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Nitropyridines: IV.* Synthesis of 3-(2-Furyl)biphenyls by Recyclization of Nitropyridinium Salts

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Abstract—The two-component Hantzsch synthesis using 3-(2-furyl)-2-nitro-1-phenylprop-2-en-1-one and various enamines gave the corresponding nitro-substituted dihydropyridines which were converted into nitropyridines and *N*-methylpyridinium salts. Recyclization of the latter by the action of aqueous–alcoholic alkali led to the formation of 3-(2-furyl)-2-nitrobiphenyl derivatives.

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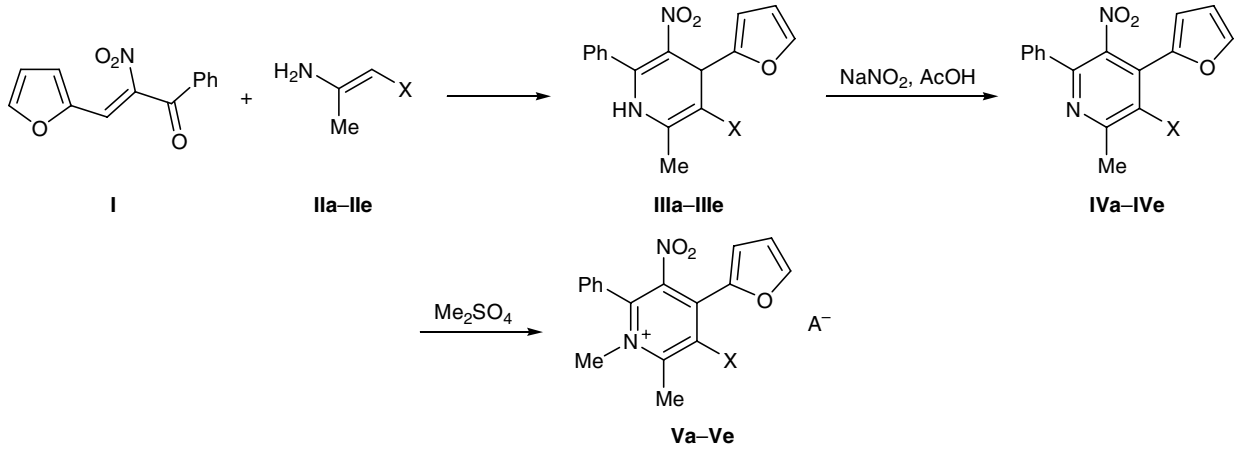
3-(2-Furyl)biphenyls are generally synthesized by cross-coupling reactions [2], cyclization of α-isonitroso-α-furoylacetone with enamines [3], and intramolecular Thorpe and Claisen cyclizations of the Michael adducts derived from alkylidenemalononitriles, furfurylidenemalononitrile, or furfurylideneacetophenone and ethyl but-2-enoate [4–6].

In the present communication we describe a new synthetic approach to 3-(2-furyl)biphenyls, which is based on recyclization of pyridinium salts **Va**–**Ve** by the action of aqueous–alcoholic alkali. The key intermediate products in the proposed reaction sequence were nitropyridines **IVa**–**IVe** which were prepared by the Hantzsch reaction of nitrochalcone **I** with enamines **IIa**–**IIe** and subsequent aromatization of 1,4-dihydropyridines **IIIa**–**IIIe** thus formed by treatment with sodium nitrite in acetic acid (Scheme 1). The alkylation of compounds **IVa**–**IVe** to pyridinium salts **Va**–**Ve** was performed by heating with 3 equiv of dimethyl sulfate.

Recyclization of pyridinium salts **Va**–**Ve** to 3-(2-furyl)biphenyl derivatives is likely to involve initial addition of hydroxide ion to the most electron-deficient carbon atom in the α-position with respect to the nitrogen atom and the nitro group. Pseudobase **A** thus formed undergoes isomerization with cleavage of the endocyclic C–N bond to give open-chain form **B**.

Scheme 1.

