ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 9, pp. 1596–1598. © Pleiades Publishing, Ltd., 2012.
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LETTERS TO THE EDITOR

Synthesis of (*E*,*E*)-N^1,N^5-Disubstituted Benzylidenenaphthalene-1,5-diamine

Yu. D. Zhikharko, N. G. Kozlov, and L. I. Basalaeva

Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus, ul. Surganova 13, Minsk, 20072 Belarus
e-mail: yurasz@yandex.by

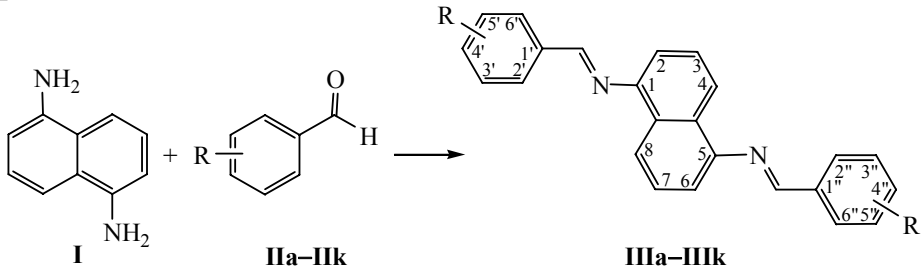
Received March 27, 2012

DOI: 10.1134/S1070363212090277

Schiff bases are widely used in organic synthesis of heterocyclic compounds [1] and secondary amines [2]. They are also applied in electronics to create the liquid-crystal monitors, sensors, and indicators and are used as dyes, luminophores, polymer stabilizers [3–5]. The azomethines also have a wide range of biological activity. The effective antidepressants, anticonvulsants, antimicrobial, hypnotic, psychotropic, nematicide, anticancer and other drugs were created on their basis. Due to the high biological activity and structural similarity with some natural compounds, they are promising to be used as plant protectors [6–10].

Aiming to search for potentially active compounds and to obtain the substrate for the synthesis of new heterocyclic compounds, we synthesized the previously undescribed azomethines of naphthalene series based on 1,5-diaminonaphthalene and mono- or disubstituted benzaldehydes.

The synthesis was performed by the short-time boiling (45–60 min) of a mixture of 1,5-diaminonaphthalene **I** and arylcarbaldehyde **II** in an ethanol solution. The reaction products, N^1,N^5-disubstituted benzylidenenaphthalene-1,5-diamines **IIIa**–**IIIk** were obtained in the yields of 55–97%.



I **IIa–IIk** **IIIa–IIIk**

II, **III**, R = H (**a**), 4-OMe (**b**), 4-NMe_2 (**c**), 4-F (**d**), 4-Cl (**e**), 4-Br (**f**), 4-NO_2 (**g**), 3,4-OCH_2O, (**h**), 3-OMe-4-OH (**i**), 3-OEt-4-OH (**j**), 3-OMe-4-OC(O)Me (**k**).

The composition and structure of the compounds obtained were confirmed by the ^{1}H NMR, IR spectroscopy and elemental analysis.

The IR spectra of compounds **IIIa**–**IIIk** contain the characteristic bands of the stretching and bending vibrations of C–H_{Ar} at 2985–2887 and 815–800 cm^{-1}, respectively. The stretching vibrations of the N=CH bond are registered as three bands of high intensity in the range of 1619–1511 cm^{-1}.

In the ^{1}H NMR spectra of **IIIa**–**IIIk** there is a singlet at 8.59 ppm belonging to the N=HC proton in the *E*-isomers. A doublet at 8.8 ppm was ascribed to the proton at the $C^{4,8}$ atoms of the naphthalene ring. The protons HC^2 and $HC^{3,6,7}$ appear as a doublet at

7.35 ppm and a triplet at 7.48 ppm, respectively. The protons of benzylidene compounds **IIIb**–**IIIg** are registered as two doublet signals at 7.91 ($C^{2',6',2'',6''}$) and 7.43 ppm ($C^{3',5',3'',5''}$). In the ^{1}H NMR spectra of compounds **IIIh**–**IIIk** containing two substituents in the aromatic ring the benzylidene protons signals are present as two doublets of doublets and a singlet at 7.12 ($C^{6',6''}$), 6.95 ($C^{5',5''}$) and 7.67 ppm ($C^{2',2''}$), respectively. The ^{1}H NMR spectrum of compound **IIIa** contains the benzylidene protons signals in the range of 8.04–8.07 ($C^{2',2'',C6',6''}$) and 7.50–7.55 ppm ($C^{3',3'',C4',4'',C5',5''}$), respectively.

