

Direct Alkylation and Phenylation of 3,8-Dibromo-1,10-phenanthroline with Grignard Reagents

Kazushige Anzai, Hiroki Fukumoto, and Takakazu Yamamoto*

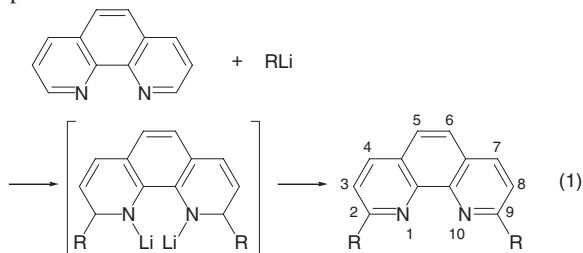
Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503

(Received November 26, 2003; CL-031151)

Reactions of alkyl and phenyl Grignard reagents with 3,8-dibromo-1,10-phenanthroline led to alkylation and phenylation at the 2-position of 1,10-phenanthroline. The prepared 2-alkyl-1,10-phenanthroline forms a 1:1 complex with Cu(II) and serves as a starting material for poly(2-alkyl-1,10-phenanthroline-3,8-diyl).

1,10-Phenanthroline (Phen) is an attractive π -conjugated ligand, and its various derivatives have been prepared to construct assembled metal complexes,¹ light emitting metal complexes,² catalysts, catenanes,^{1,3} and π -conjugated poly- and oligo-(1,10-phenanthroline)s.⁴

Introduction of substituent(s) at the 2- and/or 9-positions of Phen tunes chemical reactivity and various Phen derivatives with the substituent(s) have been prepared.^{3,5} On the other hand, 3,8-dibromophenanthrolines are considered to be important starting materials for π -conjugated oligomers and polymers of Phen.^{4,6} For introduction of alkyl and aryl group at the 2- and 9-positions, Dietrich-Buchecker and Sauvage reported the following unique reaction.⁵ Based on the reaction (1), various catenanes have been prepared.³

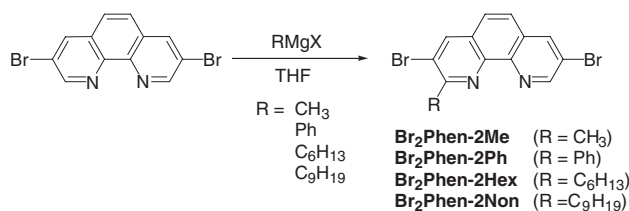


If dibromination of the obtained alkylated or arylated Phen at the 3- and 8-positions proceeds, it affords 3,8-dibromo-Phen's (Br_2Phen 's) with the alkyl or aryl group, which are expected to be important starting materials for π -conjugated oligo- and poly-Phen's. However, the bromination of the 3- and 8-positions of Phen's usually requires severe and elaborated reaction conditions.⁶ Phen is a typical electron deficient molecule due to its containing electron-withdrawing imine nitrogens, and bromination of such electron-deficient heteroaromatic compounds is difficult.⁷

Prompted by the presence of the known reaction shown in Eq 1, we tried direct alkylation and arylation of 3,8-dibromo-Phen with RLi, however, the reaction gave various uncharacterized products, presumably due to the reactions of RLi both with the C–Br bonds and at the 2- and 9-positions. By changing the reactant to RMgBr, we have found that the expected direct substitution reaction at the 2-position proceeds, and herein report the results and some chemical properties of the obtained 2-substituted-3,8-dibromo-Phen.

A THF (8.0 cm³) solution of CH_3MgBr (3.0 M, 2.4 mmol)

was added to a THF (200 cm³) solution of Br_2Phen ^{4b,6} (3.38 g, 1.0 mmol) in a Schlenk tube under N_2 at 0 °C. After the mixture was stirred for 16 h, diluted hydrochloric acid was added, and the product was extracted with chloroform. Purification by column chromatography on SiO_2 (eluent = chloroform) gave a yellowish white powder of 2-methyl- Br_2Phen (1.2 g, 34%), $\text{Br}_2\text{Phen-2Me}$. ¹H NMR (CDCl_3): δ : 9.19 (d, 2.4 Hz, 1H), 8.40 (s, 1H), 8.39 (d, 2.4 Hz, 1H), 7.73 (d, 8.8 Hz, 1H), 7.68 (d, 8.8 Hz, 1H), 3.05 (s, 3H). Anal. Found: C, 44.38; H, 2.43; N, 7.89; Br, 45.38%. Calcd for $\text{C}_{13}\text{H}_8\text{Br}_2\text{N}_2$: C, 44.35; H, 2.29; N, 7.98; Br, 45.40%. Similar reactions using PhMgBr , HexMgBr (Hex = hexyl), and NonMgBr (Non = nonyl) gave the corresponding 2-substituted 3,8-dibromo-1,10-phenanthrolines ($\text{Br}_2\text{Phen-2R}$'s).⁸



Although mono-substituted Phen's with alkyl or aryl group at the 2-position have been prepared by a ring closure reaction using 8-aminoquinolines and substituted acroleins,⁹ preparation of $\text{Br}_2\text{Phen-2R}$ has no precedent. Preparation of $\text{Br}_2\text{Phen-2R}$ by the conventional method seems to be difficult because of difficulty to prepare the corresponding starting materials.

