



Organometallic C–N coupling between *N,N'*-dichloro-*p*-benzoquinone diimine and Grignard reagents and its application to synthesis of polyanilines

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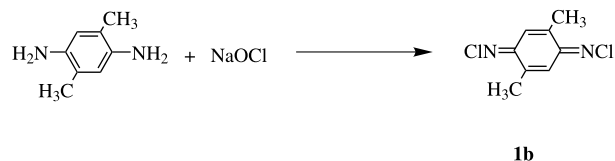
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Received 9 August 2001; revised 13 September 2001; accepted 5 October 2001

Abstract—A new C–N coupling reaction between *N,N'*-dichloro-*p*-benzoquinone diimines and aryl Grignard reagents has been developed. The new method gives *N,N'*-diaryl-*p*-benzoquinone diimines in 50–88% isolated yield. The obtained new compounds are regarded as oligomeric model compounds for pernigraniline-type polyaniline, and their chemical behavior has been investigated. New polyaniline-type polymers have been prepared by applying the developed C–N coupling reaction. © 2001 Elsevier Science Ltd. All rights reserved.

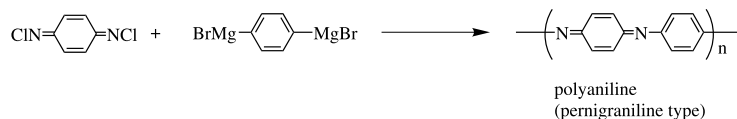
Organometallic coupling reaction between C–X (X = halogen) and C–M (M = MgX, Li, SnR₃, SiR₃, etc.) compounds has long been studied,^{1–3} and the effects of transition metal complex catalysts for the coupling reaction have been demonstrated. However, in contrast to extensive studies on the C–C coupling reaction, only limited attention has been paid to similar C–N coupling reactions between N–X and C–M compounds. In the course of our studies on electrically conducting polyanilines² and the organometallic synthesis of π -conjugated polymers,³ we considered the possibility of obtaining polyanilines, PANs, by organometallic coupling between *N,N'*-dichloro-*p*-benzoquinone diimines and aromatic diGrignard reagents, and reported that this type of polycondensation actually gave polyanilines.⁴ However, basic studies on the organometallic C–N coupling have not been reported. Herein we report the results of basic studies on the C–N coupling reaction and the chemical properties of the obtained organic compounds (Scheme 1).

N,N'-Dichloro-*p*-benzoquinone diimine with methyl substituents was prepared according to the following oxidation reaction and characterized by ¹H NMR spectroscopy and elemental analysis;⁵ preparation of *N,N'*-dichloro-*p*-benzoquinone without the methyl substituents in an analogous manner was previously reported.⁶



By using the methyl-substituted (**1b**) and non-substituted (**1a**) *N,N'*-dichloro-*p*-benzoquinone diimines, we carried out the C–N coupling reactions, which are outlined in Scheme 2.

For example, the C–N coupling reaction of the Grignard reagent of *o*-bromotoluene with **1b** was carried

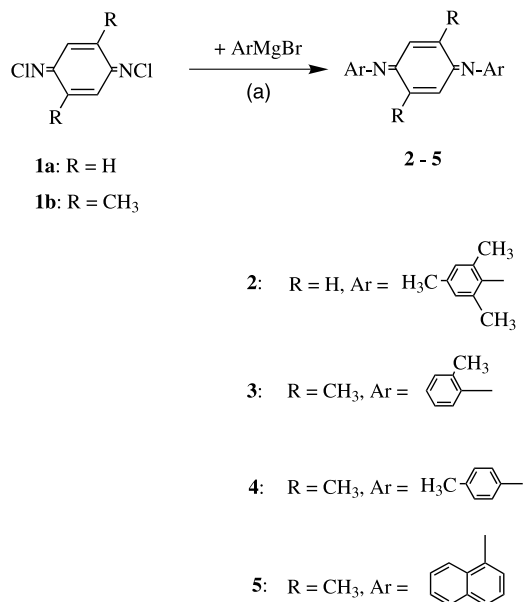


Scheme 1.