According to the ^{1}H NMR spectroscopy, the *E*,*E*-isomer is predominant. The *Z*,*Z*-isomer of azomethine is present in the reaction mixture only in trace amounts. The corresponding signals of the N=HC, $C^{2',6',2'',6''}$ and $C^{3',5',3'',5''}$ protons are shifted upfield by 0.1 ppm owing to the shielding by the naphthalene moiety.

(*E*,*E*)-N^1,N^5-Disubstituted benzilidenenaphthalene-1,5-diamines (IIIa–IIIk) *(general procedure).* A mixture of 0.01 mol of 1,5-diaminonaphthalene **I** and 0.02 mol of arylcarbaldehyde **IIa**–**IIk** was dissolved in 50–100 ml of 96% ethanol and boiled for 45–60 min. The resulting solution was allowed to stand for 20–30 h at a temperature of 20–23°C. The precipitate formed was filtered off on a glass frit filter, washed with a small amount of 96% ethanol, then with diethyl ether, and dried in a vacuum. The resulting compounds **IIIa**–**IIIk** are sufficiently pure, and the recrystallization is not required.

(*E*,*E*)-N^1,N^5-Dibenzylidenenaphthalene-1,5-diamine (IIIa). Yield 85%, dark yellow crystalline solid, mp 190°C. IR spectrum, ν, cm^{-1}: 3081, 3049, 2923, 2823, 1622, 1619, 1579. ^{1}H NMR spectrum, δ_H, ppm: 7.24 d (2H, $C^{2,6}$H, *J* 7.3 Hz), 7.50–7.55 m (6H, $C^{3',3''}$H, $C^{4',4''}$H, $C^{5',5''}$H, 2H, $C^{3,7}$H), 8.04–8.07 m (2H, $C^{2',2''}$H, 2H, $C^{6',6''}$H), 8.15 d (2H, $C^{4,8}$H, *J* 7.4 Hz), 8.69 s (2H, 2HC=N). Found, % C 86.17; H 5.41; N 8.43. $C_{24}H_{18}N_2$. Calculated, %, C 86.20; H 5.43; N 8.38.

(*E*,*E*)-N^1,N^5-Di-(4',4''-methoxybenzylidene)naphthalene-1,5-diamine (IIIb). Yield 69%, brown crystalline solid, mp 201–202°C. IR spectrum, ν, cm^{-1}: 2959, 2833, 1617, 1604, 1576, 1251, 1167, 1023. ^{1}H NMR spectrum, δ_H, ppm: 3.90 s (6H, 2OCH$_3$), 7.02 m (4H, $C^{3',3''}$H, $C^{5',5''}$H), 7.08 d (2H, $C^{2,6}$H, *J* 11.5 Hz), 7.47 t (2H, $C^{3,7}$H, *J* 4.2 Hz), 7.98 d (4H, $C^{2',2''}$H, $C^{6',6''}$H, *J* 9.6 Hz), 8.22 d (2H, $C^{4,8}$H, *J* 9.6 Hz), 8.49 s (2H, HC=N). Found, %: C 79.17; H 5.60; N 7.12 O 8.10. $C_{26}H_{22}N_2O_2$. Calculated, %: C 79.16; H 5.62; N 7.10; O 8.11.

(*E*,*E*)-N^1,N^5-Di-(4',4''-dimethylbenzylidene-amino)naphthalene-1,5-diamine (IIIc). Yield 67%, bright yellow crystalline solid, decomp. 280°C. IR spectrum, ν, cm^{-1}: 3441, 2917, 2854, 1594, 1528, 1371, 1774, 793. ^{1}H NMR spectrum, δ_H, ppm: 3.30 s (12H, CH$_3$), 7.15 d (4H, $C^{3',3''}$H, $C^{5',5''}$H, *J* 7.5 Hz), 7.30 t (2H, $C^{3,7}$H, *J* 5.2 Hz), 7.36 d (4H, $C^{2',2''}$H, $C^{6',6''}$H, *J* 7.8 Hz), 7.43 d (2H, $C^{2,6}$H, *J* 7.4 Hz), 7.65 d (2H, $C^{4,8}$H, *J* 7.7 Hz), 8.37 s (2H, HC=N). Found, %: C 79.94; H 6.75; N 13.31. $C_{28}H_{28}N_4$. Calculated, %: C 79.97; H 6.71; N 13.32.

