

## An Efficient Synthetic Method for 3,3',4,4'-Biphenyltetracarboxylic Anhydride

Yu Lin Hu, Ming Lu,\* Xiang Liu, and Peng Cheng Wang

Chemical Engineering College, Nanjing University of Science and Technology, Nanjing 210094, P. R. China

\*E-mail: luming1963@163.com

Received May 18, 2009, Accepted July 30, 2009

**Key Words:** 3,3',4,4'-Biphenyltetracarboxylic acid dianhydride. Ionic liquid. Chloromethylation. Oxidation. Dehydration

3,3',4,4'-Biphenyltetracarboxylic anhydride (BPDA) has been extensively used as an important monomer in the preparation of a variety of thermoplastics such as polyesters, polycarbonates, polyethers, epoxy resins, etc. Moreover, it is also useful in the preparation of high performance polyimides that have been widely employed in many fields such as aerospace, spaceflight, mechanical engineering, chemical engineering, microelectron and so on because of their excellent thermal, oxidative stability and excellent mechanical properties.<sup>1-5</sup>

Up to now, many publications in the open literature have been found in synthesis of 3,3',4,4'-biphenyltetracarboxylic anhydride (BPDA), and the classical method for such a synthesis constitutes the reductive coupling reaction, which starts from 4-halogeno-*o*-phthalic acid salt<sup>6,7</sup> or 4-halogeno-*o*-phthalic anhydride<sup>8,9</sup> or 4-halogeno-*o*-phthalic acid ester,<sup>10,11</sup> through a dehalogenation-dimerization reaction in the presence of palladium carbon. The oxidative coupling reaction of dimethyl phthalate (DMP) under oxygen pressure in the presence of palladium acetate is another well-known method.<sup>12,13</sup> Other notable methods to accomplish this include the coupling reaction of terephthaloyl chloride,<sup>14,15</sup> the electrolytic oxidative coupling reaction,<sup>16,17</sup> the coupling reaction of 4-(chlorocarbonyl) phthalic acid,<sup>18</sup> etc.<sup>19,20</sup> Although these methods are suitable for certain synthetic conditions sometimes, however, some of these procedures are invariably associated with one or more disadvantages such as high cost, long reaction time, low yield, use of stoichiometric and even excess amounts of reagents or catalysts, special apparatus, etc. Consequently, there is a great need to develop an efficient procedure for the synthesis of 3,3',4,4'-biphenyltetracarboxylic anhydride.

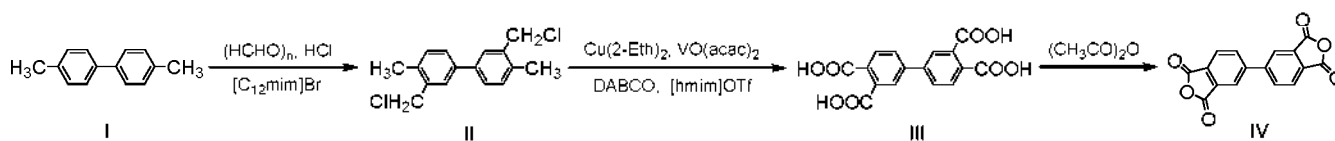
Recently, much attention has been focused on the use of ionic liquids as environmentally benign reaction media. Ionic liquids, with their unique properties, including low volatility, high polarity, good thermal stability over a wide temperature range and selective dissolving capacity by a proper choice of cations or anions,<sup>21,22</sup> have attracted increasing interest in the organic transformations as reaction medium as well as catalyst

(ligand). Various chemical reactions can be successfully performed in ionic liquids.<sup>23-25</sup> Compared with traditional organic solvents, ionic liquids have great advantages in obtaining products with high isolated yields and good to excellent selectivities, accelerating reaction rate in some cases, ease of workup, as well as recycling use with or without catalysts after simply recovery.