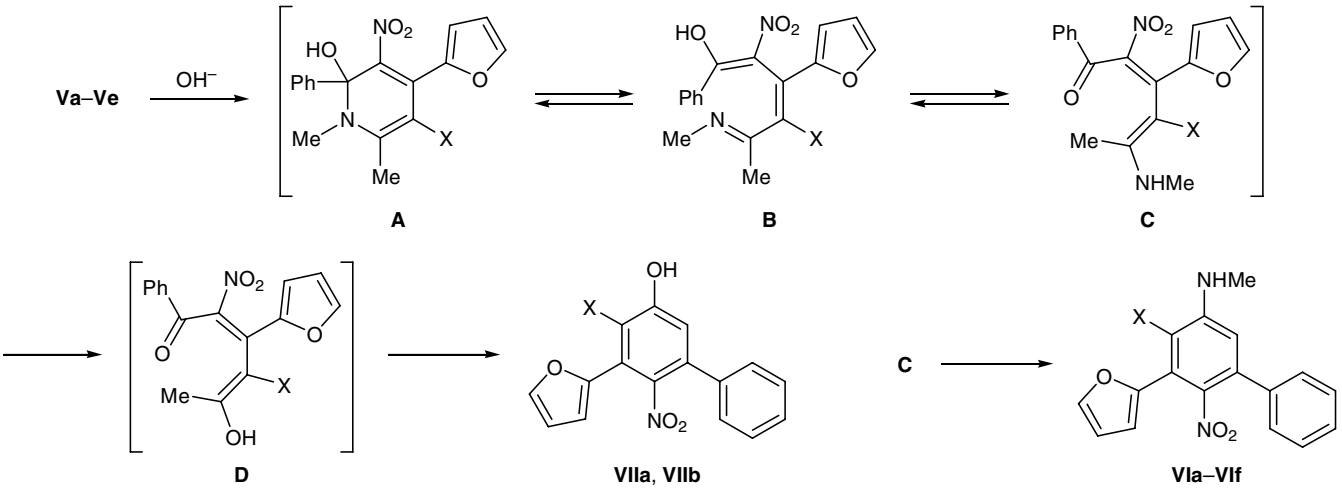


I **IIa–IIe** **IIIa–IIIe** **IVa–IVe** **Va–Ve**

X = Ac (**a**), Bz (**b**), CN (**c**), O_2N (**d**), EtOCO (**e**); A = ClO_4 (**a**, **e**), $MeSO_4$ (**b**–**d**).

* For communication III, see [1].

Scheme 2.



X = Ac (**a**), Bz (**b**), CN (**c**), O_2N (**d**), EtOCO (**e**), HOCO (**f**).

Closure of benzene ring in the latter occurs via intramolecular aldol condensation with participation of the benzoyl and methyl groups in structure **C** which is tautomeric to **B** (Scheme 2). The recyclization of quaternary salts **Vc** and **Vd** derived from 4-(2-furyl)-2-methyl-5-nitro-6-phenylpyridine-3-carbonitrile (**IVc**) and 4-(2-furyl)-2-methyl-3,5-dinitro-6-phenylpyridine (**IVd**), respectively, was completely regioselective, and the yields of 3-(2-furyl)biphenyls **VIc** and **VId** were 66 and 68%, respectively. In the reactions with 3-acetyl- and 3-benzoyl-5-nitropyridinium salts **Va** and **Vb** we obtained mixtures of two products, **VIa/VIIa** and **VIb/VIIb**. 5-Hydroxy-3-(2-furyl)biphenyls **VIIa** and **VIIb** were the minor products. Presumably, they were formed from open-chain structure **D** resulting from hydrolysis of the enamine fragment in **C**.

The structure of the newly synthesized compounds was confirmed by the IR, ^{1}H NMR, and mass spectra and elemental analyses. The IR spectra of **VIa–VIf** contained absorption bands belonging to stretching vibrations of the secondary amino group (3430–3420 cm^{-1}), cyano group (2210 cm^{-1}), carbonyl group (1680–1640 cm^{-1}), and nitro group (1530–1520 and 1360–1350 cm^{-1}). In the spectra of 3-(2-furyl)-5-hydroxy-2-nitrobiphenyls **VIIa** and **VIIb**, stretching vibrations of the hydroxy group give rise to a weak broad absorption band at a reduced frequency due to strong intramolecular hydrogen bonding with the acetyl or benzoyl carbonyl group, which is overlapped by C–H stretching vibration band near 3000 cm^{-1} [7].

