Chemistry of Heterocyclic Compounds, Vol. 45, No. 9, 2009

SYNTHESIS OF A NEW HETEROCYCLIC SYSTEM: 3-PHENYLBENZIMIDAZO[1,2-*c*]-[1,2,3]SELENADIAZOLE

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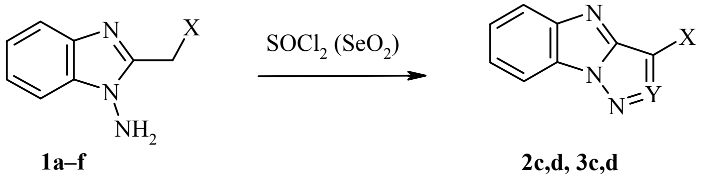
Keywords: benzimidazo[1,2-*c*]selenadiazole, benzimidazo[1,2-*c*][1,2,3]thiadiazole, selenium oxide, condensation.

The unexpected formation of benzimidazo[1,2-*c*][1,2,3]thiadiazole system as the result of the cyclization of amines **1a** or **1b** with thionyl chloride [1] has led to interest in the further study of the scope of this reaction. Amines **1** containing an active methylene group due to the presence of a phenyl, phenylamino, phenoxy, or phenylthio substituent were treated with thionyl chloride or selenium oxide. Amines **1e**,**f** underwent tar formation in all cases, while amines **1a**,**b** underwent tar formation only with selenium oxide. Amines **1c**,**d** were converted to benzimidazo[1,2-*c*][1,2,3]thiadiazoles **2c** [2] and **2d** and also a new heterocyclic system, namely, benzimidazo[1,2-*c*][1,2,3]selenadiazoles **3c**,**d**.



1 **a** X = OH, **b** X = Cl, **c** X = Ph, **d** X = SPh, **e** X = OPh, **f** X = NHPh; **2** Y = S; **3** Y = Se

The ^{1}H and ^{13}C NMR spectra were taken on a Varian Unity Inova spectrometer at 300 and 75 MHz, respectively, in DMSO-d$_6$. The residual solvent signal at δ 2.50 ppm served as the standard reference.

2-Phenylthiomethyl-1H-benzimidazole-1-amine (1d). 2-Chloromethyl-1H-benzimidazole-1-amine (**1b**) (0.32 g, 1.76 mmol) was added to a solution of sodium thiophenolate (1.8 mmol) in methanol (10 ml) and stirred for 3 h without heating. The precipitate formed was filtered off, washed with water, and recrystallized from methanol to give 0.32 g (71%) **1d**; mp 133-134°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.52 (2H, s, CH$_2$);

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1435-1436, September, 2009. Original article submitted April 24, 2009.

6.06 (2H, s, NH_2); 7.10-7.30 (3H, m, ArH); 7.35 (2H, t, *J* = 8, ArH); 7.45-7.60 (4H, m, ArH). Found, %: C 65.74; H 4.94; N 16.30. $C_{14}H_{13}N_3S$. Calculated, %: C 65.85; H 5.13; N 16.46.

3-Phenylthiobenzimidazo[1,2-*c*][1,2,3]thiadiazole (2d) was synthesized in 54% yield by heating amine **1d** in thionyl chloride at reflux for 15 min according to our previous procedure [1] and recrystallized from octane; mp 96-97°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.29 (1H, t, *J* = 8, ArH); 7.40-7.50 (3H, m, ArH); 7.54 (1H, t, *J* = 8, ArH); 7.62-7.71 (2H, m, ArH); 7.81 (1H, d, *J* = 8, H-5); 8.12 (1H, d, *J* = 8, H-8). ^{13}C NMR spectrum, δ, ppm: 113.3, 120.6, 121.3, 128.1, 128.6, 129.6, 130.0, 130.5, 131.8, 132.8, 153.2, 154.3. Found, %: C 59.28; H 2.99; N 14.56. $C_{14}H_9N_3S_2$. Calculated, %: C 59.34; H 3.20; N 14.83.

3-Phenylbenzimidazo[1,2-*c*][1,2,3]selenadiazole (3c). A mixture of 2-benzyl-1H-benzimidazole-1-amine (0.2 g, 0.89 mmol) [3], acetic acid (5 ml), and SeO_2 (0.09 g, 0.89 mmol) was heated at 65-75°C for 5 h and evaporated. Then, 10 ml water was added and the mixture was neutralized by adding sodium bicarbonate. Chromatographic separation, collecting the fraction with R_f 0.5 (1:4 ethyl acetate–toluene as eluent), gave 0.13 g (46%) **3c**; mp 146-148°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.25 (1H, t, *J* = 8, ArH); 7.48-7.62 (4H, m, ArH); 7.82 (1H, d, *J* = 8, H-5); 8.15 (1H, d, *J* = 8, H-8); 8.44 (2H, d, *J* = 8, ArH). ^{13}C NMR spectrum, δ, ppm: 113.8, 120.1, 121.1, 128.7, 128.8, 129.4, 130.1, 130.7, 132.0, 144.6, 155.2, 155.3. Found, %: C 56.68; H 3.13; N 14.15. $C_{14}H_9N_3Se$. Calculated, %: C 56.39; H 3.04; N 14.09.

3-Phenylthiobenzimidazo[1,2-*c*][1,2,3]selenadiazole (3d) was synthesized in 66% yield analogously to **3c** and recrystallized from octane; mp 146-147°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.18 (1H, t, *J* = 8, H-7); 7.49 (1H, t, *J* = 8, H-6); 7.45-7.58 (3H, m, ArH); 7.69 (1H, d, *J* = 8, H-5); 7.72-7.78 (2H, m, ArH); 8.05 (1H, d, *J* = 8, H-8). ^{13}C NMR spectrum, δ, ppm: 113.6, 119.6, 121.2, 128.2, 129.0, 130.3, 131.0, 132.2. 134.1, 141.8, 155.0, 155.4. Found, %: C 51.13; H 2.49; N 12.61. $C_{14}H_9N_3SSe$. Calculated, %: C 50.91; H 2.75; N 12.72.

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