Keywords: *N,N'*-dichloro-*p*-benzoquinone diimine; C–N coupling; polymers; nickel complex.

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Scheme 2. Reagents and conditions: (a) THF under reflux, NiCl₂(dppp).

out as follows. To a solution of *o*-bromotoluene (1.63 g, 10.0 mmol) in 10 mL of dry THF was added magnesium (0.27 g, 11 mmol). After stirring the reaction mixture under reflux for 2 h to form the Grignard reagent, dichloro[bis(1,3 - diphenylphosphino)propane]nickel(II), NiCl₂(dppp) (30 mg, 0.05 mmol) and a solution of **1b** (0.81 g, 4.0 mmol) in 10 mL of THF were added. After the reaction mixture was refluxed for 4 h under N₂, the solvent was removed by evaporation. The obtained residue was washed with diluted hydrochloric acid (about 1 M) and water. The product was purified by column chromatography on SiO₂ using CHCl₃ as an eluent. After drying under vacuum, a red powder of analytically pure **3** was obtained; yield = 0.76 g (60%). Other C–N coupling products **2**, **4** and **5** were prepared analogously in isolated yields of 88, 50 and 52%, respectively. The basicity of the coupling products seemed not high; however, the products were partly protonated with diluted hydrochloric acid and were lost during the washing with diluted hydrochloric acid, and the crude yield of the product seemed higher. Actually, neutralization of the washed solution of **3** with NH₄OH and extraction with hexane indicated that 40% yield of **3** was included in the extract, as proved by ¹H NMR spectroscopy; therefore, the C–N coupling is considered to give the product in high crude yield. All the compounds were characterized by IR and ¹H NMR spectroscopy and elemental analysis.⁵ The C–N coupling reaction proceeded even without the Ni catalyst; however, in this case the yield was lower (e.g. 40% for **3**).⁷ Similar pernigraniline-type oligomers of aniline have been prepared via different reaction routes.⁸ However, the present method can provide a wider variety of pernigraniline-type aniline dimers with various combinations of reactants, and is applicable to the preparation of new polyanilines as described below.

Table 1 summarizes optical data of **2–5**. The UV–vis absorption peaks of **2–5** appear near those of the reported

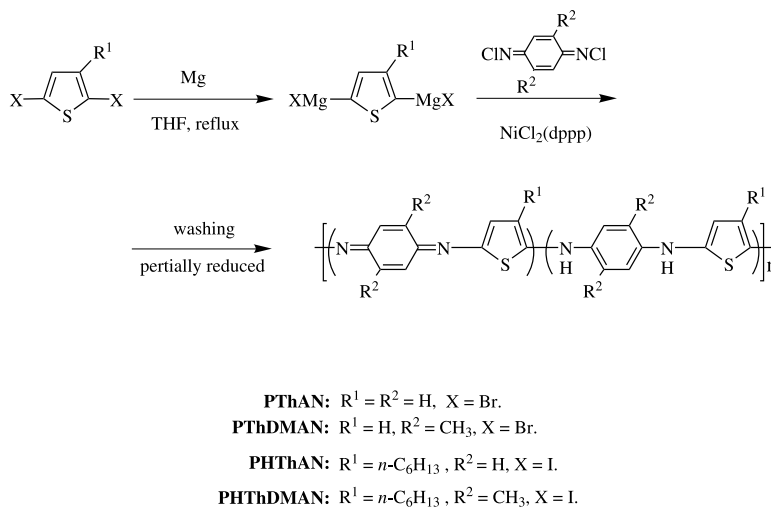
Table 1. UV–vis data of the C–N coupling products