The molecular ion peaks in the mass spectra of dihydronitropyridines **IIIa**, **IIIb**, and **IIId** had a low intensity (1–2% of the base peak), while no molecular ion peaks were found in the spectra of **IIIc** and **IIIe**. A probable reason is facile elimination of the $C_4H_3O_2$ radical under electron impact. The most abundant ions (I_{rel} = 100%) in the spectra of **IIIa**, **IIId**, and **IIIe** were $[M - C_4H_3O_2]^+$; the relative intensity of the corresponding fragment ion peak in the mass spectra of **IIIb** and **IIIc** was 89 and 46%, respectively. The mass spectra of **IIIa–IIIe** also contained strong peaks from the $[M - NO_2]^+$, $[M - HNO_2]^+$, and $[M - NO_2 - C_4H_3O]^+$ ions.

To conclude, it should be emphasized that recyclization of accessible nitropyridinium salts under mild conditions ensures preparation of 3-(2-furyl)biphenyls with various sets of substituents in the benzene ring linked to the furan ring.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker AC-200 spectrometer (200 MHz) using tetramethylsilane as internal reference. The IR spectra were measured on a Specord 75IR instrument from solutions in chloroform. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT-8200 mass spectrometer with direct sample admission into the ion source. The elemental compositions were determined on a Perkin–Elmer analyzer. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using chloroform and chloroform–ethyl acetate (9:1) as eluents. The melting points were determined on a Boetius melting point apparatus.

3-(2-Furyl)-2-nitro-1-phenylprop-2-en-1-one (**I**) was synthesized by the procedure described in [8]. Compounds **IIIe** and **IVe** [9] and 3-(2-furyl)biphenyls **VIa**, **VIb**, **VIe**, and **VIf** [10] were reported by us previously.

Dihydropyridines IIIa–IIIe (*general procedure*)**.** A solution of 2.43 g (10 mmol) of compound **I** and 10 mmol of enamine **IIa–IIe** in 15 ml of glacial acetic acid was stirred for 20 h at room temperature. The solvent was distilled off under reduced pressure, and the residue was recrystallized from ethanol.

1-[4-(2-Furyl)-2-methyl-5-nitro-6-phenyl-1,4-dihydropyridin-3-yl]ethan-1-one (IIIa). Yield 45%, yellow crystals, mp 189–190°C. IR spectrum (KBr), ν, cm^{-1}: 1320, 1490 (NO_2); 1640 (CO); 3300, 3430 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.37 s (6H, CH_3, $COCH_3$), 5.64 s (1H, 4-H), 6.15 d (1H, 3'-H, $J_{3',4'}$ = 3.1 Hz), 6.31 d.d (1H, 4'-H, $J_{4',3'}$ = 3.1, $J_{4',5'}$ = 1.8 Hz), 7.30–7.52 m (6H, C_6H_5, 5'-H), 9.44 s (1H, NH). Mass spectrum, *m/z* (I_{rel}, %): 324 (1.0) $[M]^+$, 307 (39.7) $[M - OH]^+$, 279 (29.9), 278 (74.7) $[M - NO_2]^+$, 277 (25.4) $[M - HNO_2]^+$, 262 (36.0), 241 (100) $[M - C_4H_3O_2]^+$, 235 (76.5) $[M - NO_2 - COCH_3]^+$, 211 (43.1) $[M - NO_2 - C_4H_3O]^+$, 196 (89.4) $[M - NO_2 - C_4H_3O - CH_3]^+$, 168 (39.4) $[M - NO_2 - C_4H_3O - COCH_3]^+$, 77 (49.6), 43 (92.8). Found, %: C 66.49; H 4.79; N 8.92. $C_{18}H_{16}N_2O_4$. Calculated, %: C 66.66; H 4.97; N 8.64. *M* 324.34.

