

A Facile Synthetic Method for Biphenyltetracarboxylic Dianhydrides

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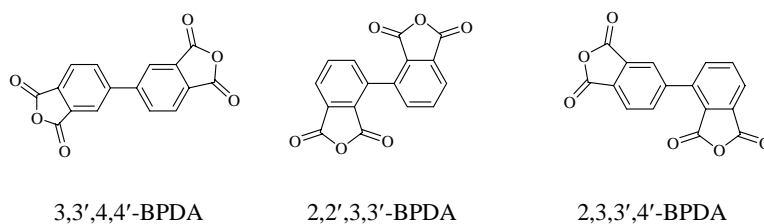
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Abstract: We report a facile and high-yielding procedure for preparing biphenyltetracarboxylic dianhydrides (BPDAs). This method relies on a nickel-catalyzed electroreductive coupling reaction of dimethyl 3-chlorophthalate (3-DMCP) and/or dimethyl 4-chlorophthalate (4-DMCP) with subsequent hydrolysis of tetra-ester and dehydration of tetra-acid.

Keywords: Biphenyltetracarboxylic dianhydrides, nickel-catalyzed, electroreductive coupling.

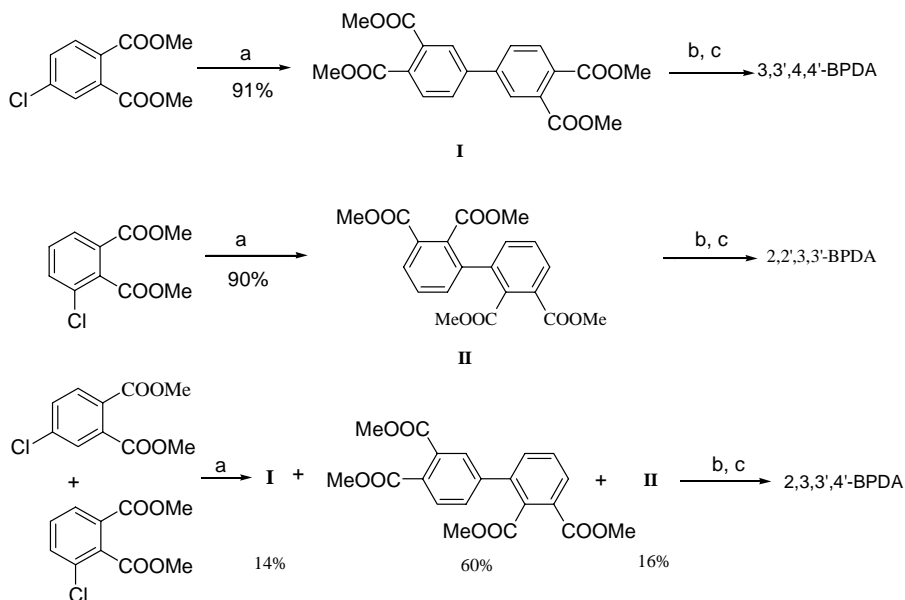
BPDAs (**Scheme 1**) are most important monomers of aromatic polyimides that can be melted and/or solution processed in the fully imidized form¹. Despite the importance of BPDAs, their synthesis remains unsatisfactory¹⁻⁵. Some time ago, Ni-catalyzed dehalogenative coupling of aryl chlorides was established as a versatile method for the synthesis of symmetrical biaryls⁶. This methodology has been employed in the synthesis of BPDAs^{1,5}. The practical application of these methods suffers from disadvantages such as harsh conditions, the use of expensive and/or toxic reagents, and tedious manipulations in the isolation of the products. Moreover, a large excess of co-reductant is required. According to a different protocol disclosed by Nédélec, Périchon and co-workers, aryl halides can be reductively coupled in a simple electro-synthesis, being catalyzed by nickel, wherein the Ni(0) moiety is generated at constant current density⁷. The main drawback of this procedure is that the organometallic compound must be prepared before the electrochemical reaction. And to our knowledge, there have been no reports on the heterocoupling between two aryl chlorides bearing electro-withdrawing groups on each aromatic ring.

Scheme 1



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Scheme 2



(a) $e/\text{NiBr}_2/\text{PPh}_3/n\text{-Bu}_4\text{NBr}/\text{DMF}$; Zinc anode/nickel foam cathode; (b) $\text{NaOH}/\text{H}_2\text{O}$; (c) H^+ ; Then dehydration.

Herein we report an extremely convenient procedure for the synthesis of BPDA (Scheme 2) starting from 3-/4-DMCP, which can easily be obtained from inexpensive 3-/4-chlorophthalic anhydride⁵ in good yield. The preparation of tetramethyl biphenyltetracarboxylic acid ester is operationally simple. DMF freshly distilled or stored over molecular sieves after prolonged time has no apparent difference on reduction yield. We used the less expensive triphenylphosphine as the ligand of the nickel complex according to Colon's research⁶, and no apparent by-product was detected.

Actually, we have studied the effects of solvent, substrate concentration, electrolyte, reaction temperature on the yield of the products⁸ and found that the temperature have a crucial effect on the yield of the coupling product. The electrochemistry cannot be carried out at room temperature owing to the poor reactivity of aryl chlorides. We have observed that the highest yields were obtained by running the reaction at 60 °C-100 °C, when the reaction was carried out at higher temperature, the yield reduced, this may cause by the deactivation of the catalyst at higher temperature.