Compounds	λ_{\max} (nm)	
	In DMF	In CF ₃ COOH
2	484	615
3	302, 452	601
4	310, 457	724
5	319, 492	750

pernigraniline-type aniline oligomers.^{8b,9} In CF₃COOH the absorption peak shifted to a longer wavelength in accord with protonation data previously reported for the pernigraniline-type oligomers.^{8b,9} Treatment of **2–5** with an aqueous solution of hydrazine under a nitrogen atmosphere afforded white solids of the corresponding reduced products, similar to the cases of the chemical reduction of aniline oligomers and polymers with oxidized structures.^{2a,8} Quantitative yield was observed for the reduction of **3**. The ¹H NMR spectrum of the reduced product showed an N–H peak at about δ 5; ¹H NMR data of the reduction products of **3** (CDCl₃, 400 MHz): δ 6.8–7.2 (m, 10H), 5.05 (br, 2H, NH), 2.26 (s, 6H), 2.22 (s, 6H). The π – π^* absorption band of **2–5** in the range of 484–492 nm (cf. Table 1) disappeared in the reaction with hydrazine, and the rate of the reaction obeyed the first-order rate law with respect to the concentration of the pernigraniline-type starting compound. The IR spectra of the reduced product showed a sharp ν (N–H) peak at about 3500 cm⁻¹. Electrochemical reduction behavior of an analogous quinodiimine-type compound (*N,N'*-diphenyl-*p*-phenylenediimine) in aqueous media has been reported.¹⁰

As described above, we previously reported the polycondensation of **1a** with the diGrignard reagent of *p*-dibromobenzene in the presence of NiCl₂(dppp).⁴ We now report preparation of polyanilines by C–N coupling of **1a** and **1b** with 2,5-dihalothiophenes, as depicted in Scheme 3. The polycondensation was carried out by using 1.0 mmol of **1a** or **1b** and 1.0 mmol of the diGrignard reagent of 2,5-dihalothiophenes in the presence of 0.03 mmol of NiCl₂(dppp) in 10 mL of THF under reflux. After 24 h, the reaction mixture was poured into diluted hydrochloric acid. After neutralization with aqueous ammonium, the polymer was separated by filtration, washed with water and MeOH, and dried under vacuum.

The obtained pernigraniline-type polymers seemed to be partly reduced to give emeraldine-type polymers on washing the polymer with hydrochloric acid, aqueous ammonia and methanol. IR (e.g. appearance of the ν (N–H) peak at about 3350 cm⁻¹), ¹H NMR and elemental analytical data⁵ supported this view. The yield of polymers was about 60%. It is known that pernigraniline-type polymers and oligomers are reduced to stable emeraldine-type compounds in aqueous media under various conditions.^{8,10} PThDMAN and PHThDMAN were partly (about 30 and 50%, respectively)



Scheme 3.

soluble in DMF; they were also partly soluble in NMP and CF_3COOH . GPC data (eluent = DMF containing 0.01 M LiBr) of **PThDMAN** and **PHThDMAN** gave a number average molecular weights of 9.2 and 9.4×10^3 , respectively. Since the soluble part and the insoluble part give the same IR spectrum, the fraction with lower molecular weights is considered to be soluble in DMF. Cyclic voltammogram of a cast film of **PHThDMAN** on a Pt plate shows an oxidation peak at 1.05 V versus Ag^+/Ag in an CH_3CN solution of $[\text{NBu}_4]\text{PF}_6$ (0.10 M). **PThAN** and **PHThAN** were slightly soluble in CF_3COOH and DMF, and determination of their molecular weights was not possible.

As described above, polyaniline-type oligomers and polymers can be prepared by the nickel complex-promoted C–N coupling reaction. The proposed polycondensation method is expected to give various new polyaniline-type polymers.

