for the chloromethylation of 2-bromoethylbenzene and found that cetyltrimethylammonium bromide (CTAB) was the most active surfactant.[12] Phase transfer catalysis (PTC) is an 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).[13] Because PTC can decrease the reaction activation energy, accelerate reaction speed, make conditions gentle and avoid side reaction to occur, it has been applied in various organic synthesis.[14-16] The reductive coupling of organic halides with active metals is an important method for the formation of carbon-carbon bonds and a number of these methods have been developed to obtain diphenylethanes from benzyl halogenation.[17-21]

The objectives of the present work are to report an improved and economic procedure for synthesis of 3,3′,4,4′-

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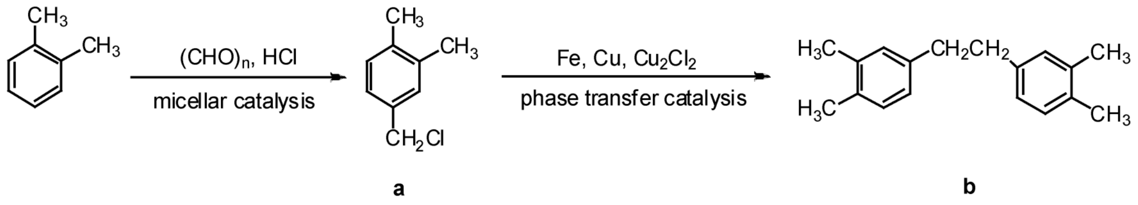
Scheme I Two-step synthesis of 3,3′,4,4′-tetramethyldiphenylethane



tetramethyldiphenylethane by self coupling reaction of 3,4-dimethylbenzyl chloride catalyzed by Cu/Cu_2Cl_2/PEG-600 and promoted by iron in aqueous media under PTC conditions and the starting material 3,4-dimethylbenzyl chloride was prepared by chloromethylation of o-xylene in CTAB micellar catalytic system (Scheme I).

RESULTS AND DISCUSSION

Preparation of 3,4-dimethylbenzyl chloride (a)

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} mol/L [22]) at a concentration of 2.57×10^{-2} mol·L^{-1} (18 CMC) proceeded very rapidly and the yield reached 89.7% in a shorter time (4 h), and the conversion was increased to 94%. After that, the conversion and the yield became level off.

Fig. 2 shows the influences 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 reaching to 18CMC. The experimental facts display distinctly the advantage of high efficiency of micellar catalysis system. When no surfactant was used or surfactant concentration was below CMC, the reaction system is a suspension (under stirring) with two phases, and the interface between oil phase and water phase is very small, so the reaction rate is very slow. However, when surfactant micelles were formed, o-xylene was solubilized into the micelles, the interface area of oil phase/water phasewas magnified suddenly and the rate of chloromethylation reaction occurred at the interface was accelerated abruptly, so the conversion showed a break point at CMC. Above CMC, the

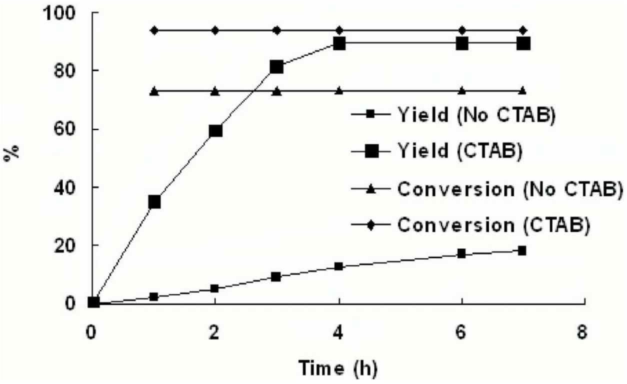


Fig. 1. Plot of the chloromethylation degree of o-xylene vs. time in presence and in absence of CTAB. Reaction conditions: O-xylene, 10.6 g (0.1 mol); paraformaldehyde, 3.15 g (0.105 mol); 20% H_2SO_4, 60 mL; AcOH, 30 mL; anhydrous hydrogen chloride gas, 60 mL/min; concentrations of CTAB, 18-fold CMC; temperature, 45 °C.

