ISSN 1070-4280, Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 8, pp. 1200–1202. © Pleiades Publishing, Inc. 2006.
Original Russian Text ©A.B. Zdravkova, N.N. Khimich, 2006, published in Zhurnal Organicheskoi Khimii, 2006, Vol. 42, No. 8, pp. 1219–1221.

Bromination of 2,2'-Bipyridile

A.B. Zdravkov[a] and N.N. Khimich[b]

[a]*St. Petersburg State University, St. Petersburg, Russia*
[b]*Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, St. Petersburg,199155 Russia*
e-mail: Khimich@isc.nw.ru

Received July 12, 2005

Abstract—A simple and convenient procedure was developed for the synthesis of 5,5'-dibromo-2,2'-bipyridyl providing the target compound in a high yield without the chromatographic separation of the reaction mixture. Polybromo derivatives of 2,2'-bipyridyl were isolated and characterized for the first time.

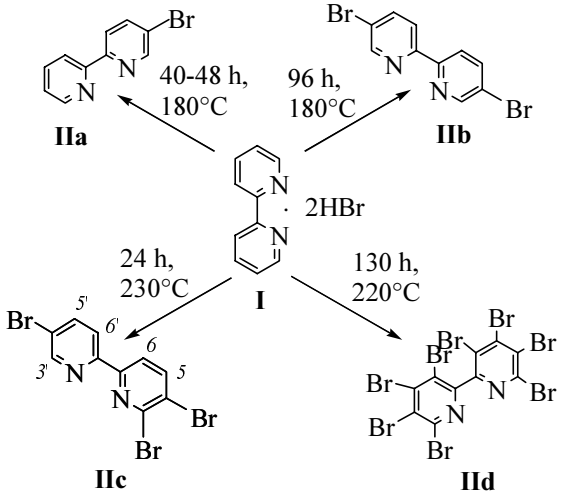
DOI: 10.1134/S1070428006080161

2,2'-Bipyridyl and its derivatives are used in preparation of transition metals bis-, tris-, and tetrakis(2,2'-bipyridyl) complexes possessing interesting photophysical, photochemical, and electrochemical properties [1–3]. The practical application of the mentioned complexes involves their insertion into a polymeric (organic or inorganic) matrix [4, 5]. The optical nanohybride materials formed (films, fibers, sol-gel glasses etc.) have a strength and a stability sufficient for their application only when the components of the system are mutually bound. The problem of the chemical binding of the complex to the polymer matrix can be solved if one of the ligands in the complex contains the 2,2'-bipyridyl with a reactive functional group.

Several methods are described for preparation of such compounds. The first procedure consists in the synthesis of substituted 2,2'-bipyridyl from 2-bromopyridines as developed by Fried and Elderfield [6]. However this reaction permits only the preparation of dialkyl derivatives in a very small yield. The modern modification of the Fried–Elderfield reaction, Negishi synthesis [7–9] provides a possibility to synthesize alkyl-, aryl-, ethynyl-, carboxy-, alkoxy-, and nitrile derivatives in high yields (55–90%) but this method has a considerable disadvantage: It is labor-consuming. Besides some reagents used in the synthesis are expensive and difficultly available.

One more approach involves a substitution of a C–H bond in the 2,2'-bipyridyl proper. Three methods of introducing substituents into 2,2'-bipyridyl are known nowadays: nitration, sulfonation, and bromination. The former two have significant drawbacks: the nitro derivatives form in low yields [10, 11], and the sulfonation is poorly reproducible [12, 13]. In this connection the bromination seems much more promising, and besides the recently developed methods of direct bromine substitution in mono- and dibromo derivatives of 2,2'-bipyridyla by an ester [14] and ethynyl [15] groups essentially raise the synthetic importance of the bromination. The bromination of 2,2'-bipyridyl was first carried out in 1938 by two methods: by direct heating of the components at 500°C, and by analogous reaction of 2,2'-bipyridyl hydrobromide in bromine vapor at 250°C [16]. Thus Burstall believed to prepare for the first time, although in a very low yield, 5- and 6-monobromo- and 5,5'- and 6,6'-dibromo-2,2'-bipyridyls. A modern modification of 2,2'-bipyridyl hydrobromide bromination was developed in 1995 [17]. It was shown that bromine atoms replaced the hydrogen only in the positions *5* and *5'*; here the 5- and 5,5'-substituted compounds were isolated in 40–50% yields. The essential disadvantage of this process is its laboriousness. The 2,2'-bipyridyl hydrobromide is obtained by the reaction of 2,2'-bipyridyl with anhydrous gaseous HBr; the developed workup of the reaction mixture is relatively complicated, and the main separation and purification procedure for the reaction products is column chromatography. Therefore the goal of the present work was the optimization of all synthesis stages for preparation of 5,5'-dibromo-2,2'-bipyridyl starting with obtaining the 2,2'-bipyridyl hydrobromide, through workup of the reaction mixture to isolation of the reaction product in an analytically pure state without subjecting it to chromatography. We also demonstrated that at raising