Obtaining $\text{Br}_2\text{Phen-2R}$ by the direct substitution reaction of Br_2Phen with the Grignard reagents will expand the scope of the chemistry of Phen. Further reaction of $\text{Br}_2\text{Phen-2Me}$ with CH_3MgBr (in a 1:2.4 molar ratio under conditions described above) gave a product which was assigned to 2,9-dimethyl-3,8-dibromo-Phen from its ¹H NMR spectrum (δ : 8.38 (s, 2H), 7.67 (s, 2H), and 3.04 (s, 6H)). However, the product was contaminated with $\text{Br}_2\text{Phen-2Me}$ (about 20 mol %), and separation of the two compounds was not possible. The mono-alkylation of Br_2Phen seems to proceed through a Grignard type reaction at the $\text{C}=\text{N}$ -bond, similar to the case of di-alkylation of Phen illustrated in Eq 1. Although the $\text{C}=\text{N}$ - group in heteroaromatic compounds is considered to have different reactivity from that of usual imine group due to the aromatization effect, the obtained results indicate the $\text{C}=\text{N}$ - group in Phen's has reactivity toward organometallic compounds, similar to usual imine groups.

$\text{Br}_2\text{Phen-2R}$'s exhibit UV-vis absorption peaks (λ_{max} = 278, 291, 279, and 279 nm for R = Me, Ph, Hex, Non, respectively) at the position with somewhat longer wavelength, compared with the corresponding non-brominated mono-substituted Phen's, Phen-2R's (e.g., λ_{max} = 285 nm for R = Ph).⁹

Addition of an acetonitrile solution of CuCl_2 to a chloroform solution of $\text{Br}_2\text{Phen-2Me}$ led to a shift of the π - π^* transition

peak to 286 nm with an isosbestic point at 281 nm. A new band appeared at 337 nm, which was assigned to an MLCT band, was located at a longer wavelength than that (298 nm) observed with a Phen–Cu(II) complex formed under similar reaction conditions, reflecting a stronger electron accepting properties of Br₂Phen-2Me than Phen. Phen usually forms a 2:1 complex with Cu(II) in the presence of excess Phen,¹⁰ the UV–vis changes observed with the Phen–CuCl₂ system agreeing with the reported results; the UV–vis changes saturated at a molar ratio of 2:1 on addition of CuCl₂, and further addition of CuCl₂ brought about new changes in the UV–vis spectrum presumably due to formation of a 1:1 complex by the reaction of the 2:1 complex with CuCl₂. On the contrary, the UV–vis changes observed with the CuCl₂–Br₂Phen-2Me system were simply explained by formation of a 1:1 complex even in the presence of an excess amount of Br₂Phen-2Me. The equilibrium constant was estimated at about $1.5 \times 10^6 \text{ M}^{-1}$ at room temperature (about 25 °C) from the UV–vis changes. The formation of a 2:1 complex seems to be retarded by a steric effect of the 2-Me group.

One of important use of Br₂Phen-2R will be the preparation of new π -conjugated polymers of 2-substituted Phen. Dehalogenative polycondensation of Br₂Phen-2Non with a zerovalent nickel complex^{4b-d} (a mixture of bis(1,5-cyclooctadiene)nickel(0), Ni(cod)₂, and 2,2'-bipyridyl, bpy) proceeded well,¹¹ similar to the case of dehalogenative polycondensation of 3,8-dibromo-1,10-phenanthroline.^{4b-d} Although non-substituted poly(1,10-phenanthroline-3,8-diyl)^{4b,c} was soluble only in acidic solvents such as formic acid, the obtained polymer with the 2-Non group, PPhen(2-Non),¹¹ was soluble in common organic solvents such as THF and chloroform due to the alkyl substitution effects and the polymer was amorphous as proved by its powder X-ray diffraction pattern. The polymer was considered to have a regio-random structure with head-to-tail and head-to-head units, which explained the amorphous structure of the polymer in the solid. The amorphous structure is usually advantageous for application of π -conjugated polymers to light emitting diodes, since such a polymer has that lower tendency to provide energy-decay routes by forming excimer-like adducts which is disadvantageous for the light emitting diode. PPhen(2-Non) exhibited photoluminescence with peak emission at 389 nm and quantum efficiency of 25% in chloroform. The quantum yield was improved from that (4%) of previously reported poly(5,6-dialkoxy-1,10-phenanthroline-3,8-diyl).^{4c}

As described above, 2-substituted 3,8-dibromophenanthrolines, Br₂Phen-2R, which are expected to serve as a ligand and starting materials for functional materials, can be prepared by direct alkylation and phenylation of Br₂Phen.