[4-(2-Furyl)-2-methyl-5-nitro-6-phenyl-1,4-dihydropyridin-3-yl]phenylmethanone (IIIb). Yield 62%, yellow crystals, mp 219–221°C. IR spectrum (KBr), ν, cm^{-1}: 1300, 1490 (NO_2); 1630 (CO); 3310, 3420 (NH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.80 s (3H, CH_3), 5.55 s (1H, 4-H), 6.11 d (1H, 3'-H, $J_{3',4'}$ = 3.1 Hz), 6.36 d.d (1H, 4'-H, $J_{4',3'}$ = 3.1, $J_{4',5'}$ = 1.8 Hz), 7.42–7.64 m (11H, C_6H_5, COC_6H_5, 5'-H), 10.00 s (1H, NH). Mass spectrum, *m/z* (I_{rel}, %): 386 (2.2) $[M]^+$, 369 (37.9) $[M - OH]^+$, 340 (65.2) $[M - NO_2]^+$, 339 (60.5) $[M - HNO_2]^+$, 303 (88.9) $[M - C_4H_3O_2]^+$, 273 (45.4) $[M - NO_2 - C_4H_3O]^+$, 272 (81.0) $[M - HNO_2 - C_4H_3O]^+$, 105 (100), 77 (84.0). Found, %: C 71.72; H 4.79; N 7.13. $C_{23}H_{18}N_2O_4$. Calculated, %: C 71.49; H 4.70; N 7.25. *M* 386.41.

4-(2-Furyl)-2-methyl-5-nitro-6-phenyl-1,4-dihydropyridine-3-carbonitrile (IIIc). Yield 60%, yellow crystals, mp 193–195°C. IR spectrum, ν, cm^{-1}: 1310, 1490 (NO_2); 2210 (CN); 3430 (NH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.11 s (3H, CH_3), 5.20 s (1H, 4-H), 6.27 d (1H, 3'-H, $J_{3',4'}$ = 3.2 Hz), 6.39 d.d (1H, 4'-H, $J_{4',3'}$ = 3.2, $J_{4',5'}$ = 1.7 Hz), 7.35–7.51 m (6H, C_6H_5, 5'-H), 9.99 s (1H, NH). Mass spectrum, *m/z* (I_{rel}, %): 260 (100) $[M - HNO_2]^+$, 224 (46.4) $[M - C_4H_3O_2]^+$, 194 (71.4) $[M - NO_2 - C_4H_3O]^+$, 193 (15.4) $[M - HNO_2 - C_4H_3O]^+$, 77 (11.0). Found, %: C 66.29; H 4.35; N 13.82. $C_{17}H_{13}N_3O_3$. Calculated, %: C 66.44; H 4.26; N 13.67.

4-(2-Furyl)-2-methyl-3,5-dinitro-6-phenyl-1,4-dihydropyridine (IIId). Yield 32%, yellow crystals, mp 194–196°C. IR spectrum, ν, cm^{-1}: 1320, 1490 (NO_2); 3420 (NH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.53 s (3H, CH_3), 5.91 s (1H, 4-H), 6.31 d (1H, 3'-H, $J_{3',4'}$ = 3.1 Hz), 6.42 d.d (1H, 4'-H, $J_{4',3'}$ = 3.1, $J_{4',5'}$ = 1.8 Hz), 7.39–7.59 m (6H, C_6H_5, 5'-H), 10.49 s (1H, NH). Mass spectrum, *m/z* (I_{rel}, %): 327 (0.5) $[M]^+$, 280 (3.3) $[M - HNO_2]^+$, 263 (2.3) $[M - HNO_2 - OH]^+$, 244 (100) $[M - C_4H_3O_2]^+$, 214 (61.4) $[M - NO_2 - C_4H_3O]^+$, 197 (14.6) $[M - C_4H_3O_2 - HNO_2]^+$, 168 (36.2) $[M - C_4H_3O_2 - NO - NO_2]^+$, 77 (14.3). Found, %: C 59.01; H 4.19; N 12.60. $C_{16}H_{13}N_3O_5$. Calculated, %: C 58.72; H 4.00; N 12.84. *M* 327.29.

Oxidation of dihydropyridines IIIa–IIIe (*general procedure*)**.** Sodium nitrite, 3 mmol, was added in portions under stirring to a suspension of 2 mmol of dihydropyridine **IIIa–IIIe** in 6 ml of glacial acetic acid, heated to 60–70°C. The mixture was then stirred for 1 h at that temperature, cooled, diluted with 3 volumes of water, and neutralized with aqueous ammonia. The precipitate was filtered off, washed with water, dried, and recrystallized from ethanol.