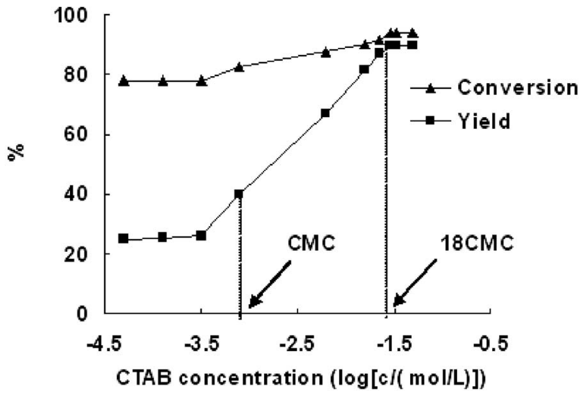


Fig. 2. Influences of concentration of CTAB on the chloromethylation. Reaction conditions: O-xylene, 10.6 g (0.1 mol); paraformaldehyde, 3.15 g (0.105 mol); 20% H_2SO_4, 60 mL; AcOH, 30 mL; anhydrous hydrogen chloride gas, 60 mL/min; temperature, 45 °C; time, 4 h.

number of micelles increased with the increasing surfactant concentration, so the rate of chloromethylation reaction speeded up and a higher conversion can be obtained. The further increase of the surfactant concentration could induce micelles to expand, which could cause slow increase of oil/water interfacial area. Therefore, at high CTAB concentration, the rate increase became gradually slow and the conversion of o-xylene did not change significantly. Besides CTAB, we also tried to use another 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 should 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.

Fig. 4 shows the influences of reaction temperature on the chloromethylation. The catalytic activity increased with the temperature to 45 °C, however, the yield was decreased with the further increase of the temperature. The yield reached maximum at 45 °C, under such temperature the conversion can be kept at the highest. These results show that the moderate temperature, such as 45 °C enhanced the chloromethylation.

The influences of the concentration of sulfuric acid at 45 °C are shown in Fig. 5. No reaction occurred in the absence of sulfuric acid, and the increase in the concentration of sulfuric acid enhanced the catalysis. The yield reached maximum at the 20% sulfuric acid, however, it decreased with further increase of the concentration of sulfuric acid. Fig. 6 shows the influences of the volume ratio of AcOH and 20% H_2SO_4 at 45 °C. In the absence of acetic acid, the chloromethylation reaction proceeded badly, only 67.7% yield was obtained and the conversion decreased to 87%, and the increase in the amount of acetic acid (i.e. the volume ratio increased) enhanced the catalysis, the yield

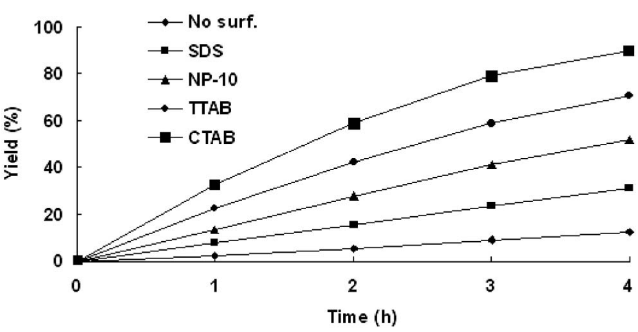


Fig. 3. Influences of different types of surfactants on the chloromethylation. Reaction conditions: O-xylene, 10.6 g (0.1 mol); paraformaldehyde, 3.15 g (0.105 mol); 20% H_2SO_4, 60 mL; AcOH, 30 mL; anhydrous hydrogen chloride gas, 60 mL/min; concentrations of surfactants: 18-fold; temperature, 45 °C; time, 4 h.

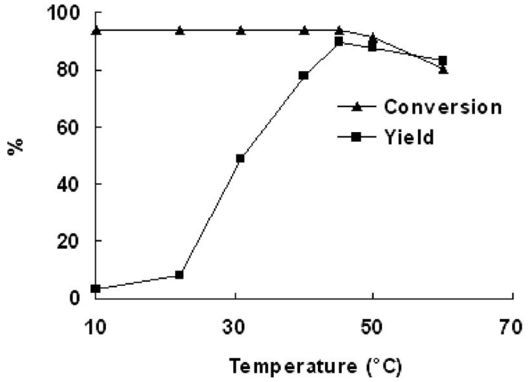


Fig. 4. Influences of temperature on the chloromethylation. Reaction conditions: O-xylene, 10.6 g (0.1 mol); paraformaldehyde, 3.15 g (0.105 mol); 20% H_2SO_4, 60 mL; AcOH, 30 mL; anhydrous hydrogen chloride gas, 60 mL/min; concentrations of CTAB: 18-fold CMC; time, 4 h.

