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# An improved synthesis of bis(cyclopentadienone)

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#### Abstract

An improved strategy for the synthesis of 3,3'-(oxy-*p*-phenylene)bis(2,4,5-triphenylcyclopentadienone) was developed, which includes three steps: Friedel–Crafts reaction, oxidation and condensation. Importantly, the use of KMnO<sub>4</sub> made the second step simple and efficient, which has potential application to synthesis of bis(cyclopentadienone)s. The course of oxidation has been confirmed by isolated intermediates.

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Cyclopentadienone could react with ethynylbenzenes [1] and acetylenes [2-4] through Diels-Alder reaction. Bis(cyclopentadienone)s are promising versatile intermediates for preparing aromatic polymers with high glass transition temperature, thermal stability and solubility, since Diels-Alder polymerization between diacetylenes and bis(cyclopentadienone) firstly developed by Stille and Noren [5]. Cyclopentadienones could be synthesized by several methods such as t-BuOK-catalyzed oxygenation of cyclopentadienones [6], coupling of propargylic alcohols with cyclopropylcarbene–chromium complexes [7], penta-carbonylation promoted silicon tethered [2 + 2 + 1] cyclocarbonylation reaction of two alkynes [8], transition metal mediated carbonylative coupling reactions and insertion of CO into zirconacyclopentadienes [9]. However, for aromatic bis(cyclopentadienone)s, one of the important raw materials for the preparation of highly aromatic polymers, there is no new synthetic method reported recently. Normally the three-step synthesis of bis(cyclopentadienones) comprises Friedel-Crafts reaction, oxidation and condensation, which suffer from serious drawbacks such as the use of hazardous reagents, complicated purification and different by-products. To solve these problems, here we describe research directed towards improving the synthesis of 3,3'-(oxy-*p*-phenylene)bis(2,4,5-triphenylcyclopentadienone) (3) from diphenyl ether (Scheme 1) by using appropriate solvents and reagents. In the conversion of deoxybenzoins to benzils,  $KMnO_4$  was firstly used as an alternative oxidant and the intermediate was successfully isolated, which helps to monitor the course of the oxidation reaction.

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Scheme 1. The present synthetic route to compound **3**: (a) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>COCl, AlCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>; HCl; NaHCO<sub>3</sub>; (b) KMnO<sub>4</sub>, TEBA, CH<sub>2</sub>Cl<sub>2</sub>, NaHCO<sub>3</sub>, H<sub>2</sub>O; HCl, NaSO<sub>3</sub>; NaHCO<sub>3</sub>; (c) 1,3-diphenylacetone, KOH, CH<sub>3</sub>CH<sub>2</sub>OH, reflux.



Fig. 1. Structure of the Friedel-Crafts reaction products according to literature method.

We have tried to obtain phenylacetylphenyl ether (1) according to literature method [10]. The molar ratio of biphenyl ether to phenyl acetyl chloride was 1:2.4, hazardous  $CS_2$  was used as solvent and  $AlCl_3$  as catalyst. Unfortunately, the product could not be separated efficiently via repeated recrystallization in benzene, and different by-products formed. Besides, the reaction mixture became sticky and hard to stir upon the addition of HCl to stop the reaction. With the combination of repeated recrystallization and column chromatography, we isolated most of the compounds. Results indicated that the mixture included di-substituted, tri-substituted and multi-substituted products as shown in Fig. 1. In the improved method,  $CH_2Cl_2$  was used as solvent in place of  $CS_2$ . We screened the molar ratio of diphenyl ether to phenylacetyl chloride in the reaction and the results showed that the 1.0:2.0 molar ratio gave the best yield by recrystallization from acetone or simple washing the product with ethanol (Table 1). Under the improved conditions, only a small amount mono-substituted by-product (4) (Fig. 2) was detected.

