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BRIEF COMMUNICATIONS

Synthesis of Di- and Triazido Derivatives of 2,4,6-Triphenylpyridine

T. N. Gavrishova, V. M. Li, and M. F. Budyka

Institute of Chemical Physics Problems, Russian Academy of Sciences, Chernogolovka, Russia

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Abstract—The possibility of obtaining new di- and triazidophenylpyridines: 4-phenyl-2,6-bis(4-azidophenyl) pyridine and 2,4,6-tris(4-azidophenyl)pyridine by a three-stage synthesis from commercially available compounds was studied.

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Aromatic azides, owing to their photochemical activity, are widely used for obtaining heterocyclic compounds [1], photoresists [2], monomers [3], and as photoaffine scores [4].

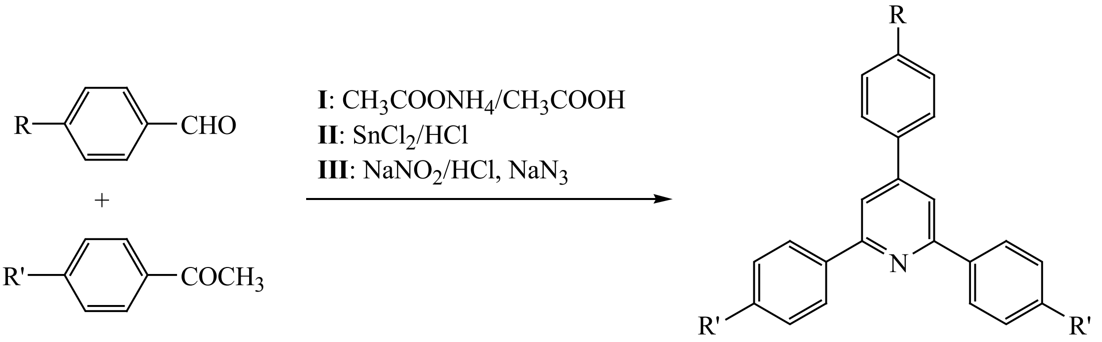
Recently attention of a number of researchers is attracted by heteroaromatic polyazides. Di- and triazidopyridines are used to generate quintet dinitrenes and septet trinitrenes [5, 6], and azidotriazines are applied as high-energy compounds [7, 8].

Using commercially available compounds (nitroacetophenone and a corresponding benzaldehyde), in the present work we have synthesized in three-stages di- and triazido derivatives of 2,4,6-triphenylpyridine (TPP) with azido groups in the *para*-position of phenyl rings: 4-phenyl-2,6-bis (4-azidophenyl)pyridine (**IIIa**) and 2,4,6-tris(4-azidophenyl)-pyridine (**IIIb**) (see the scheme).

These compounds are of interest for the study of the size effect in aromatic azides [9] and a selective photolysis of nonequivalent azido groups [10], they can be used as a support for obtaining cross-linked polymers and dendrimers [11]. High-spin polynitrenes, products of the photolysis of azides (**IIIa**) and (**IIIb**) are interesting subjects for studying regularities in the interaction of nitrene centers through an aromatic π-system and the effects of mutual orientation of nitrene centers on the spin-spin interaction [12].

To construct the triphenylpyridine framework, we used Kronke's reaction, which is a modification of the synthesis of pyridines after Chichibabin [13]. The method consists in the condensation of arylalcylketones with aromatic aldehydes in the presence of ammonium acetate in ice acetic acid [14]. To reduce the reaction duration and to increase

Scheme.



R = H, R' – NO_2 (**Ia**); R = H, R' – NH_2 (**IIa**); R = H, R' – N_3 (**IIIa**); R = R' = NO_2 (**Ib**); R = R' = NH_2 (**IIb**); R = R' = N_3 (**III**).

its selectivity, microwave radiation is used [15]. In this work 2,4,6-tris(4-nitrophenyl)pyridine and 4-phenyl-2,6-bis(4-nitrophenyl)pyridine were obtained with a yield of 71 and 64%, respectively, by the procedure given in [14].

