Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2009, **19**, 101–102
Mendeleev Communications

Synthesis and phosphorylation of 2,2′,7,7′-tetra(phenylamino)-1,1′-binaphthalene

Edward E. Nifant'ev,[a] Vera I. Maslennikova,*[a] Lyudmila V. Shelenkova,[a] Irina I. Levina[b] and Dmitrii M. Polekhin[a]

[a] *Department of Chemistry, Moscow State Pedagogical University, 119021 Moscow, Russian Federation. Fax: +7 499 248 0162; e-mail: him-vim@mail.ru*
[b] *N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 137 4101; e-mail: ibcp@sky.chph.ras.ru*

DOI: 10.1016/j.mencom.2009.03.017

The reaction of 2,2′,7,7′-tetrahydroxydinaphthylmethane with aniline in the presence of aniline salts involves the rupture of C–C bonds and the elimination of a methylene bridge and is completed by the formation of 2,2′,7,7′-tetra(phenylamino)-1,1′-binaphthalene, the phosphorylation of which with 2-chloro-1,3,2-dioxaphosphinane and dichloroisopropyl phosphite yields original polycyclic phosphamide architectures.

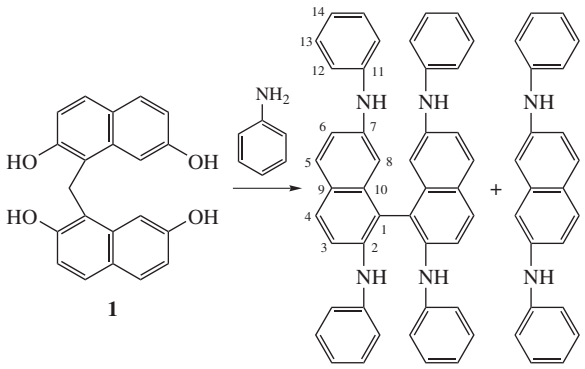
Due to high complexation ability, polyaminoaromatic compounds are perspective building blocks for the design of complex supramolecular systems.[1] The most easy and convenient synthesis of these substances is the amination of polyhydroxyaromatic analogues. The direct transformation of phenols and naphthols to corresponding amino derivatives is performed using numerous methods differing in reagents, preferred substrates and techniques.[2–9] However, the substitution of an amino group for hydroxyl is of practical importance only for the simplest derivatives of naphthalene and resorcinol. The amination of more complicated hydroxyl aromatic compounds is still not understood.

In this work, 2,2′,7,7′-tetrahydroxydinaphthylmethane **1** was used as a substrate for amination. The point of departure in our work was the use of a German patent of 1893,[10] which indicated the possibility of amination of tetrahydroxydinaphthylmethane **1**, but the structure of tetraamination products was not established. The method is easy for carrying out, and it does not require expensive reagents and catalysts.

According to the patented procedure,[10] a mixture of dinaphthylmethane **1**, aniline, and aniline hydrochloride was heated to 200 °C for 6 h. The study of the isolated products by NMR spectroscopy† and mass spectrometry showed that the reaction proceeded unusually, with the rupture of C–C bonds and the elimination of a methylene bridge. A new C–C bond formed between two α-naphthyl fragments. Finally, the reaction was completed by the formation of 2,2′,7,7′-tetra(phenylamino)-1,1′-binaphthalene **2** (green powder, mp 132–134 °C) (Scheme 1).

Signals of aromatic protons and NH groups were detected in the ^{1}H NMR spectrum of binaphthalene **2**, and only signals from carbon atoms of aromatic rings were identified in its ^{13}C NMR spectrum. No signals of methylene bridge atoms were found in any of these spectra.

Along with binaphthalene **2**, a small amount of 2,7-bis(phenylamino)naphthalene **3** was present in the reaction mixture. The yield of tetraamine **2** was 38.4%, and that of diamine **3** was 3%.