In the oxidation step, the most commonly used oxidants are toxic selenium dioxide and expensive *N*,*N*-diethyl-4nitrosoaniline [10]. In case of selenium dioxide, the reduced red powder of Se with unpleasant odor is very difficult to remove from the product. In case of *N*,*N*-diethyl-4-nitrosoaniline, the crude product is a intractable black sticky material. Herein, in the synthesis of 4-phenylglyoxalylphenyl ether (**2**), KMnO<sub>4</sub> was employed as oxidant. The reaction preceded smoothly and efficiently at 39 °C (Table 2). The reaction monitored by TLC shows that an intermediate (**5**) exists (Fig. 3), and the intermediate has been successfully separated. The conversion of **1** to the intermediate could be achieved in a few minutes, while the conversion from the intermediate to **2** was relatively slow, implying that oxidation of the first methylene group raised activation energy of oxidation of the second methylene group. Under proper conditions, **1** completely converts into **2** through the process of intermediate.

Catalyzed by KOH in ethanol, condensation between bisbenzils and 1,3-diphenylacetone depends on the temperature critically. When the temperature of adding KOH was controlled precisely at 75 °C, target product **3** could be prepared in a good yield.

 Table 1

 Data for the modified Friedel–Crafts reaction.

Entry	Molar ratio <sup>a</sup>	Refluxing time (h)	Yield (crude product) (%)	Yield (pure product)	Purification			
1	1:1.94	1.5	84.7	72.4	Washed with ethanol/recrystallized from acetone			
2	1:2.06	2.5	94.3	>84.6	Washed with ethanol			
3	1:2.0	3	88.7	86.9	Washed with ethanol			

The concentration of biphenyl ether in CH<sub>2</sub>Cl<sub>2</sub> (500 mL) was 0.32 M.

<sup>a</sup> Molar ratio of biphenyl ether to phenylacetyl chloride.



Fig. 2. Structure of the mono-substituted by-product (4) in improved Friedel-Crafts reaction.

Table 2 Effect of reaction conditions on the results in the oxidation reaction.

Entry	Concentration of 1 (mol/L)	[1]:[KMnO <sub>4</sub> ]:[NaHCO <sub>3</sub> ]:[TEA]	Temperature (°C)	Time (h)	Yield (%)	TLC results			
						$O^a$	$R^{b}$	$I^c$	P
1	0.138	1:3.17:1.21:0.46	r.t.	60	51	_	+	+	+
2	0.132	1:3.26:1.25:0.48	r.t.	48	54	_	+	+	+
3	0.069	1:4.6:1.21:1.38	r.t.	36	>56	_	+	+	+
4	0.062	1:9.19:1.23:1.41	r.t.	35	>62.4	_	_		
5	0.062	1:4.67:1.27:1.40	39	15	>58	_	_		•
6	0.109	1:2.58:2.32:1.93	39	12	52	_		+	+
7	0.059	1:4.61:2.31:2.77	39	5	92.3		_		•
8	0.109	1:4.59:2.31:1.93	39	4	>93.4		_		
9	0.059	1:4.64:2.31:1.94	39	6	>87		_		•
10	0.059	1:4.6:2.3:1.93	39	6.5	88.3		_		•
11	0.063	1:4.58:2.32:1.93	39	6	90.1		_	_	•
12	0.083	1:4.6:2.3:1.93	39	6	90.1		_	_	•
13	0.106	1:4.6:2.3:1.93	39	4	>93.8		_		
14	0.059	1:4.59:2.29:2.75	39	5.5	93.4		_		
15	0.059	1:4.61:2.31:2.77	39	5	92.3		_		•

+, visible; -, invisible; ■, an extremely light spot; ●, a thick and round spot.

<sup>a</sup> A spot which does not move.

<sup>b</sup> The spot corresponding to **1**.

<sup>c</sup> The spot corresponding to **5**.

<sup>d</sup> The spot corresponding to **2**.



Fig. 3. Structure of the intermediate (5) in the improved oxidation reaction.

In conclusion, we report an efficient and mild synthesis method to prepare 3,3'-(oxy-*p*-phenylene)bis(2,4,5-triphenylcyclopentadienone).

