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Hexaalkoxytriphenylenes Synthesized from Facile Solvent-Free Oxidative Coupling Trimerization

Weibin Bai^{ab} & Jinhuo Lin^{ab}

^a College of Chemistry and Material Science, Fujian Normal University, Fuzhou, China

^b Key Laboratory of Polymer Materials , Fuzhou , China Published online: 25 Feb 2011.

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HEXAALKOXYTRIPHENYLENES SYNTHESIZED FROM FACILE SOLVENT-FREE OXIDATIVE COUPLING TRIMERIZATION

Weibin Bai and Jinhuo Lin

College of Chemistry and Material Science, Fujian Normal University, Fuzhou, China and Key Laboratory of Polymer Materials, Fuzhou, China

GRAPHICAL ABSTRACT



Abstract By grinding 1,2-dialkoxybenzene with anhydrous $FeCl_3$ powder using a glass pestle in a mortar at ambient temperature under solvent-free conditions, hexaalkoxytriphenylenes were obtained in good yield (up to 90%) in 30 min. The solvent-free oxidative coupling reaction is a facile, efficient, "green-chemistry" method.

Keywords Green chemistry; hexaalkoxytriphenylene; oxidative coupling; solvent-free

Discotic liquid crystals are usually composed of molecules with a disc-like core and aliphatic tails. In recent years, the discotic liquid crystals have attracted much attention as novel organic semiconductors. Triphenylene derivatives are the most widely studied discotic mesogens because of their ability to form highly ordered columnar structures with overlapping π -electron systems. Especially hexasubstituted triphenylene discotic liquid crystals have been drawing attention as photoconductors, molecular wires and fibers, light-emitting diodes, and photovoltaic cells.^[1]

By three consecutive Scholl reactions of 1,2-dimethoxybenzene, the hexamethoxytriphenylene was synthesized previously in H_2SO_4 using chloranil or iron chloride as oxdidant.^[2] Because triphenylene derivatives show mesomorphism only

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Address correspondence to Weibin Bai, College of Chemistry and Material Science, Fujian Normal University, China and Key Laboratory of Polymer Materials, Fuzhou 350007, China. E-mail: bai-wb@163.com

when the six peripheral alkoxy chains have a minimum of four carbon atoms (i.e., butoxy chains),^[3] the reaction is more or less limited to the production of hexamethoxytriphenylene. If the long-chain derivatives are prepared, it is necessary to replace the alkoxy groups to give different hexaalkoxytriphenylene discotics. The method of cyclic anodic trimerization could be extended to other dialkoxybenzenes to form hexaalkoxytriphenylene discotics directly,^[4] but this slow reaction could be applied on a very small scale and is limited in its use.

With the oxidative coupling reaction researched further, the use of FeCl₃ as oxidant was reported to synthesize the hexahexyloxytriphenylenes with 20% yield by the trimerization of 1,2-dihexyloxybenzene in 70% H_2SO_4 at 80 °C.^[5] The synthetic route was improved further to obtain better yields.^[6] Cooke et al. reported good yields could be obtained using FeCl₃ supported on alumina, which could also avoid the application of mineral acids.^[7] However, the preparation of alumina/FeCl₃ catalyst is not facile, and the hazardous organic solvents are still unavoidable. Recently, oxidative coupling trimerization has developed into the most commonly used method to prepare different triphenylene derivatives.^[8]

In addition to FeCl₃, VOCl₃,^[9] and MoCl₅^[3] also have been used as oxidants for the trimerization. The novel reagents could increase the yields under very mild conditions with or without acid catalyst in a short time at room temperature. However, the high price and toxicity hazard limited the application of the reagent of VOCl₃ and MoCl₅.

Solvent-free oxidative coupling reaction cannot only reduce pollution of organic solvents such as dichloromethane and nitromethane^[10] but also can overcome the problem of insolubility of the reagents in organic solvents. Furthermore, because molecules in a crystal are arranged tightly and regularly, a solvent-free organic reaction occurs more efficiently and more selectively.^[11] Here, we report a novel, solvent-free oxidative coupling trimerization to prepare hexaalkoxytriphenylenes with anhydrous iron chloride as the oxidant. By comparison with the previous preparation methods, the solvent-free grinding method cannot only avoid the poisonous organic solvents and mineral acids but also can obtain good yields, so the whole process is simple, mild, cost-efficient, and environmentally friendly, which will have some social and economic benefits. The reaction is shown in Scheme 1.