1-[4-(2-Furyl)-2-methyl-5-nitro-6-phenylpyridin-3-yl]ethan-1-one (IVa). Yield 60%, colorless crystals, mp 124–126°C. IR spectrum, ν, cm^{-1}: 1340, 1530 (NO_2); 1700 (CO). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.25 s (3H, $COCH_3$), 2.63 s (3H, CH_3), 6.56 d.d (1H, 4'-H, $J_{4',3'}$ = 3.4, $J_{4',5'}$ = 1.7 Hz), 6.77 d (1H, 3'-H, $J_{3',4'}$ = 3.4 Hz), 7.43–7.65 m (6H, C_6H_5, 5'-H). Mass spectrum, *m/z* (I_{rel}, %): 322 (2.5) $[M]^+$, 306 (7.6) $[M - O]^+$, 305 (39.0) $[M - OH]^+$, 277 (33.3) $[M - OH - CO]^+$, 263 (11.6), 249 (12.2), 235 (13.8), 207 (11.4), 206 (10.3), 105 (18.5), 77 (17.1), 43 (100), 28 (10.0). Found, %: C 67.39; H 4.23; N 8.38. $C_{18}H_{14}N_2O_4$. Calculated, %: C 67.07; H 4.38; N 8.69. *M* 322.32.

[4-(2-Furyl)-2-methyl-5-nitro-6-phenylpyridin-3-yl]phenylmethanone (IVb). Yield 48%, colorless crystals, mp 101–103°C. IR spectrum, ν, cm^{-1}: 1340, 1530 (NO_2); 1670 (CO). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.52 s (3H, CH_3), 6.30 d.d (1H, 4'-H, $J_{4',3'}$ = 3.5, $J_{4',5'}$ = 1.8 Hz), 6.62 d.d (1H, 3'-H, $J_{3',4'}$ = 3.5, $J_{3',5'}$ = 0.7 Hz), 7.29 d.d (1H, 5'-H, $J_{5',4'}$ = 1.8, $J_{5',3'}$ = 0.7 Hz), 7.40–7.81 m (10H, C_6H_5, COC_6H_5). Mass

spectrum, *m/z* (I_{rel}, %): 384 (12.2) $[M]^+$, 368 (11.6) $[M - O]^+$, 367 (40.8) $[M - OH]^+$, 339 (27.3) $[M - OH - CO]^+$, 311 (21.3), 105 (100), 77 (99.0), 28 (21.2). Found, %: C 71.77; H 4.48; N 7.20. $C_{23}H_{16}N_2O_4$. Calculated, %: C 71.87; H 4.20; N 7.29. *M* 384.39.

4-(2-Furyl)-2-methyl-5-nitro-6-phenylpyridine-3-carbonitrile (IVc). Yield 53%, colorless crystals, mp 152–154°C. IR spectrum, ν, cm^{-1}: 1340, 1540 (NO_2); 2220 (CN). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.93 s (3H, CH_3), 6.66 d.d (1H, 4'-H, $J_{4',3'}$ = 3.7, $J_{4',5'}$ = 1.7 Hz), 7.42 d (1H, 3'-H, $J_{3',4'}$ = 3.7 Hz), 7.45–7.63 m (5H, C_6H_5), 7.68 d (1H, 5'-H, $J_{5',4'}$ = 1.7 Hz). Mass spectrum, *m/z* (I_{rel}, %): 305 (7.4) $[M]^+$, 289 (19.6) $[M - O]^+$, 288 (100) $[M - OH]^+$, 261 (15.4), 260 (85.7) $[M - OH - CO]^+$, 248 (13.3), 247 (18.4) $[M - NO - CO]^+$, 232 (34.4), 206 (30.5), 205 (15.0), 152 (17.1), 151 (18.5), 105 (19.9), 77 (36.1), 63 (12.8), 55 (19.9), 43 (29.1), 39 (17.0) 28 (21.5). Found, %: C 66.61; H 3.56; N 13.66. $C_{17}H_{11}N_3O_3$. Calculated, %: C 66.88; H 3.63; N 13.76. *M* 305.29.