To reduce nitro-substituted phenylpyridines up to corresponding aminophenylpyridines, instead of expensive palladium on coal and highly toxic hydrazine hydrate applied in [14], we used $SnCl_2$ in HCl. 4-Phenyl-2,6-bis(4-aminophenyl)pyridine (**IIa**) and 2,4,6-tris(4-aminophenyl)pyridine (**IIb**) were obtained with almost quantitative yields.

The target azides, 4-phenyl-2,6-bis(4-azidophenyl)-pyridine (**IIIa**) and 2,4,6-tris(4-azidophenyl)pyridine (**IIIb**) were obtained with yields of more than 70% by diazotization of amines (**IIa**) and (**IIb**) with the subsequent treatment by sodium azide. The azides represent white crystalline substances decomposing on light.

The IR spectrum of diazide (**IIIa**) contained intensive absorption bands at 2118 and 1281 cm^{-1} characteristic for the azido group and characteristic out-of-plane CH vibrations of the monosubstituted benzene at 759 and 693 cm^{-1}. In the IR spectrum of triazide (**IIIb**), the azido group bands (2127 and 1296 cm^{-1}) were shifted to high frequencies and the out-of-plane CH vibrations of the monosubstituted benzene at 759 and 693 cm^{-1} disappeared. The ^1H NMR spectrum of azide (**IIIa**) contained a singlet of two pyridine protons in the region of 7.84 ppm, a doublet of four *ortho*-protons of azidophenyl groups in the region of 8.21 ppm, a doublet of four *meta*-protons of azidophenyl groups in the region of 7.15 ppm, a doublet of two *ortho*-protons of the phenyl group in the region of 7.84 ppm, and a multiplet of three *para*- and *meta*-protons of the phenyl group in the region of 7.44-7.60 ppm.

The ^1H NMR spectrum of azide (III) contained a singlet of two pyridine protons in the region of 7.78 ppm, a doublet of four *ortho*-protons of azidophenyl groups in the region of 8.19 ppm, a doublet of two *ortho*-protons of an azidophenyl group in the region of 7.72 ppm, and a multiplet of six *meta*-protons of azidophenyl groups in the region of 7.12-7.24 ppm

EXPERIMENTAL

The ^1H NMR spectra were recorded on Varian VXR-400 and Bruker DPX 200 spectrometers (working frequency of 400 and 200 MHz, respectively) in $CDCl_3$ and DMSO-d_6, using TMS as the interior standard. The values of chemical shifts are given on the δ scale (ppm). Electrospray (ES) mass spectra were obtained using an original time-of-flight mass spectrometer with an orthogonal input of ions [16]. The mass spectra were recorded in the mode of positive ions, which represented protonated molecules of analyzed compounds. A self-made electrospray ion source of the “microspray” type with a metal emitter (needle) with the internal diameter of 0.1 mm was used. The end of the emitter was sharpened by means of fine sandpaper. A solution of a sample under study was delivered with a rate of 0.35 μl min^{-1} using a KD Scientific syringe pump. The voltage fed to the electrospray emitter was +2.8 kV.

The IR spectra for solid substances were taken in KBr pellets on a Spectrum BX-2 spectrometer with Fourier transformation, melting points were determined on a Boetius stage with a heating rate of 4 deg min^{-1}.

The TLC analysis was carried out on ALUGRAM SIL G/UV_{254} TLC plates, and the developing process was fulfilled in UV light or in a cell with iodine vapor.

2,4,6-Tris(4-nitrophenyl)pyridine (Ia) and 4-phenyl-2,6-bis(4-nitrophenyl)pyridine (Ib) were obtained by the procedure described in [14] with yields of 71 and 64%, respectively. The physicochemical characteristics (data on melting points, NMR and IR spectra) corresponded to those given in [14, 15].