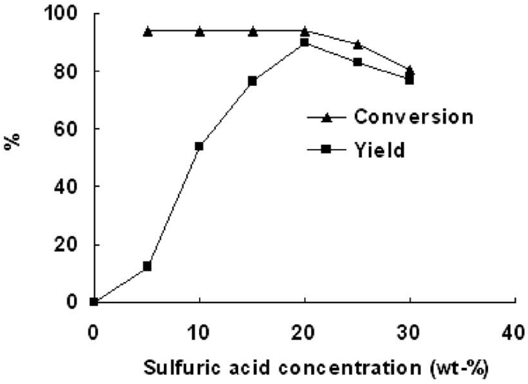


Fig. 5. Influences of concentration of sulfuric acid on the chloromethylation. Reaction conditions: O-xylene, 10.6 g (0.1 mol); paraformaldehyde, 3.15 g (0.105 mol); AcOH, 30 mL; anhydrous hydrogen chloride gas, 60 mL/min; concentrations of CTAB: 18-fold CMC; temperature, 45 °C; time, 4 h.

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 seem stable. One possibility for the role of acetic acid may be due to the enhancement of solubility to prompt the contact of paraformaldehyde with o-xylene by the solvation, however, further studies are necessary for the clarification of the mechanism.

Preparation of 3,3′,4,4′-tetramethyldiphenylethane (b)

In the process of reductive coupling, 3,4-dimethylbenzyl chloride was initially carried out by vigorously stirring the two phase system (**a** and 100 mL H_2O) at 80 °C in the absence of phase transfer catalyst (PTC) and the yield was only 90% (Table 1, entry 1) after 2 h. Using PEG-600 (1.2 mmol) as phase transfer catalyst under the same conditions, **b** was obtained in a higher yield 96.5% (Table 1, entry 2). Besides PEG-600, we also tried to use CTAB, TTAB, TBAB and TEAB as phase transfer catalysts in this coupling reaciton. However, the yields were 94.5%, 93%, 92.7% and 92.2%, respectively (Table 1, entries 3-6). Thus, based on the results obtained, the best phase transfer catalyst is PEG-600.

Table 2 shows the influences of Cu and Cu_2Cl_2 on the reaction. In the absence of Cu and Cu_2Cl_2, the reaction proceeded very slowly, only 17.5% yield was obtained (Table 2, entry 1) after 4 h, and the addition of Cu (0.15 g) or Cu_2Cl_2 (0.2 g) to it resulted in the increase of the yield, **b** could be obtained in a higher yield 45.2% (Table 2, entry 2) or 43.0% (Table 2, entry 6) under the same conditions. The yield can be greatly improved when the combined use of Cu and Cu_2Cl_2, and it reached maximum (96.5%) in a shorter time (2 h) when the addition of Cu (0.15 g) and Cu_2Cl_2 (0.2 g) (Table 2, entry 3). However, further addition the amount of Cu (Table 2, entries 7, 8) or Cu_2Cl_2 (Table 2, entries 4, 5), under the same conditions, the yield was not enhanced significantly. Therefore, the optimal reaction conditions were observed in Table 2, entry 3.

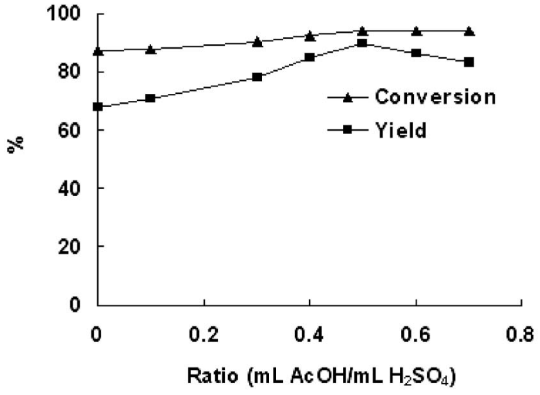


Fig. 6. Influences of volume ratio of acetic acid and sulfuric acid on the chloromethylation. Reaction conditions: O-xylene, 10.6 g (0.1 mol); paraformaldehyde, 3.15 g (0.105 mol); anhydrous hydrogen chloride gas, 60 mL/min; concentrations of CTAB: 18-fold CMC; temperature: 45 °C; time: 4 h.