1 **2** **3**

Scheme 1

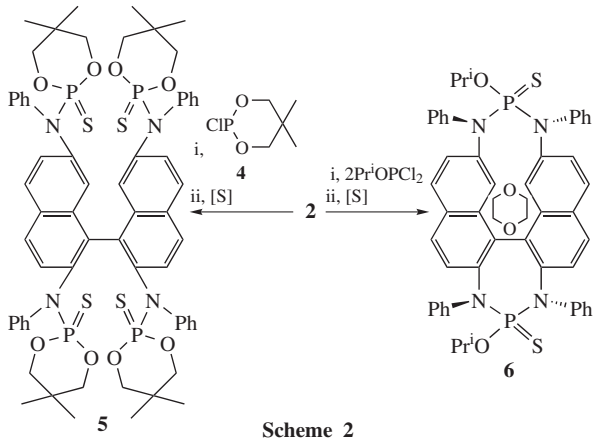
The microwave irradiation of the reaction mixture increased the yield of binaphthalene **2** to 51%, reduced the reaction time to 2 h and decreased the process temperature to 145 °C.‡ However, the yield of compound **3** also increased proportionally. When aniline hydrochloride was replaced by aniline hydrophosphite, no diamine **3** was found in the reaction mixture, but the amount of gum increased appreciably, which decreased the yield of target compound **2** to 26%.

Since oligophosphorylated derivatives of **2** may be useful for the design of macroheterocyclic receptor systems and ligands for metal complex catalysts, we started investigating the phosphorylation of this compound. In distinction from tetrahydroxydinaphthylmethane **1**,[11,12] tetraaminobinaphthalene **2** did not react with phosphorous amides in the temperature range 20–100 °C. The ^{31}P NMR spectra of reaction mixtures remained unchanged for a month. Therefore, trivalent phosphorus acid chlorides, which have a higher reactivity, were used as reagents in this case.

The phosphorylation of binaphthalene **2** by 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphinane **4** was performed in acetonitrile in the presence of triethylamine at 20–25 °C and the reagent ratio **2**:**4** = 1:6 (Scheme 2).

† ^{1}H NMR ([$^2H_6$]acetone) δ: 6.89 (tt, 4H, H^{14}, $^3J_{HH}$ 7.4 Hz, $^4J_{HH}$ 2.1 Hz), 7.09 (dd, 4H, $H^{3,6}$, $^3J_{HH}$ 8.9 Hz, $^4J_{HH}$ 2.1 Hz), 7.23–7.30 (m, 16H, $H^{12,13}$), 7.34 (d, 2H, H^8, $^4J_{HH}$ 2.2 Hz), 7.53 (br. s, 4H, NH), 7.64 (d, 4H, $H^{4,5}$, $^3J_{HH}$ 8.8 Hz). ^{13}C NMR ([$^2H_6$]acetone) δ: 109.80 (s, C^{12} or C^{16}), 117.80 (s, C^1 or C^8), 118.49 (s, C^{14}), 121.16 (s, C^3 or C^6), 125.10 (s, C^{10}), 129.42 (s, C^4 or C^5), 129.91 (s, C^{13} or C^{15}), 136.97 (s, C^9), 142.69 (s, C^2 or C^7), 144.24 (s, C^{11}). MS (MALDI), *m/z*: 618 [M$^+$], 619 [M + H$^+$].

‡ Reactions were performed in a Bruker MWS-3 microwave digestion system with optical temperature control.



Scheme 2

At the end of the reaction, the signal of phosphinane **4** with δ 147 ppm disappeared and a singlet with δ 120 ppm appeared in the ^{31}P NMR spectrum of the reaction mixture. Sulfur was added to the resulting product without isolation from the reaction mixture. The data of elemental analysis, MALDI, and ^{1}H NMR spectroscopy for the synthesized compound corresponded to those of perphosphorylated derivative **5**.§ The yield of thionamidophosphate **5** (white powder, mp 186–188 °C) was 54%.

To obtain a more complex architecture, we studied the reaction of binaphthalene **2** with dichloroisopropyl phosphite at the reagent ratio **2**:Pr^{i}OPCl$_2$ = 1:2 (Scheme 2). The reaction proceeded in pyridine at room temperature for 4 h. After the completion of phosphorylation, which was evidenced by the disappearance of isopropyldichlorophosphite signal with δ 181 ppm from the ^{31}P NMR spectrum of the reaction mixture and the appearance of a singlet signal at 160 ppm, sulfur was added to the reaction mixture. Cyclophosphorylated product **6** (brown oil) was isolated using column chromatography, but its yield was only 5%. Studies of **6** by mass spectrometry and ^{1}H NMR spectroscopy have shown that compound **6** formed a dioxane complex. Dioxane was shielded by the field of aromatic rings of macrocycle **6**, that results in big signal shift for the methylene protons toward the high-field region ($\Delta\delta$ –2.46).¶

This work was supported in part by the Russian Foundation for Basic Research (project no. 06-03-32354a).