Molecular oxygen may serve as superior oxidant that is of lower cost, greater abundance, and improved safety contrast to other oxidizing reagents (KMnO<sub>4</sub>, MnO<sub>2</sub>, CrO<sub>3</sub>, etc.).<sup>26</sup> Furthermore, the use of molecular oxygen as the primary oxidant may also have the advantage that water is the sole final byproduct. Thus, catalytic aerobic oxidation represents a promising protocol for organic synthesis and industrial applications. Accordingly, there has been concerted effort directed at developing various transition metals (copper, vanadium, palladium, etc.)<sup>27-30</sup> to catalyze aerobic oxidation. Vanadyl acetylacetonate (VO(acac)<sub>2</sub>)<sup>31-34</sup> and copper (II) 2-ethylhexanoate (Cu(2-Eth)<sub>2</sub>)<sup>35-37</sup> have been extensively used in organic chemistry as reagents in the epoxidation of allylic alcohols, showing to be highly active, stereo- and regioselective catalysts. 1,4-diazabicyclo-[2.2.2]octane (DABCO) has been extensively used as a catalyst in Suzuki-Miyaura reaction, Baylis-Hillman reaction, epoxidation reaction, complexing ligand, etc.<sup>38-40</sup>

The objectives of the present work are to report an efficient and economic procedure for synthesis of 3,3',4,4'-biphenyltetracarboxylic anhydride by aerobic oxidation reaction of 3,3'-bis(chloromethyl)-4,4'-dimethylbiphenyl catalyzed by VO(acac)<sub>2</sub>/Cu(2-Eth)<sub>2</sub>/DABCO in [hmim]OTf and a subsequent dehydration of tetra-acid upon heating with acetic anhydride, and the starting material 3,3'-bis(chloromethyl)-4,4'-dimethylbiphenyl was prepared by chloromethylation of 4,4'-dimethylbiphenyl catalyzed by [C<sub>12</sub>mim]Br in aqueous media (Scheme 1).

The chloromethylation of 4,4'-dimethylbiphenyl was initially carried out at 75 °C in the presence and absence of 1-dodecyl-3-methylimidazolium bromide ([C<sub>12</sub>mim]Br). As shown in Table 1, in the absence of [C<sub>12</sub>mim]Br, the reaction proceeded



Scheme 1. Three-step synthesis of BPDA

**Table 1.** Chloromethylation of 4,4'-dimethylbiphenyl catalyzed by ionic liquids<sup>a</sup>

Entry	Ionic liquid	Ionic liquid (equiv.)	Time (h)	Yield (%) <sup>b</sup>
1	[C <sub>12</sub> mim]Br	0	24	7
2	[C <sub>12</sub> mim]Br	0.02	16	32
3	[C <sub>12</sub> mim]Br	0.10	14	77
4	[C <sub>12</sub> mim]Br	0.12	12	82
5	[C <sub>12</sub> mim]Br	0.13	12	82
6	[C <sub>12</sub> mim]Br	0.15	12	82
7	[C <sub>12</sub> mim]Br	0.12	10	78
8	[C <sub>12</sub> mim]Br	0.11	12	80
9	[C <sub>12</sub> mim]Br	0.12 <sup>c</sup>	12	82
10	[C <sub>12</sub> mim]Br	0.12 <sup>d</sup>	12	81
11	[C <sub>4</sub> mim]Br	0.12	12	32
12	[C <sub>6</sub> mim]Br	0.12	12	51
13	[C <sub>8</sub> mim]Br	0.12	12	63
14	[C <sub>10</sub> mim]Br	0.12	12	72

<sup>a</sup>Reaction conditions: 4,4'-dimethylbiphenyl 0.1 mol, paraformaldehyde 0.4 mol, 80% H<sub>2</sub>SO<sub>4</sub> 10 mL, AcOH 5 mL, 75 °C. <sup>b</sup>Isolated yield. <sup>c</sup>The second run. <sup>d</sup>The third run.

very slowly, the yield was only 7% after 24 h (entry 1). Reaction performed with [C<sub>12</sub>mim]Br, the yield increased to 32% in a shorter time (16 h) when only 0.02 equiv was used (Table 1, entry 2). The yield increased with the amount of [C<sub>12</sub>mim]Br and reached maximum (82%) at the 0.12 equiv of [C<sub>12</sub>mim]Br (Table 1, entry 4). However, further addition the amount of [C<sub>12</sub>mim]Br, under the same conditions, the yield was not enhanced significantly (Table 1, entries 5 and 6). The subsequent experiments on optimum conditions revealed that 12 h and 0.12 equiv of the promoter were necessary to complete the reaction. Because when 10 h or 0.11 equiv of the promoter was used, the yields were 78% and 80%, respectively (Table 1, entries 7 and 8). In addition, the ionic liquid could be typically recovered and reused with no appreciable decrease in yields and reaction rates (Table 1, entries 9 and 10). Besides [C<sub>12</sub>mim]Br, we also tried to use another types of ionic liquids