Table 1. PTC catalyzed self coupling of 3,4-dimethylbenzyl chloride with Fe and Cu/Cu_2Cl_2 in aqueous media[a]

Entry	Phase transfer catalyst	Amount (mmol)	Yield (%)[b]
1			90.0
2	PEG-600	1.2	96.5
3	CTAB	1.2	94.5
4	TTAB	1.2	93.0
5	TBAB	1.2	92.7
6	TEAB	1.2	92.2

[a] Reaction conditions: 3,4-dimethylbenzyl chloride, 15.4 g (0.1 mol); Fe, 3.37 g (0.06 mol); Cu_2Cl_2, 0.2 g (0.001 mol); Cu, 0.15 g (0.0024 mol); H_2O, 100 mL; temperature, 80 °C; time: 2 h.

[b] Isolated yield.

Table 2. Cu/Cu_2Cl_2 catalyzed self coupling of 3,4-dimethylbenzyl chloride with Fe and PEG-600 in aqueous media[a]

Entry	Cu (g)	Cu_2Cl_2 (g)	Yield (%)[b]
1			17.5
2	0.15		45.2
3	0.15	0.2	96.5
4	0.15	0.25	96.6
5	0.15	0.3	96.7
6		0.2	43.0
7	0.2	0.2	96.5
8	0.25	0.2	96.6

[a] Reaction conditions: 3,4-dimethylbenzyl chloride, 15.4 g (0.1 mol); Fe, 3.37 g (0.06 mol); PEG-600, 0.73 g (1.2 mmol); H_2O, 100 mL; temperature, 80 °C; time: 2 h.

[b] Isolated yield.

The influences of iron powder on the reaction are shown in Table 3. In this reaciton, the role of iron powder is as an inevitable reductant, we found its physical and chemical forms have great influences on the reaction. Using soft gray iron powder (0.06 mol) as reductant, **b** could be obtained in a high yield 96.5% (Table 3, entry 5), however, when we use wrought iron powder and steel powder as reductant, under the same conditions, the yields were

Table 3. Fe reduced self coupling of 3,4-dimethylbenzyl chloride catalyzed by Cu/Cu_2Cl_2/PEG-600 in aqueous media[a]

Entry	Reductant (Fe)	Ratio (mol Fe/mol **a**)	Yield (%)[b]
1	Wrought Iron Powder	0.6	74.0
2	Steel Powder	0.6	78.3
3	Soft Gray Iron Powder	0.4	65.0
4	Soft Gray Iron Powder	0.5	87.5
5	Soft Gray Iron Powder	0.6	96.5
6	Soft Gray Iron Powder	0.65	96.6
7	Soft Gray Iron Powder	0.7	96.7

[a] Reaction conditions: 3,4-dimethylbenzyl chloride, 15.4 g (0.1 mol); Cu_2Cl_2, 0.2 g (0.001 mol); Cu, 0.15 g (0.0024 mol); PEG-600, 0.73 g (1.2 mmol); H_2O, 100 mL; temperature, 80 °C; time: 2 h.

[b] Isolated yield.

merely 74.0% and 78.3%, respectively (Table 3, entries 1, 2). From these results, it was observed that the best reductant is soft gray iron powder. Also, the amount of iron powder has great influences on the reaction. The yield increased with the ratio of Fe and **a** (i.e. the amount of Fe increased) and reached maximum at 0.6 of the ratio (Table 3, entry 5), and further addition the amount of Fe, under the same conditions, the yield was not enhanced significantly (Table 3, entries 6, 7).