References

1 J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, J. Wiley & Sons, Chichester, 2000.
2 N. L. Drake, *Org. React.*, 1942, **1**, 105.
3 K. Tang and H. Zhang, *Tetrahedron Lett.*, 2002, **43**, 7163.
4 A. Canete, M. X. Melendrez, C. Saitz and A. L. Zanocco, *Synth. Commun.*, 2001, **31**, 2143.
5 Z. Liu and R. C. Larock, *J. Org. Chem.*, 2006, **71**, 3198.
6 J. Louie, M. S. Driver, B. C. Hamann and J. F. Hartwig, *J. Org. Chem.*, 1997, **62**, 1268.
7 J. Ahman and S. L. Buchwald, *Tetrahedron Lett.*, 1997, **38**, 6363.
8 E. S. Semichenko, A. L. Gomonova, N. A. Gavrilova and G. A. Suboch, *Zh. Org. Khim.*, 2008, **44**, 659 (*Russ. J. Org. Chem.*, 2008, **44**, 647).
9 E. Yu. Belyaev and B. V. Gidaspov, *Aromaticheskie nitrozosoedineniya* (*Aromatic Nitroso Compounds*), Teza, St. Petersburg, 1996, p. 208 (in Russian).
10 *DAHL and COMP in BARMEN*, Patent Fortschr Tecrfabenfarb, Verw. Industrierweige, DE 75755, 1893.
11 V. I. Maslennikova, T. Yu. Sotova, L. K. Vasyanina, K. A. Lyssenko, M. Yu. Antipin, S. O. Adamson, A. I. Dementyev, W. D. Habicher and E. E. Nifantyev, *Tetrahedron*, 2007, **63**, 4162.
12 E. E. Nifant'ev, V. I. Maslennikova, T. Yu. Sotova, L. K. Vasyanina and L. V. Shelenkova, *Dokl. Akad. Nauk*, 2007, **414**, 343 [*Dokl. Chem.* (*Engl. Transl.*), 2007, **414**, 132].

Received: 15th October 2008; Com. 08/3228

§ ^{31}P NMR (MeCN) δ: 65.3. ^{1}H NMR ([$^2H_6$]acetone) δ: 0.69 (s, 12H, Me), 0.88 (s, 12H, Me), 3.80 [dd, 8H, OCH$_2$(e), $^2J_{HH}$ 21.6 Hz, $^3J_{PH}$ 11.3 Hz], 4.34 [dd, 8H, OCH$_2$(a), $^3J_{PH}$ 7.3 Hz], 7.22 (t, 4H, H^{14}, $^3J_{HH}$ 8.8 Hz), 7.33 (dd, 8H, H^{13}, $^3J_{HH}$ 7.3 Hz, $^4J_{HH}$ 2.2 Hz), 7.44–7.49 (m, 8H, H^{12}, 4H, H^{3,6}), 7.73 (d, 4H, H^{4,5}, $^3J_{HH}$ 8.8 Hz), 7.83 (s, 2H, H^8). MS (MALDI), *m*/*z*: 1195 [M – Ph].

¶ ^{31}P NMR (CHCl$_3$) δ: 63.2. ^{1}H NMR (CDCl$_3$) δ: 1.06 (d, 6H, CH*Me*, $^3J_{HH}$ 6.0 Hz), 1.25 (s, 8H, OCH$_2$ dioxane), 1.30 (d, 6H, CH*Me*, $^3J_{HH}$ 6.4 Hz), 4.81 (m, 2H, C*H*Me$_2$, $^3J_{PH}$ 10.7 Hz), 6.98 (tt, 4H, H^{14}, $^3J_{HH}$ 7.4 Hz, $^4J_{HH}$ 1.3 Hz), 7.16 (dd, 4H, H^{3,6}, $^3J_{HH}$ 7.7 Hz), 7.23–7.31 (m, 16H, H^{12,13}), 7.38 (d, 2H, H^8, $^4J_{HH}$ 2.2 Hz), 7.66 (d, 4H, H^{4,5}, $^3J_{HH}$ 8.4 Hz). MS (MALDI), *m*/*z*: 992 [M + $C_4H_8O_4$].