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Eco-friendly N–N coupling of aminofuroxans into azofuroxans under the action of electrogenerated hypohalites

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Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 (300.13 and 75.47 MHz, respectively) and Bruker AC-200 (200.13 and 50.32 MHz, respectively) spectrometers and referenced to residual solvent peak. The chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. The IR spectra were recorded on a Bruker "Alpha" spectrometer in the range 400-4000 cm^{-1} (resolution 2 cm^{-1}). Elemental analyses were performed by the CHN Analyzer Perkin-Elmer 2400. The melting points were determined on Stuart SMP20 apparatus and are uncorrected. Analytical thin-layer chromatography (TLC) was carried out on Merck 25 TLC silica gel 60 F_{254} aluminum sheets. The visualization of the TLC plates was accomplished with a UV light. Column chromatography was performed on silica gel 60 A (0.060-0.200 mm, Acros Organics). Galvanostatic electrolysis (a current controlled electrolysis) was performed in an undivided temperature-controlled (25 °C) glass cell, using a B 5-8 current source (Russia). The electric circuit contained a coulometer devised at the Special design bureau of the Institute of Organic Chemistry of the Russian Academy of Sciences. A magnetic stirrer was used to stir the solution during the electrolysis.

All solvents were purified and dried using standard methods prior to use. All standard reagents were purchased from Aldrich or Acros Organics and used without further purification. Aminofuroxans **1a** [S1], **1b** [S2], **1c** [S3] and **4** [S1] were synthesized as reported.

Synthesis of 4-aminofuroxans 1d,e.

The corresponding amine (12 mmol) was added to a magnetically stirred suspension of 4-amino-3-azidocarbonylfuroxan [S3] (1.0 g, 5.9 mmol) in a mixture of THF (1 ml) and H_2O (5 ml) at 20 °C. The reaction mixture was stirred for 1 h, then diluted with H_2O (20 ml) and stirred for 20 min. The solid formed was filtered off, washed with H_2O and dried in air.

4-Amino-3-(*N*,*N*-diethylcarbamoyl)furoxan 1d. Yield 0.40 g (34%). White solid. Mp. 78-80 °C. R_f 0.37 ($CHCl_3$-EtOAc, 10:1). IR (KBr): 3304, 3212, 2954, 2928, 1650, 1628, 1536, 1480, 1452, 1340, 1218, 1150, 1002, 973, 815 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 1.24 (t, 6H,

^{3}J 6.5 Hz), 3.35 (q, 2H, ^{3}J 6.5 Hz), 3.51 (q, 2H, ^{3}J 6.5 Hz), 4.80 (br s, 2H). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$) δ_C: 12.5, 14.3, 40.3, 42.8, 106.3, 156.2, 156.6. Calcd for $C_7H_{12}N_4O_3$ (%): C, 42.00; H, 6.04; N, 27.99. Found (%): C, 41.84; H, 5.92; N, 28.16.

4-Amino-3-(morpholin-4-ylcarbonyl)furoxan 1e. Yield 0.76 g (60%). White solid. Mp. 114-116 °C. R_f 0.31 ($CHCl_3$-EtOAc, 10:1). IR (KBr): 3315, 3215, 2928, 2912, 2878, 1646, 1615, 1540, 1472, 1312, 1225, 1162, 980, 820 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ_H: 3.36 (br s, 2H), 3.59-3.66 (m, 6H), 6.45 (s, 2H). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, DMSO-d_6) δ_C: 42.3, 46.3, 65.5, 66.3, 106.0, 154.2, 156.0. Calcd for $C_7H_{10}N_4O_4$ (%): C, 39.25; H, 4.71; N, 26.16. Found (%): C, 39.38; H, 4.54; N, 26.33.

Azofuroxans **2a** [S4], **2b** [S4], **2c** [S3] and **5** [S4] are known compounds and the physical and spectral data are identical to those reported in literature.

4,4'-(Diazene-1,2-diyl)bis[3-(*N*,*N*-diethylcarbamoyl)furoxan] 2d. Yield 0.17 g (42%). Orange solid. Mp. 159-161 °C.R_f 0.23 ($CHCl_3$). IR (KBr): 2952, 2922, 1660, 1610, 1542, 1485, 1420, 1356, 1233, 1112, 944, 836 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ_H: 1.27 (t, 6H, ^{3}J 6.2 Hz), 3.39 (q, 2H, ^{3}J 6.2 Hz). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, DMSO-d_6) δ_C: 12.6, 14.5, 41.4, 42.5, 102.9, 153.6, 155.9. Calcd for $C_{14}H_{20}N_8O_6$ (%): C, 42.42; H, 5.09; N, 28.27. Found (%): C, 42.25; H, 4.90; N, 28.49.