Fig. 7 shows the influences of reaction temperature on the yield. The catalytic activity increased with the increase in the temperature to 80 °C, at lower temperatures such as 50 °C, the reaction proceeded slowly and only 36% yield was obtained. The yield reached the maximum at 80 °C and then, decreased when at higher temperature. The influences of the reaction time are shown in Fig. 8. The yield increased with the increase of the reaction time, and reached maximum at 2 h.

Mechanism of reaction

It can be observed that the reaction for the formation of 3,3′,4,4′-tetramethyldiphenylethane consists of multiple reaction steps, and they can be divided basically into two types of reactions: chloromethylation of o-xylene and reductive coupling of 3,4-dimethylbenzyl chloride. Despite the absence of any supporting evidence and the detailed pathways is not clear, we envision a plausible mechanism that explains the peculiar effectiveness of the excellent procedure, key steps are proposed on the basis of the related literatures,[12,23-26] our observations and obtained results (Scheme II). Accordingly, CTAB micellar-catalyzed chloromethylation of o-xylene proceed by a similar mechanism as shown in a reported literature[12] and possibly consists of four steps: the electrophilic substitution reaction (steps 1 and 2) to form 3,4-dimethylphenyl methanol (**II**) and then the nucleophilic substitution reaction (steps 3 and 4) to form 3,4-dimethylbenzyl chloride (**V**). The self coupling of 3,4-dimethylbenzyl chloride possibly consists of five steps (steps 5-9).[23-26] Initially, Cu_2Cl_2 act as a source of Cu^+, **V** reacts with Cu^+ to form transition state (**VI**) and then, the **VI** eliminated Cu^+ to yield benzyl free radical (**VII**), then **VII** reacts with each other through self coupling to from the

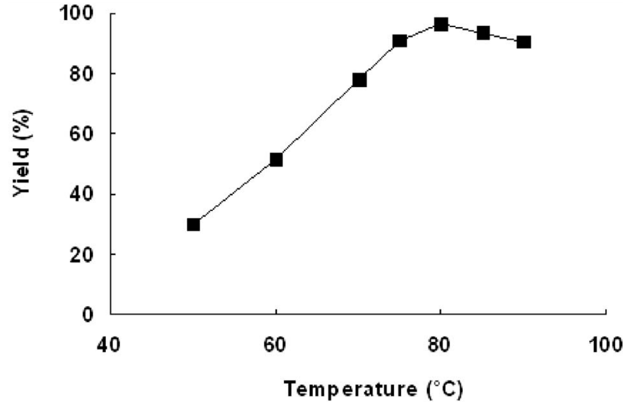


Fig. 7. Influences of temperature on the coupling. Reaction conditions: 3,4-dimethylbenzyl chloride, 15.4 g (0.1 mol); Fe, 3.37 g (0.06 mol); Cu_2Cl_2, 0.2 g (0.001 mol); Cu, 0.15 g (0.0024 mol); PEG-600, 0.73 g (1.2 mmol); H_2O, 100 mL; time: 2 h.