### 1. Experimental

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker DRX400MHz spectrometer. FT-IR was recorded on IR spectrometer 4000. Elemental analyses were obtained from Flash EA1112 Elemental Analyzer. Melting points were determined using an X-4 micro-melting point apparatus. Differential scanning calorimetry (DSC) was done on a Mettler-Toledo DSC822e at a heating rate of 10 °C/min under N<sub>2</sub> atmosphere. The peak of the exotherm determined by DSC was also taken as the melting point. UV–vis spectra were recorded on a TU-1901 UV–vis spectrometer. Analytical thin-layer chromatography (TLC) was performed on silica gel plates precoated with a fluorescent indicator. Visualization was effected with ultraviolet light. Mass spectra were recorded on APEXII FT-ICR and BIFLEX III MALDI-TOF spectrometer.

Preparation of 4-phenylacetylphenyl ether (1). In a typical protocol, anhydrous aluminum chloride (42.67 g, 0.32 mol) was dissolved in 400 mL of dry  $CH_2Cl_2$  under stirring and cooled in an ice bath. A solution of diphenyl ether (27.23 g, 0.16 mol) and phenylacetyl chloride (49.47 g, 0.32 mol) in dichloromethane (100 mL) was then slowly

added over a 1 h period at 0.5–1.5 °C. The resulting suspension was stirred for 2 h at room temperature, then refluxed for 3 h. 50 mL of concentrated hydrochloric acid in 50 mL of distilled water was added dropwise to the above mixture under vigorous stirring in an ice bath. The mixture was allowed to stand at room temperature. The resulting precipitate was collected by filtration. The organic layer was neutralized with aqueous solution of NaHCO<sub>3</sub> and washed with distilled water. The solvent was removed by rotary evaporation. The yellowish solid was combined with the precipitate and washed with hot ethanol and dried in a vacuum oven to give 4-phenylacetylphenyl ether (1) as a white solid (56.6 g, 87%). Mp: 175.2 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS):  $\delta$  4.25(s, 4H, –CH<sub>2</sub>–), 7.05(d, 4H, aromatics), 7.34(m, 10H, aromatics), 8.03(d, 4H, aromatics). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS):  $\delta$  45.53, 118.88, 127.00, 128.78, 129.43, 131.11, 132.51, 132.54, 134.58, 160.20, 196.15, 196.17. MS(ESI): Calcd. for C<sub>28</sub>H<sub>22</sub>O<sub>3</sub> *m/z*: 315, Found 315. Elem. anal. calcd. for C<sub>28</sub>H<sub>22</sub>O<sub>3</sub>: C, 82.74; H, 5.46. Found: C, 82.66; H, 5.46.

*Preparation of mono-substituted product* (4). Evaporation of ethanol afforded the mono-substituted product (4). <sup>1</sup>H NMR (DMSO– $d_6$ ):  $\delta$  4.27(s, 2H), 7.02(d, 2H, aromatics), 7.10(d, 2H, aromatics), 7.44–7.22(m, 8H, aromatics), 8.04(d, 2H, aromatics). <sup>13</sup>C NMR (DMSO– $d_6$ ):  $\delta$  45.42, 117.30, 120.31, 126.90, 128.73, 128.86, 129.44, 130.09, 130.12, 131.00, 131.19, 134.80, 162.10, 196.21. MS: Calcd. for C<sub>20</sub>H<sub>16</sub>O<sub>2</sub> *m/z*: 288.1, Found: 289.1. Elem. anal. calcd. for C<sub>20</sub>H<sub>16</sub>O<sub>2</sub>: C, 83.31; H, 5.59. Found: C, 83.67; H, 5.66.