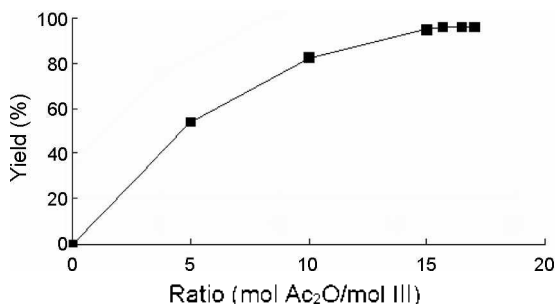
such as 1-butyl-3-methylimidazolium bromide ([C<sub>4</sub>mim]Br), 1-hexyl-3-methylimidazolium bromide ([C<sub>6</sub>mim]Br), 1-methyl-3-octylimidazolium bromide ([C<sub>8</sub>mim]Br) and 1-decyl-3-methylimidazolium bromide [C<sub>10</sub>mim]Br as catalysts in the reaction (Table 1, entries 11-14). It was observed that [C<sub>12</sub>mim]Br demonstrated the best performance. The experimental facts displayed distinctly the advantage of high efficiency of [C<sub>12</sub>mim]Br catalysis. A review of the literature<sup>41</sup> shows that ILs based on 1-alkyl-3-methylimidazolium cation ([C<sub>n</sub>mim]<sup>+</sup>) possess inherent amphiphilic character when their alkyl group is a longer hydrocarbon chain, so the role of [C<sub>12</sub>mim]Br in the reaction probably lies in the fact that it behaves like a classical surfactant and forms aggregates in water at low concentrations and self-assembles to form lyotropic mesophases at higher concentrations. When no surfactant ([C<sub>12</sub>mim]Br) was used or surfactant concentration was below critical micelle concentration (CMC), the reaction system was a suspension (under stirring) with two phases, and the interface between oil phase and water phase was very small, so the reaction rate was very slow and a low yield was obtained, whilst the concentration was above CMC, the number of micelles increased with the increasing surfactant concentration (i.e. the amount of [C<sub>12</sub>mim]Br increased), so the rate of chloromethylation speeded up and a higher yield could 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 concentration, the rate increase became gradually slow and the yield did not change significantly (Table 1, entries 4-6 and 8).

The oxidation of 3,3'-bis(chloromethyl)-4,4'-dimethylbiphenyl was tested in the presence of DABCO at 120 °C, and the results are summarized in Table 2. No reaction occurred in the absence of VO(acac)<sub>2</sub> (Table 2, entry 1) and very low yield of 3,3',4,4'-biphenyltetracarboxylic acid was obtained (13% yield after 48 h) in the absence of copper (II) 2-ethylhexanoate (Table 2, entry 8). It can be observed that both VO(acac)<sub>2</sub> and copper (II) 2-ethylhexanoate as catalysts are crucial for this reaction. Besides [hmim]OTf, other ionic liquids have been tried for the reaction system (Table 2, entries 3-5). Among all investigated ionic liquids, [hmim]OTf demonstrated the best performance. Finally, we also tried to use another types of

**Table 2.** Aerobic oxidation of 3,3'-bis(chloromethyl)-4,4'-dimethylbiphenyl into 3,3',4,4'-biphenyltetracarboxylic acid in ionic liquids<sup>a</sup>