the reaction temperature and time occurred further bromination of 5,5'-dibromo-2,2'-bipyridyl, and thus we for the first time isolated and characterized polybromo derivatives of 2,2'-bipyridyl.



The structure of the newly synthesized bromides was established by means of ^{1}H and ^{13}C NMR spectroscopy, and the composition was confirmed by elemental analysis. The melting points and ^{1}H NMR spectra of mono- and dibromides obtained were consistent with the published data [17].

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker DPX-300 (at 300.13 and 75.5 MHz respectively) from solutions of compounds in DMSO-d_6 or $CDCl_3$, internal reference TMS. ^{13}C NMR spectrum of perbromide **IId** was registered in concn. H_2SO_4, internal reference DMSO-d_6. Elemental analysis was carried out on a CHN analyzer Hewlett Packard 185B. The bromine content in perbromo-2,2'-bipyridyl was determined by Scheniger burn/titration method [titration with solution of mercury(II) nitrate]. The purity of compounds obtained was checked by TLC on Silica Gel 60 $_{F254}$ plates. The separation by column chromatography was performed using silica gel L40/60 (40–60 μm).

2,2'-Bipyridyl hydrobromide (I). To 40 ml of solution of 10 g (64 mmol) of 2,2'-bipyridyl in methanol was added 29 g (2.2 equiv) of 40% water solution of HBr. The solvent was distilled off in a vacuum, the residue was dried at 120°C for 12 h. Yield 20.08 g (98%).

General bromination procedure for 2,2'-bipyridyl. A mixture of 2,2'-bipyridyl hydrobromide and bromine was maintained in a pressure reactor of stainless steel with the Teflon lining. The reaction time and temperature is given on the scheme. The cooled molten product was recrystallized from 40 ml of boiling DMF. The crystals and filtrate obtained on cooling were neutralized with a aqueous-alcoholic KOH solution and worked up as described further.

5-Bromo-2,2'-bipyridyl (IIa) was obtained from 18 g (56.6 mmol) 2,2'-bipyridyl hydrobromide and 20 g (0.125 mmol) of bromine. The crystals obtained by the general procedure were dissolved in 15 ml of DMF and reprecipitated with 60 ml of ethanol to obtain 3.8 g (21%) of analytically pure 5,5'-dibromo-2,2'-bipyridyl. Filtrate (DMF–ethanol) was diluted with a three-fold volume of water, the separated crystals were filtered off to obtain 2.7 g (20%) of analytically pure compound **IIa**.

5,5'-Dibromo-2,2'-bipyridyl (IIb) was obtained from 12 g (37.7 mmol) of 2,2'-bipyridyl hydrobromide and 20 g (125 mmol) of bromine. The crystals obtained were dissolved in 15 ml of DMF and reprecipitated with 60 ml of ethanol to obtain 6.35 g (53.6%) of analytically pure compound **IIb**.