4-Phenyl-2,6-bis(4-aminophenyl)-pyridine (IIa) and 2,4,6-tris(4-aminophenyl)pyridine (IIb). A mixture of 0.003 mol of a corresponding nitrophenylpyridine and 0.015 mol of $SnCl_2$ in 50 ml of concentrated HCl was heated within 3.5 h, then cooled. The resulting precipitate was filtered, washed out by concentrated hydrochloric acid, and dried up in air. The resulting hydrochloride was treated by an aqueous soda solution; the precipitate was filtered, washed out by water, dried up in a drying box, and recrystallized from ethanol.

Yield of **IIa** 94%, beige crystals, mp 210°C with decomposition (from ethanol) (mp 208°C [1]).

Yield of **IIb** 96%, beige crystals, mp 263°C with decomposition (from ethanol). IR spectrum, ν (cm^{-1}): 3400 cm^{-1} (NH_2). ^1H NMR spectrum (200 MHz, DMSO-d_6, TMS), δ, ppm (*J*, Hz): 7.97 (4H, d, $J = 8.3$, C_6H_4), 7.55–7.80 (4H, pyridine-H, C_6H_4), 6.55–6.80 (6H, m, C_6H_4), 5.45 (2H, br.s, NH_2), 5.39 (4H, br.s, NH_2). Found (%): C 78.76, H 5.89, N 16.03; m/z 353.172, $[M + H]^+$. $C_{23}H_{20}N_4$. Calculated (%): C 78.38, H 5.72, N 15.90; M = 352.169.

4-Phenyl-2,6-bis(4-azidophenyl)pyridine (IIIa) and 2,4,6-tris(4-azidophenyl)pyridine (IIIb). Water, 4 ml, then concentrated hydrochloric acid, 2 ml, were added to 0.50 mmol of corresponding bis- or trisaminophenylpyridine. The resulting solution was cooled to 0°C and diazotized by a $NaNO_2$ solution (1.00 mmol for bis-aminophenylpyridine and 1.50 mmol for trisaminophenylpyridine) in 3 ml of H_2O. Within 30 min the solution was cooled to 1°C, and 0.5 ml of concentrated hydrochloric acid and 1 ml of water were added to it with stirring. Then a solution of 1.00 or 1.50 mmol of NaN_3 in 3 ml of H_2O was added and, within a few minutes of that, an excess amount of an azide. The precipitate was filtered off and twice recrystallized from petroleum ether. White crystals of a corresponding azide were obtained (darken in the course of time).

Yield of **IIIa** 77%, white crystals, mp 128°C with decomposition (from petroleum ether). IR spectrum, ν (cm^{-1}): 2117, 1281 (N_3). ^1H NMR spectrum (400 MHz, $CDCl_3$, TMS), δ, ppm (*J*, Hz): 8.21 (4H, d, $J = 8.7$, C_6H_4), 7.84 (2H, s, pyridine), 7.73 (2H, d, $J = 8.5$, C_6H_5), 7.44–7.60 (3H, m, C_6H_5), 7.16 (4H, d, $J = 8.7$, C_6H_4). Found (%): C 71.14, H 3.75, N 24.98; m/z 390.149, $[M + H]^+$. $C_{23}H_{15}N_7$. Calculated (%): C 70.94, H 3.88, N 25.18, M = 389.139.

Yield of **IIIb** 72%, white crystals, mp 145°C with decomposition (from petroleum ether). IR spectrum, ν (cm^{-1}): 2127, 1296 (N_3). ^1H NMR spectrum (400 MHz, $CDCl_3$, TMS), δ, ppm (*J*, Hz): 8.19 (4H, d, $J = 8.9$, C_6H_4), 7.78 (2H, s, pyridine), 7.72 (2H, d, $J = 8.7$, C_6H_4), 7.12–7.24 (6H, m, C_6H_4). Found (%): C 64.36, H 3.47, N 32.33; *m/z* 431.147, $[M + H]^+$. $C_{23}H_{14}N_{10}$. Calculated (%): C 64.18, H 3.28, N 32.54; M = 430.140.

CONCLUSION

New di- and triazidophenylpyridines have been obtained by the three-stage synthesis from commercially available compounds.

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