Entry	Catalyst	Cocatalyst	Ionic liquid	Time (h)	Yield (%) <sup>b</sup>
1		copper (II) 2-ethylhexanoate	[hmim]OTf	48	0
2	VO(acac) <sub>2</sub>	copper (II) 2-ethylhexanoate	[hmim]OTf	24	94
3	VO(acac) <sub>2</sub>	copper (II) 2-ethylhexanoate	[bmpyr]NTf <sub>2</sub>	48	71
4	VO(acac) <sub>2</sub>	copper (II) 2-ethylhexanoate	[bmim]PF <sub>6</sub>	48	37
5	VO(acac) <sub>2</sub>	copper (II) 2-ethylhexanoate	[bmpy]PF <sub>6</sub>	48	16
6	VO(acac) <sub>2</sub>	copper (II) 2-ethylhexanoate	[hmim]OTf <sup>c</sup>	24	94
7	VO(acac) <sub>2</sub>	copper (II) 2-ethylhexanoate	[hmim]OTf <sup>d</sup>	24	93
8	VO(acac) <sub>2</sub>		[hmim]OTf	48	13
9	VO(acac) <sub>2</sub>	Cu(acac) <sub>2</sub>	[hmim]OTf	24	54
10	VO(acac) <sub>2</sub>	Cu(OAc) <sub>2</sub>	[hmim]OTf	24	63
11	VO(acac) <sub>2</sub>	Pb(OAc) <sub>2</sub>	[hmim]OTf	24	77

<sup>a</sup>Reaction conditions: 3,3'-bis(chloromethyl)-4,4'-dimethylbiphenyl 0.05 mol, VO(acac)<sub>2</sub> 7 mmol, DABCO 13 mmol, ionic liquid 0.05 mol, 1 atm O<sub>2</sub>, 120 °C. <sup>b</sup>Isolated yield. <sup>c</sup>The second run. <sup>d</sup>The third run.



**Figure 1.** Influences of the amount of acetic anhydride on the dehydration. Reaction conditions: 3,3',4,4'-biphenyltetracarboxylic acid 0.05 mol, reflux, 3 h.

cocatalysts such as  $\text{Cu}(\text{acac})_2$ ,  $\text{Cu}(\text{OAc})_2$  and  $\text{Pb}(\text{OAc})_2$  in the reaction, under the same conditions, however, the yields were merely 54%, 63% and 77%, respectively (Table 2, entries 9-11). The best cocatalyst is copper(II) 2-ethylhexanoate. Therefore, the optimal reaction conditions were observed in Table 2, entry 2. In addition, the catalytic system could be typically recovered and reused with no appreciable decrease in yields and reaction rates (Table 2, entries 6 and 7).

During the process of dehydration, the acetic anhydride had great influences on the reaction, which is shown in Figure 1. No reaction occurred in the absence of acetic anhydride, and the increase in the amount of acetic anhydride (i.e. the ratio increased) enhanced the activity of dehydration. The yield reached maximum at 15.7 of the ratio. Further addition the amount of acetic anhydride, under the same conditions, the yield was not enhanced significantly.

In conclusion, we have developed an efficient synthetic pathway for the preparation of 3,3',4,4'-biphenyltetracarboxylic anhydride starting from commercially available 4,4'-dimethylbiphenyl in three steps in a 74% total yield. Compared to the synthetic methods reported in previous literatures,<sup>6-20</sup> not only was the yield of product greatly improved, but also the operating units were easy workup. One of the noticeable points in our paper was that the catalysts are easy to handle and could be recycled and reused without any significant loss of catalytic activity, and another glittery point was that the facile manipulations in the isolation of the products. Judging from the conditions employed, this method showed has great prospects in industrial applications.

## Experimental Section

**General.** All the used chemicals were from commercial sources without any pretreatment. All reagents were of analytical grade. The ionic liquids were synthesized according to the literature procedures.<sup>42-45</sup> The required substrates (**II-IV**) were prepared according to the related methods.<sup>37,46,47</sup> The target substrates were characterized by Elemental analysis, <sup>1</sup>H NMR, <sup>13</sup>C NMR or compared with their authentic samples.

**Preparation of 3,3'-bis(chloromethyl)-4,4'-dimethylbiphenyl (II, New Compound).** A mixture of compound **I** (18.2 g, 0.1 mol), paraformaldehyde (12.0 g, 0.4 mol), aqueous  $\text{H}_2\text{SO}_4$  (80%, 10 mL), AcOH 5 mL and ionic liquid  $[\text{C}_{12}\text{mim}]\text{Br}$  (4.0 g, 0.012 mol) were added in a 100-mL round flask equipped with reflux