We are grateful to Mr. T. Iijima of our laboratory and Mr. M. Takeuchi of Showa Denko K. K. for helpful discussion and experimental support.

References and Notes

- 1 a) M. Munakata, L. P. Wu, and T. Kuroda-Sowa, *Adv. Inorg. Chem.*, **46**, 173 (1999). b) S. Kitagawa and M. Kondo, *Bull. Chem. Soc. Jpn.*, **71**, 1739 (1998). c) R. P. Kingsborough and T. M. Swager, *Prog. Inorg. Chem.*, **48**, 123 (1999).
- 2 T. Tsutsui, N. Nakada, S. Saito, and E. Ogino, *Appl. Phys. Lett.*, **65**, 1868 (1994).
- 3 G. Bidan, B. Divisia-Blohom, M. Lapkowski, J.-M. Kern, and J.-P. Sauvage, *J. Am. Chem. Soc.*, **114**, 5958 (1992).
- 4 a) H. S. Joshi, R. Jamshidi, and Y. Tor, *Angew. Chem., Int. Ed.*, **38**, 2722 (1999). b) Y. Saitoh and T. Yamamoto, *Chem. Lett.*, **1995**, 785. c) T. Yamamoto, Y. Saitoh, K. Anzai, H. Fukumoto, T. Yasuda, Y. Fujiwara, B.-K. Choi, and K. Kubota, *Macromolecules*, **36**, 6722 (2003). d) T. Yasuda and T. Yamamoto, *Macromolecules*, **36**, 7513 (2003). e) M. Al-Higari, E. Birckner, B. Heise, and E. Klemm, *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 4442 (1999).
- 5 C. O. Dietrich-Buchecker, P. A. Marnot, and J. P. Sauvage, *Tetrahedron Lett.*, **23**, 5291 (1982).
- 6 Y. Saitoh, T. Koizumi, K. Osakada, and T. Yamamoto, *Can. J. Chem.*, **75**, 1336 (1997).
- 7 G. R. Newkome and W. W. Paudler, "Contemporarybrack-Heterocyclic Chemistry," John Wiley, New York (1982).
- 8 R = Ph: yield = 25%. Anal. Found: C, 52.04; H, 2.18; N, 6.75; Br, 38.62%. Calcd for C₁₈H₁₀Br₂N₂: C, 52.21; H, 2.43; N, 6.77; Br, 38.59%. R = Hex: yield = 12%. Anal. Found: C, 51.04; H, 4.46; N, 6.65%. Calcd for C₁₈H₁₈Br₂N₂: C, 51.21; H, 4.30; N, 6.64; Br, 37.86%. R = Non: yield = 9%. Anal. Found: C, 54.32; H, 5.33; N, 6.06; Br, 34.42%. Calcd for C₂₁H₂₄Br₂N₂: C, 54.33; H, 5.21; N, 6.03; Br, 34.42%. NMR data agreed with the structures of the products.
- 9 a) P. Belser, S. Bernhard, and U. Guerig, *Tetrahedron*, **52**, 2937 (1996). b) C. Bonnefous, A. Chouai, and R. P. Thummel, *Inorg. Chem.*, **40**, 5851 (2001). c) H. Irving, M. J. Cabell, and D. H. Mellor, *J. Chem. Soc.*, **1953**, 3417. d) R. W. Sonntag, *Inorg. Chem.*, **19**, 1977 (1980).
- 10 a) C. M. Harris, T. N. Lockyer, and H. Wateman, *Nature*, **192**, 425 (1961). b) J. Hall, N. Marchant, and R. A. Plownam, *Aust. J. Chem.*, **16**, 34 (1963).
- 11 Reaction conditions: Br₂Phen-2Non:Ni(cod)₂ = 1:1.33 molar ratio at 60 °C in DMF for 36 h. PPhen(2-Non): ¹H NMR (CDCl₃): δ : 9.8–9.4 (m, 1H, H at the 9-position), 8.7–8.1 (m, 2H, Hs at the 4,7-positions), 8.0–7.5 (2H, Hs at the 5,6-positions), 3.4–2.8 (m, 2H), 2.1–1.7 (m, 2H), 1.7–0.6 (m, 15H). Elemental analysis indicated that the polymer contained no bromine. IR data of the polymer agreed with the structure of poly(2-nonyl-1,10-phenanthroline-3,8-diyl). Number- and weight-averaged molecular weights = 8300 and 11000, respectively, as determined by gel permeation chromatography (eluent = hexafluoroisopropanol). Yield = 51%; a part of the polymer seemed to be lost during repeated reprecipitation (THF-aqueous ammonia (twice), THF-dil. (2–3 M) hydrochloric acid (twice), THF-aqueous ammonia (twice), and THF-H₂O).