(*E*,*E*)-N^1,N^5-Di-(4',4''-fluorobenzilidene)naphthalene-1,5-diamine (IIId). Yield 90%, dark yellow crystalline solid, mp 202–203°C. IR spectrum, ν, cm^{-1}: 3063, 3039, 2923, 2877, 2856, 1623, 1591, 1506, 1225, 1150, 1092. ^{1}H NMR spectrum, δ_H, ppm: 7.22 d (2H, $C^{2,6}$H, *J* 7.8 Hz), 7.34–7.37 m (4H, $C^{3',3''}$H, $C^{5',5''}$H, *J* 7.5 Hz), 7.50 t (2H, $C^{3,7}$H, *J* 4.5 Hz), 8.07–8.13 m (4H, $C^{2',2''}$H, $C^{6',6''}$H, 2H, $C^{4,8}$H), 8.66 s (2H, 2HC=N). Found, %: C 77.86; H 4.32; F 10.26; N 7.55. $C_{24}H_{16}F_2N_2$. Calculated, %: C 77.82; H 4.35; F 10.26; N 7.56.

(*E*,*E*)-N^1,N^5-Di-(4',4''-chlorobenzylidene)naphthalene-1,5-diamine (IIIe). Yield 97%, bright yellow crystalline solid, mp 199–200°C. IR spectrum, ν, cm^{-1}: 3035, 2921, 2871, 1622, 1591, 1567, 1084, 1012, 824, 787. ^{1}H NMR spectrum, δ_H, ppm: 7.27 d (2H, $C^{2,6}$H, *J* 8.7 Hz), 7.53 t (2H, $C^{3,7}$H, *J* 5.6 Hz), 7.62 d (4H, $C^{3',3''}$H, $C^{5',5''}$H, *J* 8.7 Hz), 8.07 d (4H, $C^{2',2''}$H, $C^{6',6''}$H, *J* 8.7 Hz), 8.16 d (2H, $C^{4,8}$H, *J* 10.0 Hz), 8.72 s (2H, HC=N). Found, %: C 71.46; H 3.98; Cl 17.60; N 6.96. $C_{24}H_{16}Cl_2N_2$. Calculated, %: C 71.47; H 4.00; Cl 17.58; N 6.95.

(*E*,*E*)-N^1,N^5-Di-(4',4''-bromobenzylidene)naphthalene-1,5-diamine (IIIf). Yield 75%, bright yellow crystalline solid, mp 222–223°C. IR spectrum, ν, cm^{-1}: 3076, 3041, 3020, 2921, 2878, 1621, 1578, 1564, 1065, 1006, 786. ^{1}H NMR spectrum, δ_H, ppm: 7.11 d (2H, $C^{2,6}$H, *J* 8.3 Hz), 7.50 t (2H, $C^{3,7}$H, *J* 5.0 Hz), 7.66 d (4H, $C^{3',3''}$H, $C^{5',5''}$H, *J* 8.6 Hz), 7.90 d (4H, $C^{2',2''}$H, $C^{6',6''}$H, *J* 8.7 Hz), 8.23 d (2H, $C^{4,8}$H, *J* 8.3 Hz), 8.52 s (2H, HC=N). Found, %: C 58.58; H 3.24; Br 32.48; N 5.70. $C_{24}H_{16}Br_2N_2$. Calculated, %: C 58.56; H 3.28; Br 32.47; N 5.69.

(*E*,*E*)-N^1,N^5-Di-(4',4''-nitrobenzilidene)naphthalene-1,5-diamine (IIIg). Yield 76%, red-orange

crystalline solid, mp >300°C. IR spectrum, ν, cm^{-1}: 3095, 3073, 3050, 2923, 2845, 1624, 1597, 1517, 1341, 839, 796. ^1H NMR spectrum, δ_H, ppm: 7.48 t (2H, $C^{3,7}H$, *J* 4.0 Hz), 7.56 d (2H, $C^{2,6}H$, *J* 6.7 Hz), 7.78 d (4H, $C^{3',3''}H$, $C^{5',5''}H$, *J* 7.9 Hz), 7.83 d (2H, $C^{4,8}H$, *J* 8.0 Hz), 8.05 d (4H, $C^{2',2''}H$, $C^{6',6''}H$, *J* 7.9 Hz), 8.76 s (2H, HC=N). Found, % C: 67.95; H 3.81; N 13.18; O 15.06. $C_{24}H_{16}N_4O_4$. Calculated, %: C 67.92; H 3.80; N 13.20; O 15.08.

(*E*,*E*)-N^1,N^5-Di-(benzo[*d*][1,3]dioxol-5-yl-methylene)naphthalene-1,5-diamine (IIIh). Yield 64%, pale yellow crystalline solid, mp 237–238°C. IR spectrum, ν, cm^{-1}: 3069, 3041, 2966, 2903, 2875, 1621, 1599, 1578, 1486, 1447, 1249. ^1H NMR spectrum, δ_H, ppm: 6.12 s (4H, $2OCH_2O$), 7.07 d (2H, $C^{5',5''}H$, *J* 8.2 Hz), 7.19 d (2H, $C^{6',6''}H$, *J* 6.8 Hz), 7.47–7.50 m (2H, $C^{2,6}H$, 2H, $C^{3,7}H$), 7.62 s (2H, $C^{2',2''}H$), 8.12 d (2H, $C^{4,8}H$, *J* 9.1 Hz), 8.57 s (2H, HC=N). Found, %: C 73.94; H 4.31; N 6.60; O 15,14. $C_{26}H_{18}N_2O_4$. Calculated, %: C 73.92; H 4.29; N 6.63; O 15.15.