4-(2-Furyl)-2-methyl-3,5-dinitro-6-phenylpyridine (IVd). Yield 43%, colorless crystals, mp 141–142°C. IR spectrum, ν, cm^{-1}: 1350, 1540 (NO_2). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.66 s (3H, CH_3), 6.78–6.81 m (1H, 4'-H), 6.95 d (1H, 3'-H, $J_{3',4'}$ = 3.5 Hz), 7.51–7.69 m (5H, C_6H_5), 8.09 s (1H, 5'-H). Mass spectrum, *m/z* (I_{rel}, %): 325 (49.9) $[M]^+$, 309 (2.4) $[M - O]^+$, 308 (16.0) $[M - OH]^+$, 297 (9.6) $[M - CO]^+$, 280 (17.6) $[M - OH - CO]^+$, 234 (33.5), 221 (38.2), 220 (37.2), 206 (63.1), 193 (30.9), 192 (40.6), 180 (35.4), 167 (30.7), 166 (39.9), 163 (34.4), 152 (43.3), 140 (73.7), 139 (54.0), 127 (43.9), 126 (55.4), 105 (72.1), 104 (73.1), 83 (66.4), 81 (46.7), 77 (100), 63 (49.0), 55 (72.2), 51 (41.0), 39 (37.8), 29 (18.1) 28 (28.4), 27 (37.2). Found, %: C 58.98; H 3.60; N 12.69. $C_{16}H_{11}N_3O_5$. Calculated, %: C 59.08; H 3.41; N 12.92. *M* 325.28.

Alkylation of pyridines IVa–IVe (*general procedure*). A mixture of 5 mmol of pyridine **IVa**–**IVe** and 1.9 ml (20 mmol) of dimethyl sulfate was heated for 20–24 h at 100°C. The mixture was cooled and washed with anhydrous diethyl ether (3×10 ml). Methyl pyridinium sulfates **Vb**–**Vd** crystallized from the mixture and were filtered off. In the synthesis of salts **Va** and **Ve**, the oily residue was dissolved in 5 ml of water, a saturated aqueous solution of 0.64 g (5.3 mmol) of sodium perchlorate was added, and the precipitate was filtered off, dried, and recrystallized from ethanol.

3-Acetyl-4-(2-furyl)-1,2-dimethyl-5-nitro-6-phenylpyridin-1-ium perchlorate (Va). Yield 83%, colorless crystals, mp 271–274°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.57 s (3H, $COCH_3$), 2.79 s (3H, CH_3), 3.83 s (3H, CH_3), 6.90–6.98 m (1H, 4'-H), 7.16 d (1H, 3'-H, $J_{3',4'}$ = 3.7 Hz), 7.53–7.86 m (5H, C_6H_5), 8.31 s (1H, 5'-H). Found, %: C 51.93; H 3.81; N 6.36. $C_{19}H_{17}ClN_2O_8$. Calculated, %: C 52.25; H 3.92; N 6.41.

3-Benzoyl-4-(2-furyl)-1,2-dimethyl-5-nitro-6-phenylpyridin-1-ium methyl sulfate (Vb). Yield 85%, colorless crystals, mp 230–232°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.71 s (3H, CH_3), 3.38 s (3H, $CH_3SO_4^-$), 3.89 s (3H, CH_3), 6.72 d.d (1H, 4'-H, $J_{4',3'}$ = 4.0, $J_{4',5'}$ = 1.8 Hz), 6.98 d (1H, 3'-H, $J_{3',4'}$ = 4.0 Hz), 7.60–8.05 m (11H, C_6H_5, COC_6H_5, 5'-H). Found, %: C 58.69; H 4.33; N 5.47. $C_{25}H_{22}N_2O_8S$. Calculated, %: C 58.82; H 4.34; N 5.49.

3-Cyano-4-(2-furyl)-1,2-dimethyl-5-nitro-6-phenylpyridin-1-ium methyl sulfate (Vc). Yield 80%, colorless crystals, mp 177–179°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.17 s (3H, CH_3), 3.35 s (3H, $CH_3SO_4^-$), 3.87 s (3H, CH_3), 7.10–7.16 m (1H, 4'-H), 7.53–7.80 m (5H, C_6H_5), 8.11 d (1H, 3'-H, $J_{3',4'}$ = 3.7 Hz), 8.43 s (1H, 5'-H). Found, %: C 53.23; H 4.09; N 9.78. $C_{19}H_{17}N_3O_7S$. Calculated, %: C 52.90; H 3.97; N 9.74.