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- Spectroscopic and elemental analytical data for **1b** and the C–N coupling products. **1b**: $^1\text{H NMR}$ (CDCl_3 ; 400 MHz) δ 7.27 (m, 2H, $J = 4.0$ Hz), 2.24 (d, 6H, $J = 1.4$ Hz). Anal. calcd for $\text{C}_8\text{H}_8\text{Cl}_2\text{N}_2$: C, 47.32; H, 3.97; N, 13.92; Cl, 34.80. Found: C, 47.47; H, 4.03; N, 13.95; Cl, 34.48%. **2**: $^1\text{H NMR}$ (CDCl_3 ; 400 MHz) δ 7.17 (d, 0.6H, $J = 2$ Hz, *cis*-quinoide-H), 6.94 (dd, 1.4H, $J = 2.8$ Hz, 10 Hz, *trans*-quinoide-H), 6.89 (s, 2.8H, *trans*-ArH), 6.84 (s, 1.2H, *cis*-ArH), 6.48 (dd, 1.4H, $J = 2.8$ Hz, 10 Hz, *trans*-quinoide-H), 6.23 (d, 0.6H, $J = 2$ Hz, *cis*-quinoide-H), 2.30 (s, 4.2H, *trans*-quinoide- CH_3), 2.26 (s, 1.8H, *cis*-quinoide- CH_3), 1.91 (s, 8.4H, *trans*-quinoide- CH_3), 1.87 (s, 3.6H, *cis*-quinoide- CH_3). Anal. calcd for $\text{C}_{24}\text{H}_{26}\text{N}_2$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.51; H, 7.74; N, 8.17%. **3**: $^1\text{H NMR}$ (CDCl_3 ; 400 MHz) δ 7.24 (d, 2H, $J = 8.0$ Hz), 7.20 (t, 2H, $J = 8.0$ Hz), 7.07 (t, 2H, $J = 8.0$ Hz), 6.64 (d, 2H, $J = 8.0$ Hz), 6.54 (d, 2H, $J = 1.6$ Hz), 2.15 (d, 6H, $J = 1.6$ Hz, CH_3), 2.12 (s, 6H, CH_3). Anal. calcd for $\text{C}_{22}\text{H}_{22}\text{N}_2$: C, 84.04; H, 7.05; N, 8.91. Found: C, 84.04; H, 7.16; N, 8.70%. **4**: $^1\text{H NMR}$ (CDCl_3 ; 400 MHz) δ 7.18 (d, 4H, $J = 8.0$ Hz), 6.74 (d, 4H, $J = 8.0$ Hz), 6.68 (s, 2H), 2.37 (s, 6H, CH_3), 2.12 (s, 6H, CH_3). Anal. calcd for $\text{C}_{22}\text{H}_{22}\text{N}_2$: C, 84.04; H, 7.05; N, 8.91. Found: C, 84.00; H, 7.28; N, 8.63%. **5**: $^1\text{H NMR}$ (CDCl_3 ; 400 MHz) δ 7.87 (d, 2H, $J = 8.0$ Hz), 7.81 (d, 2H, $J = 8.0$), 7.69 (d, 2H, $J = 8.0$), 7.54–7.44 (m, 6H), 6.79 (d, 2H, $J = 8.0$ Hz), 2.14 (s, 6H, CH_3). Anal. calcd for $\text{C}_{28}\text{H}_{22}\text{N}_2$: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.80; H, 5.85; N, 7.21%. **PHThDMAN**: $^1\text{H NMR}$ (CF_3COOD , 400 MHz) δ 7.2–8.5 (br, 6H, Ph-H and N-H), 7.3 (br, 2H, Th-H), 3.5 (m, 4H, CH_2), 2.9 (m, 12H, Ph- CH_3), 1.9 (m, 16H, CH_2), 1.2 (m, 6H, CH_3). Anal. calcd for $((\text{C}_{18}\text{H}_{22}\text{N}_2\text{S})(\text{C}_{18}\text{H}_{24}\text{N}_2\text{S}) \cdot \text{H}_2\text{O})_n$: C, 70.09; H, 7.84; N, 9.08. Found: C, 70.19; H, 7.34; N, 8.66%. **PThDMAN**: Anal. calcd for $((\text{C}_{12}\text{H}_{10}\text{N}_2\text{S})(\text{C}_{12}\text{H}_{12}\text{N}_2\text{S}) \cdot 2\text{H}_2\text{O})_n$: C, 61.78; H, 5.62; N, 12.01. Found: C, 61.93; H, 5.61; N, 11.81%.
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7. The Ni-promoted C–N coupling is considered to proceed according to a catalytic cycle involving (i) oxidative addition of the N–Cl bond to Ni to form a Ni(Cl)(–N=) species; (ii) arylation of the Ni(Cl)(–N=) species with ArMgBr to afford a Ni(Ar)(–N=) species, and (iii) reduction elimination of the final product from the intermediate Ni(Ar)(–N=) species, similar to the Ni-promoted C–C coupling reaction.^{1b}
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