(*E*,*E*)-N^1,N^5-Di-(4',4''-hydroxy-3',3''-methoxybenzylidene)naphthalene-1,5-diamine (IIIi). Yield 53%, pale yellow crystalline solid, mp 204°C. IR spectrum, ν, cm^{-1}: 3388, 3314, 3068, 2959, 2933, 1634, 1600, 1512, 1283, 1252, 1028. ^1H NMR spectrum, δ_H, ppm: 3.86 s (6H, OCH_3), 6.55 d (2H, $C^{5',5''}H$, *J* 9.0 Hz), 6.90 d (2H, $C^{6',6''}H$, *J* 10.0 Hz), 7.42 d (2H, $C^{2,6}H$, *J* 6.1 Hz), 7.49 t (2H, $C^{3,7}H$, *J* 4.5 Hz), 7.64 s (2H, $C^{2',2''}H$), 8.10 d (2H, $C^{4,8}H$, *J* 8.9 Hz), 8.51 s (2H, HC=N), 9.78 (2H, OH). Found, %: C 73.24; H 5.22; N 6.54; O 15,01. $C_{26}H_{22}N_2O_4$. Calculated, %: C 73.23; H 5.20; N 6.57; O 15.01.

(*E*,*E*)-N^1,N^5-Di-(4',4''-hydroxy-3',3''-ethoxybenzylidene)naphthalene-1,5-diamine (IIIj). Yield 80%, dark yellow crystalline solid, mp 204–206°C. IR spectrum, ν, cm^{-1}: 3314, 3076, 2984, 2931, 2887, 1618, 1589, 1511, 1280, 1250, 1038. ^1H NMR spectrum, δ_H, ppm: 1.36 t (6H, $OCH_2\underline{CH_3}$, *J* 4.0 Hz), 1.36 q (4H, $2O\underline{CH_2}CH_3$, *J* 3.0 Hz), 6.92 d (2H, $C^{5',5''}H$, *J* 9.1 Hz), 7.14 d (2H, $C^{6',6''}H$, *J* 8.2 Hz), 7.41 d (2H, $C^{2,6}H$, *J* 10.0 Hz), 7,47 t (2H, $C^{3,7}H$), 7.62 s (2H, $C^{2',2''}H$), 8.10 d (2H, $C^{4,8}H$, *J* 9.1 Hz), 8.49 s (2H, HC=N), 9.71 (2H, OH). Found, %: C 73.97; H 3.81; N 6.18; O 15,04. $C_{28}H_{26}N_2O_4$. Calculated, %: C 73.99; H 3.77; N 6.16; O 14.08.

(*E*,*E*)-N^1,N^5-Di-(4',4''-acetoxy-3',3''-methoxybenzylidene)naphthalene-1,5-diamine (IIIk). Yield 61%, pale yellow crystalline solid, mp 250°C. IR spectrum, ν, cm^{-1}: 3419, 2953, 2933, 1763, 1626, 1601, 1506, 1280, 1259, 1192. ^1H NMR spectrum, δ_H, ppm: 2.28 s [6H, $OC(O)CH_3$], 3.88 s (6H, OCH_3), 7.24 d (2H, $C^{6',6''}H$, *J* 9.1 Hz), 7.27 d (2H, $C^{5',5''}H$, *J* 10.0 Hz), 7.53 t (2H, $C^{3,7}H$, *J* 4.4 Hz), 7.61 d (2H, $C^{2,6}H$, *J* 8.2 Hz), 7.81 s (2H, $C^{2',2''}H$), 8.17 d (2H, $C^{4,8}H$, *J* 9.1 Hz), 8.68 s (2H, HC=N). Found, %: C 70.54; H 5.17; N 5.51; O 18,79. $C_{30}H_{26}N_2O_6$. Calculated, %: C 70.58; H 5.13; N 5.49; O 18.80.

The IR spectra were recorded on a Nicolet Protege-460 Fourier spectrometer from KBr pellets. The ^1H NMR spectra were taken on a Brucker Avance spectrometer (500 MHz) relative to internal TMS using DMSO-d_6 as a solvent. The elemental analysis was performed on a VarioMICRO Superuser CHNS analyzer. The melting points were determined on a Koeffler bench.

ACKNOWLEDGMENTS

This work was financially supported by the Belarus Republic Foundation for Basic Research (grant no X11M-028).

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