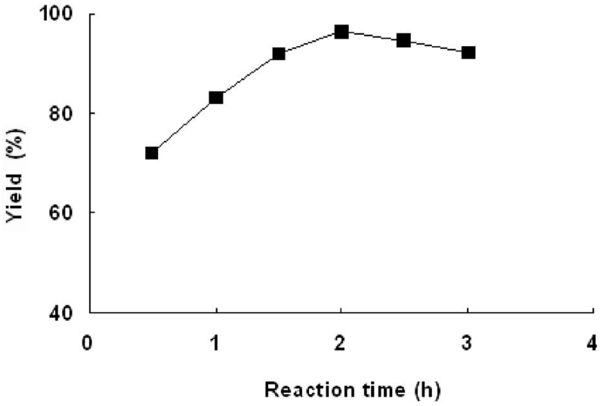
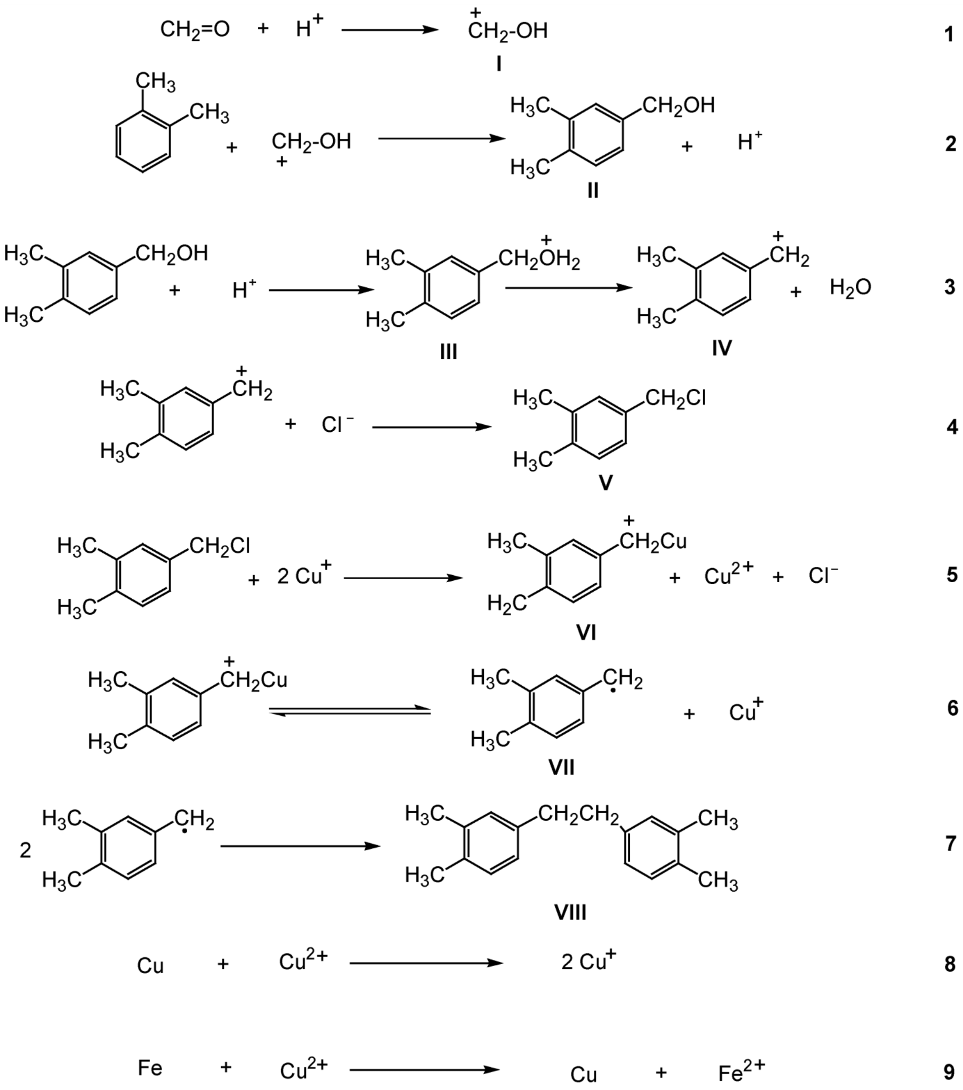


Fig. 8. Influences of reaction time on the coupling. Reaction conditions: 3,4-dimethylbenzyl chloride, 15.4 g (0.1 mol); Fe, 3.37 g (0.06 mol); Cu_2Cl_2, 0.2 g (0.001 mol); Cu, 0.15 g (0.0024 mol); PEG-600, 0.73 g (1.2 mmol); H_2O, 100 mL; temperature, 80 °C.

Scheme II A possible reaction mechanism



desired product **VIII**. The self coupling of complex **VII** occurs continuously via the oxidation-reduction reactions (steps 8 and 9) and the reduction of Cu^{2+} by iron (step 9) likely initiates the catalytic reaction.

CONCLUSION

A facile and improved procedure for the synthesis of 3,3′,4,4′-tetramethyldiphenylethane has been developed in this paper, which is prepared by CTAB micellar-catalyzed chloromethylation with o-xylene as starting material for the first time with subsequent self coupling reaciton catalyzed by Cu/Cu_2Cl_2/PEG-600 and promoted by iron in aqueous media.