It is worth mentioning that a good selectivity of the unsymmetrical cross-coupling is observed when the electroreductive coupling was carried out between 3-DMCP and 4-DMCP, relatively low homocoupling of the 3-DMCP and 4-DMCP occurred. The reason may be that 3-DMCP is more reactive than 4-DMCP⁹. Regarding the mechanism of the reaction⁶, the reaction most likely proceeded *via* the oxidative addition of 3-DMCP onto nickel (0). The second step could be either oxidative addition onto 4-DMCP or a nucleophilic substitution.

Typical experimental procedure is as follows: The electrochemical cell, equipped

with a pierced rubber stopper carrying a zinc rod anode (diam. 1 cm), a copper wire and a jaw-clip holding the nickel foam cathode (20 cm²) wrapped around the anode in a cylindrical fashion (anode-cathode distance ≈ 1 cm), as well as gas inlet and outlet tube, was flushed with argon. DMF (40 mL) was added through syringe and *n*-Bu₄NBr (0.1 mmol) was used as supporting electrolyte. NiBr₂ (1.5 mmol), PPh₃ (6.0 mmol) and 3- or 4-DMCP (15 mmol) were added to this solution in the case of homocoupling reaction, and NiBr₂ (1.5 mmol), PPh₃ (6.0 mmol), 3-DMCP (7.5 mmol) and 4-DMCP (7.5 mmol) in the case of heterocoupling reaction. After passing argon for 10 min, a constant current of 0.20 A was applied at 60 °C and the reaction was monitored by TLC. The end point was indicated by a color change from wine-red to dark brown. The coupling yields are determined by HPLC using biphenyl as the internal reference and compared with the authentic sample. HPLC analysis conditions were: Hypersil CN (250 × φ 4.6 mm) column, an eluent with 8:2 *n*-hexane + isopropanol at 0.8 mL/min, a GILSON UV-117 Interlligent UV-vis detector with detection at 254 nm.

After electrolysis, the solution was quenched with 1 mol/L HCl. The precipitate, separated by filtration, was added to the stirred solution of NaOH (0.3 mol) in water (50 mL), and the mixture was heated to reflux for 4 h. After cooling, the mixture was filtrated to remove the PPh₃, and the filtrate was acidified with conc. HCl to pH ≤ 1. The precipitate was filtrated off, washed with H₂O several times, and dried in an oven at 100 °C to afford 3,3',4,4'- or 2,2',3,3'-biphenyltetracarboxylic acid which was heated slowly to dehydrated and sublimated under reduced pressure to afford 3,3',4,4'-BPDA or 2,2',3,3'-BPDA as a colorless crystals. 3,3',4,4'-BPDA: Yield 78%; m.p. 297 °C (lit.⁵ mp 297-298 °C); IR (KBr/cm⁻¹): 1776 and 1848 (C=O), 1263 (C-O-C); ¹H-NMR (600MHz, DMSO-d₆, δ_{ppm}): 8.60 (d, 2H, J=1.2Hz), 8.47 (dd, 2H, J=7.8, 1.2Hz), 8.21 (d, 2H, J=7.8Hz). Anal. Calcd. for C₁₆H₆O₆ (294.23): C, 65.32, H, 2.05; Found, C, 65.19, H, 1.95. 2,2',3,3'-BPDA: Yield 75%; m.p. 268 °C (lit.¹ mp. 268-269 °C); IR (KBr/cm⁻¹): 1776 and 1848 (C=O), 1263 (C-O-C); ¹H-NMR (600MHz, DMSO-d₆, δ_{ppm}): 8.35 (dd, 2H, J=6.8, 2.0Hz), 8.22-8.28 (m, 4H). Anal. Calcd. for C₁₆H₆O₆ (294.23): C, 65.32, H, 2.05; Found, C, 65.19, H, 1.95.

While for the 2,3,3',4'-BPDA, owing to the large solubility of the corresponding tetra-acid in water, the procedure was slightly different. After hydrolyzation, the solution was acidified to pH ≤ 1 and then filtrated to remove 3,3',4,4'- and 2,2',3,3'-biphenyltetracarboxylic acid which are insoluble in water. Xylene was added to the filtrate, and the mixture was refluxed with stirring until no more water appeared in the trap. The hot solution was filtrated and the filtrate was cooled. The precipitate was separated by filtration, dried in vacuum to afford 2,3,3',4'-BPDA as a colorless crystals. Yield 40%; mp. 198 °C (lit.¹⁰ mp. 195.5-197 °C); IR (KBr/cm⁻¹): 1776 and 1848 (C=O), 1263 (C-O-C); ¹H-NMR (600MHz, DMSO-d₆, δ_{ppm}): 8.41 (d, 1H, J=1.2 Hz), 8.27 (dd, 1H, J=7.8, 1.2Hz), 8.23 (d, 1H, J=7.8Hz), 8.18 (dd, 1H, J=7.2, 1.2 Hz), 8.11 (t, 1H, J= 7.2Hz), 8.07 (dd, 1H, J=7.2, 1.2Hz). Anal. Calcd. for C₁₆H₆O₆ (294.23): C, 65.32, H, 2.05; Found, C, 65.19, H, 1.95.

In the present experiments, good yields of homocoupling or heterocoupling products were obtained very easily. Further optimization aimed at the practical conditions for these reactions is currently under active progress in our laboratory.

Acknowledgments

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