4-(2-Furyl)-1,2-dimethyl-3,5-dinitro-6-phenylpyridin-1-ium methyl sulfate (Vd). Yield 94%, colorless crystals, mp 201–203°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.90 s (3H, CH_3), 3.37 s (3H, $CH_3SO_4^-$), 3.90 s (3H, CH_3), 6.98–7.05 m (1H, 4'-H), 7.39 d (1H, 3'-H, $J_{3',4'}$ = 3.9 Hz), 7.54–7.87 m (5H, C_6H_5), 8.41 s (1H, 5'-H). Found, %: C 47.50; H 3.67; N 9.16. $C_{18}H_{17}N_3O_9S$. Calculated, %: C 47.89; H 3.80; N 9.31.

3-Ethoxycarbonyl-4-(2-furyl)-1,2-dimethyl-5-nitro-6-phenylpyridin-1-ium perchlorate (Ve). Yield 85%, colorless crystals, mp 241–243°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.31 t (3H, CH_3CH_2O, J = 7.1 Hz), 2.88 s (3H, CH_3), 3.83 s (3H, CH_3), 4.55 q (2H, OCH_2, J = 7.1 Hz), 6.95 d.d (1H, 4'-H, $J_{4',3'}$ = 3.9, $J_{4',5'}$ = 1.7 Hz), 7.24 d (1H, 3'-H, $J_{3',4'}$ = 3.9 Hz), 7.59–7.75 m (5H, C_6H_5), 8.33 d (1H, 5'-H, $J_{5',4'}$ = 1.7 Hz). Found, %: C 51.51; H 4.07; N 5.75. $C_{20}H_{19}ClN_2O_9$. Calculated, %: C 51.46; H 4.10; N 6.00.

3-(2-Furyl)biphenyls VIa–VIf, VIIa, and VIIb (*general procedure*). Pyridinium salt **Va**–**Ve**, 1 mmol, was dispersed in 4 ml of ethanol, 1.8 ml (5 mmol) of 10% aqueous sodium hydroxide was added, and the mixture was stirred at room temperature for a time indicated below and was then diluted with water. The

precipitate of biphenyl **VIa–VIe** was filtered off and washed with water. Biphenylcarboxylic acid **VIf** was isolated by acidification with 50% aqueous acid of the filtrate obtained after separation of biphenyl **VIe**. 5-Hydroxybiphenyls **VIIa** and **VIIb** were isolated in a similar way from the filtrates obtained after separation of products **VIa** and **VIb**. Compounds **VIa–VIf**, **VIIa**, and **VIIb** were purified by recrystallization from ethanol.

3-(2-Furyl)-5-methylamino-2-nitrobiphenyl-4-carbonitrile (VIc). Yield 66% (reaction time 4 h), yellow crystals, mp 185–186°C. IR spectrum, ν, cm^{-1}: 1350, 1520 (NO_2); 2210 (CN); 3430 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.99 d (3H, NHC**H**$_3$, J = 5.1 Hz), 5.23 br.s (1H, N**H**CH_3), 6.54 s (1H, 6-H), 6.56 d (1H, 4'-H, $J_{4',5'}$ = 1.7 Hz), 6.97 d (1H, 3'-H, $J_{3',4'}$ = 3.4 Hz), 7.32–7.45 m (5H, C_6H_5), 7.55 d.d (1H, 5'-H, $J_{5',4'}$ = 1.7, $J_{5',3'}$ = 0.7 Hz). Mass spectrum, *m/z* (I_{rel}, %): 319 (37.6) $[M]^+$, 302 (33.7) $[M - OH]^+$, 291 (45.1), 275 (28.1), 274 (100) $[M - OH - CO]^+$, 262 (27.0), 259 (41.4), 247 (69.2), 246 (85.7), 232 (27.4), 231 (44.3), 230 (20.9), 220 (27.8), 219 (60.1), 218 (28.9), 206 (24.7), 205 (60.6), 193 (27.0), 192 (33.0), 190 (34.2), 77 (23.5), 28 (27.5). Found, %: C 67.61; H 4.24; N 13.35. $C_{18}H_{13}N_3O_3$. Calculated, %: C 67.71; H 4.10; N 13.16. *M* 319.32.