4,4'-(Diazene-1,2-diyl)bis[3-(morpholin-4-ylcarbonyl)furoxan] 2e. Yield 0.29 g (69%). Orange solid. Mp. 203-205 °C.R_f 0.14 ($CHCl_3$). IR (KBr): 2924, 2908, 2880, 1652, 1610, 1555, 1482, 1299, 1203, 1116, 992 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ_H: 3.50-3.55 (m, 8H), 3.63-3.69 (m, 8H). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, DMSO-d_6) δ_C: 46.2, 46.7, 66.0, 66.7, 102.3, 152.8, 153.1. Calcd for $C_{14}H_{16}N_8O_8$ (%): C, 39.63; H, 3.80; N, 26.41. Found (%): C, 39.81; H, 4.03; N, 26.17.

3-[(2-Oxido-3-phenyl-1,2,5-oxadiazol-4-yl)diazenyl]-4-phenylfuroxan 3a. Yield 0.081 g (23%). Orange solid. Mp. 140-142 °C.R_f 0.70 ($CHCl_3$). IR (KBr): 2916, 2892, 1642, 1608, 1550, 1425, 1306, 1150, 1026, 960, 823cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ_H: 7.48-7.55 (m, 6H), 7.70 (d, 2H, ^{3}J 7.4 Hz), 7.76 (d, 2H, ^{3}J 7.2 Hz). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, DMSO-d_6) δ_C: 104.2, 124.1, 124.5, 124.9, 125.6, 126.1, 129.0, 129.2, 129.8, 130.8, 147.9, 148.6. Calcd for $C_{16}H_{10}N_6O_4$ (%): C, 54.86; H, 2.88; N, 23.99. Found (%): C, 55.03; H, 2.71; N, 24.13.

3-Methyl-4-[(4-methyl-2-oxido-1,2,5-oxadiazol-3-yl)diazenyl]furoxan 3b. Yield 0.020 g (9%). Orange solid. Mp. 111-113 °C. R_f 0.58 ($CHCl_3$). IR (KBr): 2920, 1650, 1612, 1543, 1420, 1312, 1135, 1026, 960, 823 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ_H: 2.41 (s, 3H), 2.57 (s, 3H). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, DMSO-d_6) δ_C: 9.0, 10.4, 105.4, 126.7, 148.5, 150.6. Calcd for $C_6H_6N_6O_4$ (%): C, 31.87; H, 2.67; N, 37.16. Found (%): C, 31.73; H, 2.55; N, 36.98.

3-Methoxycarbonyl-4-[(4-methoxycarbonyl-2-oxido-1,2,5-oxadiazol-3-yl)diazenyl]furoxan 3c.

Yield 0.082 g (26%). Orange solid. Mp. 138-140 °C. R_f 0.35 ($CHCl_3$). IR (KBr): 2912, 1680, 1646, 1602, 1525, 1460, 1390, 1212, 1136, 990 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) δ_H: 3.90 (s, 3H), 4.01 (s, 3H). $^{13}C\{^1H\}$ NMR (75.5 MHz, DMSO-d_6) δ_C: 53.3, 54.3, 104.8, 125.2, 156.0, 156.6, 161.3, 161.8. Calcd for $C_8H_6N_6O_8$ (%): C, 30.58; H, 1.92; N, 26.75. Found (%): C, 30.74; H, 2.05; N, 26.49.

3-(*N*,*N*-Diethylcarbamoyl)-4-{[4-(*N*,*N*-diethylcarbamoyl)-2-oxido-1,2,5-oxadiazol-3-yl]diazenyl}furoxan 3d.

Yield 0.11 g (28%). Orange solid. Mp. 130-132 °C. R_f 0.42 ($CHCl_3$). IR (KBr): 2950, 2912, 2892, 1646, 1622, 1545, 1495, 1420, 1306, 1253, 1118, 1025, 982, 808 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) δ_H: 1.10 (t, 3H, ^3J 6.5 Hz), 1.32 (t, 3H, ^3J 6.2 Hz), 3.36 (q, 2H, ^3J 6.5 Hz), 3.54 (q, 2H, ^3J 6.2 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, DMSO-d_6) δ_C: 12.7, 12.9, 14.5, 14.8, 41.6, 42.5, 42.9, 43.0, 103.2, 126.4, 153.9, 156.0, 158.8, 158.9. Calcd for $C_{14}H_{16}N_8O_8$ (%): C, 42.42; H, 5.09; N, 28.27. Found (%): C, 42.59; H, 4.92; N, 28.11.

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