condenser and oil-bath. Anhydrous hydrogen chloride gas was bubbled into the flask at the flow rate of 60 mL/min. The reaction mixture was stirred for 12 h at 75°C, the reaction progress was monitored by TLC and HPLC. After the reaction completed, the mixture was cooled and filtered and extracted with methylene chloride ( $3 \times 20$  mL). The organic phases were combined and rinsed with  $\text{NaHCO}_3$  solution (20%,  $3 \times 20$  mL) and water ( $3 \times 20$  mL), then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated and the crude product was recrystallized from hexane and methylene chloride afforded a white powder 22.9 g, yield 82%, m.p. 99 - 101 °C; <sup>1</sup>H NMR (400 MHz,  $\delta$  in ppm from TMS in  $\text{CDCl}_3$ ): 2.48 (s, 3H,  $\text{CH}_3$ ), 4.66 (s, 2H,  $\text{CH}_2$ ), 4.68 (s, 2H,  $\text{CH}_2$ ), 7.25-7.41 (m, 6H, aromatic); <sup>13</sup>C NMR (400MHz,  $\delta$  in ppm from TMS in  $\text{CDCl}_3$ ): 18.5, 44.1, 128.1, 129.6, 130.5, 135.6, 137.7, 139.2. Analysis Calcd for  $\text{C}_{16}\text{H}_{16}\text{Cl}_2$ : C, 68.79; H, 5.79; Cl, 25.42. Found: C, 68.82; H, 5.78; Cl, 25.40.

**Preparation of 3,3',4,4'-biphenyltetracarboxylic acid (III).** A mixture of compound **II** (14.0 g, 0.05 mol),  $\text{VO}(\text{acac})_2$  (1.86 g, 7 mmol),  $\text{Cu}(\text{2-Eth})_2$  (2.45 g, 7 mmol), DABCO (1.45 g, 13 mmol), and  $[\text{hmim}]\text{OTf}$  (15.8 g, 0.05 mol) were added in a 100-mL round flask equipped with reflux condenser and oil-bath. The round flask was capped with a rubber septum, and the reaction mixture was vigorously stirred at 120 °C under 1 atm  $\text{O}_2$  for 24 h, the reaction progress was monitored by TLC and HPLC. After the reaction completed, the mixture was extracted with methylene chloride ( $3 \times 20$  mL). The combined organic phases was concentrated in vacuo. The residue was recrystallized from distilled water afforded a white powder 15.5 g, yield 94%, m.p. > 330 °C (lit.<sup>12</sup> m.p. > 330 °C); <sup>1</sup>H NMR (400 MHz,  $\delta$  in ppm from TMS in  $\text{DMSO}-d_6$ ): 8.09 (dd, 2H), 8.16 (d, 2H, aromatic), 8.54 (d, 2H, aromatic), 12.3-13.7 (s, 4H); <sup>13</sup>C NMR (400 MHz,  $\delta$  in ppm from TMS in  $\text{DMSO}-d_6$ ): 130.7, 131.4, 132.0, 133.7, 133.9, 147.1, 167.8, 168.3. Analysis Calcd for  $\text{C}_{16}\text{H}_{10}\text{O}_8$ : C, 58.22; H, 3.06; O, 38.73. Found: C, 58.19; H, 3.05; O, 38.76.

**Preparation of BPDA (IV).** In a 250-mL round flask, compound **III** (16.5 g, 0.05 mol) was added to the stirred solution containing acetic anhydride (80 mL, 0.784 mol). The suspension was gradually heated to reflux for 3 h, the reaction progress was monitored by TLC and HPLC. After the reaction completed, the mixture was cooled, the precipitate was filtered off, dried in vacuum, afford a white powder 14.1 g, yield 96%, m.p. 299 - 301 °C (lit.<sup>13</sup> m.p. 298.5 - 300 °C); <sup>1</sup>H NMR (400 MHz,  $\delta$  in ppm from TMS in  $\text{DMSO}-d_6$ ): 7.99 (d, 2H, aromatic), 8.04 (d, 2H, aromatic), 8.11 (dd, 2H, aromatic); <sup>13</sup>C NMR (400 MHz,  $\delta$  in ppm from TMS in  $\text{DMSO}-d_6$ ): 130.2, 130.5, 130.9, 131.3, 134.2, 146.9, 162.7, 162.9. Analysis Calcd for  $\text{C}_{16}\text{H}_6\text{O}_6$ : C, 65.29; H, 2.07; O, 32.65. Found: C, 65.32; H, 2.06; O, 32.62.

**Acknowledgments.** We thank Ministry of Education of the Republic of China and Natural Science Foundation of Jiangsu Province for support of this research.

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