5-(2-Furyl)-*N*-methyl-4,6-dinitrobiphenyl-3-amine (VId). Yield 68% (reaction time 2 h), yellow crystals, mp 162–164°C. IR spectrum, ν, cm^{-1}: 1360, 1530 (NO_2); 3430 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.99 d (3H, NHC**H**$_3$, J = 5.1 Hz), 6.48 d.d (2H, NH, 4'-H, $J_{4',3'}$ = 3.4, $J_{4',5'}$ = 1.7 Hz), 6.61 d.d (1H, 3'-H, $J_{3',4'}$ = 3.4, $J_{3',5'}$ = 0.7 Hz), 6.76 s (1H, 6-H), 7.35–7.49 m (5H, C_6H_5), 7.51 d.d (1H, 5'-H, $J_{5',4'}$ = 1.7, $J_{5',3'}$ = 0.7 Hz). Mass spectrum, *m/z* (I_{rel}, %): 339 (75.9) $[M]^+$, 322 (27.4) $[M - OH]^+$, 294 (13.8) $[M - OH - CO]^+$, 276 (9.2) $[M - NO_2 - OH]^+$, 248 (32.9), 247 (33.9) $[M - 2NO_2]^+$, 222 (30.9), 221 (48.3), 220 (100) $[M - 2NO_2 - HCN]^+$, 219 (69.1), 208 (40.7), 207 (53.0), 206 (52.9), 205 (67.2), 193 (77.8), 192 (57.7), 191 (58.5), 180 (54.2), 77 (42.2), 55 (37.9), 28 (34.3). Found, %: C 60.14; H 3.85; N 12.68. $C_{17}H_{13}N_3O_5$. Calculated, %: C 60.18; H 3.86; N 12.38. *M* 339.31.

1-[3-(2-Furyl)-5-hydroxy-2-nitrobiphenyl-4-yl]-ethan-1-one (VIIa). Yield 14% (reaction time 4 h), colorless crystals, mp 155–157°C. IR spectrum, cm^{-1}: 1370, 1530 (NO_2); 1650 (CO). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.90 s (3H, $COCH_3$), 6.57 d.d (1H, 4'-H, $J_{4',3'}$ = 3.3, $J_{4',5'}$ = 1.8 Hz), 6.69 d (1H, 3'-H, $J_{3',4'}$ = 3.3 Hz), 7.10 s (1H, 6-H), 7.37–7.46 m (5H, C_6H_5), 7.64 s (1H, 5'-H), 11.92 s (1H, OH). Mass spectrum, *m/z* (I_{rel}, %): 323 (4.1) $[M]^+$, 306 (12.5) $[M - OH]^+$, 278 (29.5) $[M - OH - CO]^+$, 277 (6.1) $[M - NO_2]^+$, 276 (17.6) $[M - HNO_2]^+$, 264 (20.8), 251 (41.6), 236 (51.9), 208 (21.6), 180 (36.9), 176 (18.7), 165 (24.3), 152 (21.3), 139 (18.0), 77 (17.6), 43 (100). Found, %: C 66.56; H 4.22; N 4.22. $C_{18}H_{13}NO_5$. Calculated, %: C 66.87; H 4.05; N 4.33. *M* 323.30.

1-[3-(2-Furyl)-5-hydroxy-2-nitrobiphenyl-4-yl]-phenylmethanone (VIIb). Yield 12% (reaction time 18 h), colorless crystals, mp 180–181°C. IR spectrum, ν, cm^{-1}: 1360, 1530 (NO_2); 1630 (CO). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.03 d.d (1H, 4'-H, $J_{4',3'}$ = 3.5, $J_{4',5'}$ = 1.8 Hz), 6.35 d (1H, 3'-H, $J_{3',4'}$ = 3.5 Hz), 7.12–7.55 m (12H, C_6H_5, COC_6H_5, 6-H, 5'-H), 9.66 s (1H, OH). Mass spectrum, *m/z* (I_{rel}, %): 385 (7.3) $[M]^+$, 368 (5.0) $[M - OH]^+$, 356 (7.4), 340 (23.0) $[M - OH - CO]^+$, 339 (10.5) $[M - NO_2]^+$, 338 (29.5) $[M - HNO_2]^+$, 328 (31.4) $[M - CO - CHO]^+$, 312 (40.1), 105 (78.5), 77 (100), 28 (18.0). Found, %: C 71.39; H 3.79; N 3.31. $C_{23}H_{15}NO_5$. Calculated, %: C 71.68; H 3.92; N 3.63. *M* 385.38.

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