One of the noticeable points in our paper was that the CTAB micellar-catalyzed chloromethylation of o-xylene was carried out successfully. The conversion for **a** in the micellar solutions could be remarkably improved to 94% contrast to other procedures catalyzed by lewis acids, ionic liquids or rare-earth metal triflates whose conversion for **a** was usually 72~80%,[27-32] which demonstrated the high efficiency for the chloromethylation of o-xylene. Another glittery point in our paper was that we have developed a new and efficient procedure for the preparation of **b** from **a** via a self coupling catalyzed by Cu/Cu_2Cl_2/PEG-600 and promoted by iron in aqueous media under PTC conditions. The good yields obtained in all cases, makes this self coupling procedure very attractive.

In conclusion, we have developed an excellent procedure for the preparation of 3,3′,4,4′-tetramethyldiphenylethane in two steps in a 86.5% total yield. Judging from the conditions employed, this method showed has great prospects in industrial applications.

EXPERIMENTAL

Materials and apparatus

Cetyltrimethylammonium bromide (CTAB), tetraethylammonium bromide (TEAB), tetrabutylammonium bromide (TBAB), tetradecyltrimethylammonium bromide (TTAB), nonylphenol polyoxyethylene ether (NP-10), sodium dodecyl sulfonates (SDS) and (polyethylene glycol 600) PEG-600 purchased from Aldrich Chemical Co., Inc. 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, America), consisting of a pump (P680) and ultraviolet-visible light detector (UVD) system (170U). The experiments were performed on Diacovery C18 column, ∅ 4.6 × 150 mm. Elemental analysis were performed on a Vario EL III instrument (Elmentar Anlalysensy Teme GmbH, Germany).

Preparation of 3,4-dimethylbenzyl chloride (a)

A mixture of o-xylene (10.6 g, 0.1 mol), CTAB (0.8 g, 2.3 mmol), 20% H_2SO_4 60 mL and HAc 30 mL was stirred in 250 mL round flask for 2 h at room temperature in order to solubilize fully o-xylene 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. The mixture was stirred for 4 additional hours at 45 °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 × 20 mL). The combined organic phases was washed to neutral with 20% $NaHCO_3$ solution (3 × 20 mL) and water (3 × 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-dimethylbenzylchloride (**a**, a colorless liquid, 13.8 g, yield 89.7%). ^1H NMR (400 MHz, δ in ppm from TMS in $CDCl_3$): 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 (400 MHz, δ in ppm from TMS in $CDCl_3$): 21.9, 22.5, 46.8, 126.1, 129.7, 130.5, 135.8, 137.1, 137.5. Anal. Calcd for $C_9H_{11}Cl$: C, 69.86; H, 7.18; Cl, 22.96. Found: C, 69.90; H, 7.17; Cl, 22.93.

Preparation of 3,3′,4,4′-tetramethyldiphenylethane (b)

A mixture of Fe (3.37 g, 0.06 mol), Cu_2Cl_2 (0.2 g, 0.001 mol), Cu (0.15 g, 0.0024 mol), PEG-600 (0.73 g, 1.2 mmol) and H_2O 100 mL was stirred in 250 mL round flask. Then 3,4-dimethylbenzyl chloride (15.4 g, 0.1 mol) was added dropwise when the temperature reached to 80 °C. After that the mixture was stirred for 2 additional hours at 80 °C, the reaction progress was monitored by TLC and HPLC, then cooled to room temperature and filtered, the filtrate obtained was extracted with dimethylbenzene (3 × 10 mL), the residue was dissolved with ethanol and dimethylbenzene and filtered. The combined organic phases was dried over anhydrous Na_2SO_4. The solvent was removed and the crude product was recrystallized from ethanol and dimethylbenzene afforded a white powder (**b**, 11.5 g, yield 96.5%, m.p. 87-89 °C, lit.[8] m.p. 88-90 °C). ^1H NMR (400 MHz, δ in ppm from TMS in $CDCl_3$): 2.55 (s, 3H, CH_3), 2.83 (s, 2H, CH_2), 6.94-7.08 (m, 3H, Ar-H), ^{13}C NMR (400 MHz, δ in ppm from TMS in $CDC1_3$): 22.1, 22.8, 38.6, 125.7, 130.2, 135.1, 135.7, 137.4, 140.1. Anal. Calcd for C_8H_{22}: C, 90.68; H, 9.32. Found: C, 90.70; H, 9.30.

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