*Preparation of 4-phenylglyoxalylphenyl ether* (2). In a typical protocol, to a 1000 mL three-necked flask equipped with a condenser and a stirrer, **1** (15.12 g) and CH<sub>2</sub>Cl<sub>2</sub> (350 mL) was added, followed by the addition of a solution of NaHCO<sub>3</sub> (7.4 g) and tetraethylammonium bromide (TEBA) (15.12 g) in 220 mL of water, then KMnO<sub>4</sub> (27.63 g) was added to the above mixture accompanied by vigorous stirring. After stirring at 39 °C for 4 h, the reaction mixture was allowed to cool to room temperature. The resulting dark brown suspension was poured into a 2000 mL beaker containing 100 mL of ice water, 200 mL of concentrated hydrochloric acid and 52.0 g of anhydrous Na<sub>2</sub>SO<sub>3</sub>. The color faded rapidly and disappeared finally. The mixture was allowed to stand at room temperature. The yellow organic layer was neutralized with aqueous solution of NaHCO<sub>3</sub> and washed with water for several times. Removal of the solvent by rotary evaporation afforded a bright yellow powder (more than 15.16 g, yield: higher than 94%). Mp: 106 °C. <sup>1</sup>H NMR: δ 7.14(d, 4H, aromatics), 7.53(t, 4H, aromatics), 7.67(t, 2H, aromatics), 7.98(d, 4H, aromatics), 8.01(d, 4H, aromatics). Elem. anal. calcd. for C<sub>28</sub>H<sub>18</sub>O<sub>5</sub>: C, 77.41; H, 4.18. Found: C, 77.47; H, 4.47.

*Preparation of the intermediate* (5). In order to determine the structure of the intermediate, we conduct the reaction at room temperature and stop the reaction at initial stage (before the formation of 2). By column chromatography, with CH<sub>2</sub>Cl<sub>2</sub> as the eluent, we successfully separated the intermediate from **1**. The results of <sup>1</sup>H NMR, <sup>13</sup>C NMR, dept and MS clearly confirmed the structure of the intermediate. <sup>1</sup>H NMR (DMSO–*d*<sub>6</sub>):  $\delta$  4.38(s, 2H), 7.33–7.20(m, 9H, aromatics), 7.62(t, 2H, aromatics), 7.79(t, 1H, aromatic), 7.92(d, 2H, aromatics), 7.99(d, 2H, aromatics), 8.14(d, 2H, aromatics). <sup>13</sup>C NMR (DMSO–*d*<sub>6</sub>):  $\delta$  45.06, 119.39, 120.02, 126.97, 128.23, 128.78, 129.95, 130.09, 130.16, 131.61, 132.70, 132.97, 133.25, 135.52, 135.99, 159.23, 162.15, 193.72, 195.13, 196.78. dept (DMSO–*d*<sub>6</sub>):  $\delta$  45.05(CH<sub>2</sub>), 119.39, 120.02, 126.97, 128.78, 129.95, 130.09, 130.16, 131.62, 132.98, 136.00 (18CH, aromatics). MS(ESI): Calcd. for C<sub>28</sub>H<sub>20</sub>O<sub>4</sub> *m/z*: 420, Found 443.5(420 plus 23 of Na).

*Preparation of* 3,3'-(*oxy-p-phenylene*)*bis*(2,4,5-*triphenylcyclopentadienone*) (**3**). In a typical protocol, to a 1000 mL three-necked flask equipped with a condenser and a stirrer, were added **2** (9.57 g, 0.022 mol), 1,3-diphenylacetone (9.50 g, 0.045 mol) and absolute ethanol (633 mL). The mixture was heated to 75 °C, then a solution of KOH (4.2 g, 0.063 mol) in water (22.3 mL) was added. The mixture immediately turned to red then to black. The temperature was raised to 78 °C within 3 min. The mixture was heated at reflux for 45 min, then allowed to cool to room temperature. The precipitate was collected by filtration and washed with water and ethanol to give crude product of **3**. Further purification by washing with toluene and ethanol gave pure **3**. Mp: 273 °C. <sup>1</sup>H NMR: δ 6.78(d, 4H, aromatics), 6.88(d, 4H, aromatics), 6.94(d, 4H, aromatics), 7.18–7.28(26H, aromatics). <sup>13</sup>C NMR: δ 118.31, 125.11, 125.49, 127.52, 128.06, 128.13, 128.22, 128.57, 129.38, 130.14, 130.64, 130.81, 131.20, 133.10, 153.75, 154.08, 156.74, 200.15. Elem. anal. calcd. for C<sub>58</sub>H<sub>38</sub>O<sub>3</sub>: C, 88.98; H, 4.89. Found: C, 88.87; H, 4.92. MS(MALDI-TOF): Calcd for C<sub>58</sub>H<sub>38</sub>O<sub>3</sub> 782, Found 782.8.

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