5,5',6-Tribromo-2,2'-bipyridyl (IIc) was obtained from 5 g (15.6 mmol) of 2,2'-bipyridyl hydrobromide and 15 g (93.8 mmol) of bromine. To the filtrate obtained by the general procedure was added 300 ml of water. The crystals formed were filtered off and subjected to column chromatography. The isolated product was twice recrystallized from toluene. Yield 280 mg (4.5%), mp 175–177°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.95 d.d (1H, H^{52}, J_1 2.5, J_2 8.5 Hz), 8.01 d (1H, H^{62}, J 8.5 Hz), 8.24 d (1H, H^5, J 8.5 Hz), 8.30 d (1H, H^6, J 8.5 Hz), 8.71 d (1H, $H^{3'}$, J 2.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 121.1, 122.5, 123.0, 124.4, 140.1, 142.9, 143.3, 150.8, 152.7, 154.8. Found, %: C 30.65; H 1.49; N 7.07. $C_{10}H_5Br_3N_2$. Calculated, %: C 30.55; H 1.28; N 7.13.

Perbromo-2,2'-bipyridyl (IId) was obtained from 4 g (12.5 mmol) of 2,2'-bipyridyl hydrobromide and 20 g (125 mmol) of bromine. The crystals obtained were twice recrystallized from toluene. Yield 0.9 g (7.5%). To the neutralized filtrate was added 300 ml of water. The separated precipitate was filtered off, dissolved in 30 ml of chloroform and reprecipitated into 60 ml of ethanol. The precipitate was twice recrystallized from toluene. Thus were obtained 5 g more of perbromo-2,2'-bipyridyl (overall yield 50%), mp 303–305°C. ^{13}C NMR spectrum (H_2SO_4), δ, ppm: 128.4, 136.8, 138.7, 139.7, 155.8. Found, %: C 15.68; Br 81.12; N 3.19. $C_{10}Br_8N_2$. Calculated, %: C 15.25; Br 81.19; N 3.56.

The authors are grateful to E.G. Rumyantseva for performing the elemental analyses.

The study was carried out under a financial support of the Russian Foundation for Basic Research (grant no. 06-03-33002-a).

REFERENCES

1. Ikeda, S. and Senna, M., *J. Mater. Chem*., 2004, vol. 14, no. 6, p. 1071.
2. Farah, A.A., Veinot, J.G.C., Najman, M., and Pietro, W.J., *Pure Appl. Chem*., 2000, vol. A37, vol. 11, p. 1507.
3. Harriman, A., Ziessel, R., Moutet, J-C., and Saint-Aman, E., *Phys. Chem. Chem. Phys*., 2003, vol. 5, no. 8, p. 1593.
4. Matsui, K. and Momose, F., *Chem. Mater*., 1997, vol. 9, p. 2588.
5. Ahmad, M., Mohammad, N., and Abdullah, J., *J. Non-Cryst. Sol*., 2001, vol. 290, p. 86.
6. Fried, J. and Elderfield, R.C., *J. Org. Chem*., 1941, vol. 6, p. 567.
7. Smith, A.P., Savage, S.A., Love, J.C., and Fraser, C.L., *Org. Synth*., 2002, vol. 78, p. 51.
8. Lutzen, A. and Hapke, M., *Eur. J. Org. Chem*., 2002, p. 2292.
9. Lutzen, A. and Hapke, M., *Eur. J. Org. Chem*., 2003, p. 3948.
10. Haginiva, J., *J. Pharm. Soc. Jpn*., 1955, vol. 75, p. 731.
11. Maerker, M. and Case, F.H., *J. Am. Chem. Soc.,* 1958, vol. 80, p. 2745.
12. Pirzada, N.H., Pojer, P.M., and Summers, L.A., *Z. Naturforsch*., 1976, vol. 31b, p. 115.
13. Ostroshchenko, O.S., Kurbatov, Yu.V., and Sadykov, A.S., *Nauchn. Tr. Tashkentsk. Gos. Un.,* 1964, vol. 263, p. 27.
14. Ziessel, R., *J. Org. Chem*., 2000, vol. 65, p. 7757.
15. Groshenny, V., Romero, F.M., and Ziessel, R., *J. Org. Chem*., 1997, vol. 62, p. 1491.
16. Burstall, F.H., *J. Chem. Soc.,* 1938, p. 1662.
17. Romero, F.M. and Ziessel, R., *Tetrahedron Lett.,* 1995, vol. 36, p. 6471.