Table 1 shows the yields of different hexaalkoxytriphenylenes obtained depending on the rection time and the molecular ratio of 1,2-dialkoxybenzenes



Scheme 1. Solvent-free oxidative coupling trimerization of 1,2-dialkoxybenzenes.

Entry	R	Ratio ^a	Time (min)	Yield (%)
1	C ₄ H ₉	1:2	30	56.0
2	C_4H_9	1:2	40	49.0
3	C_4H_9	1:3	20	71.0
4	C_4H_9	1:3	30	77.3
5	C_4H_9	1:3	40	82.5
6	C_4H_9	1:4	20	84.3
7	C_4H_9	1:4	30	93.0
8	C_4H_9	1:4	40	95.4
9	C_4H_9	1:5	20	79.0
10	C_4H_9	1:5	30	82.0
11	C_4H_9	1:5	40	82.0
12	$C_{6}H_{13}$	1:3	30	66.6
13	$C_{6}H_{13}$	1:4	30	75.9
14	$C_{6}H_{13}$	1:4	40	80.0
15	C_2H_5	1:3	30	63.9
16	C_2H_5	1:4	30	63.7

Table 1. Preparation of triphenylene derivatives using FeCl₃ by solvent-free oxidative coupling trimerization

^aMolecular ratio of 1,2-dialkoxybenzenes and FeCl₃.

and FeCl₃. As shown in Table 1, anhydrous FeCl₃ as oxidation could give yields of about 50% at room temperature when the molecular ratio is 1:2 and the reaction time is more than 30 min. The result indicates that reaction was initiated by grinding, which generated cation radicals mechanically. In addition, the solvent-free oxidative reaction offered good yields with theoretical amount of oxidant. The yields of 77.3, 66.6, and 63.9% were obtained for 1,2-dibutoxybenzene, 1,2-dihexyloxybenzene, and 1,2-diethoxybenzene, respectively (entries 4, 12, and 15). It also can be seen that the ratio of the oxidation and the reaction time could effect the reaction obviously. As the amount of FeCl₃ is increased, the yields increase too. A yield of 90% is obtained for 1,2-dibutoxybenzene with 4 molecular equivalents of FeCl₃ (entries 7 and 8). When the ratio is 1:5, the yield decreases, indicating that excess of oxidant holds back the trimerization process. So does the time. The yields could not increase significantly after 30 min.

In conclusion, we have described a novel, solvent-free oxidative coupling trimerization to synthesize hexaalkoxytriphenylenes by grinding 1,2-dialkoxybenzenes. At room temperature, good yields can be obtained by anhydrous FeCl₃ as the oxidant without any acid catalyst. The solvent-free oxidative coupling trimerization is facile, efficient, time-saving, and environmentally friendly.

The synthetic procedure is illustrated by the trimerization of 2,3,6,7,10,11hexabutoxytriphenylene as an example: 0.44 g (2 mmol) of 1,2-dibutoxybenzene and 1.30 g (8 mmol) of anhydrous FeCl₃ powder were added into a mortar. After grinding for about 30 min with a glass pestle, the mixture was put into cold ethanol containing 5% hydrochloric acid and then stirred for 5 min. The crude product was collected by filtration, then washed several times with cold ethanol; the refined product was filtered and recrystallizated in the ethanol, yielding 0.41 g (93%) of hexabutoxytriphenylene. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.81 (s, H¹, 6H), δ 4.23 (t, H², 12H, J = 6.4), δ 1.94 (m, H³, 12H, J = 4.8), δ 1.58 (m, H⁴, 12H, J = 1.6), $\delta 1.02$ (t, H⁵, 18H, J = 2.8). Elemental analysis (calculated for C₄₂H₆₀O₆), C: calc. 76.33%, found 76.39%; H: calc. 9.15%, found 9.27%. The purity of the product is 99.05% as measured by high-performance liquid chromatography.

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