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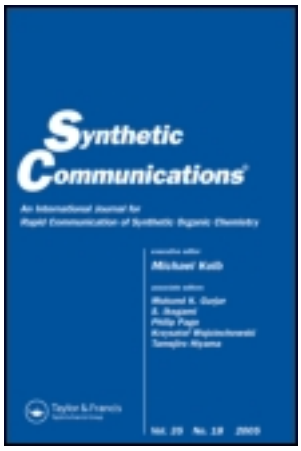

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Synthesis of 3,3′-bi-1,2,4-Triazolo[4,5-a]-benzimidazole, 5,5′-bi-1,3,4-Thiadiazole, and Thiazolo[3,2-a]benzimidazole Derivatives

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ABSTRACT

A series of novel 3,3′-bi-1,2,4-triazolo[4,5-a]benzimidazole and thiazolo[3,2-a]-benzimidazole derivatives were synthesized via the reaction of *bis*-hydrazonoyl chlorides with 2-methylthiobenzimidazole and with benzimidazol-2-thiol, respectively. A direct synthesis of 5,5′-bi-1,3,4-thiadiazole and 4,5-*bis*-phenylhydrazono-2,3,4,5-tetrahydrothiazole derivatives is also described.

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Key Words: *bis*-Hydrazonoyl chlorides; Biheterocycles; Thiazoles; Benzothiazoles; Benzimidazoles.

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Bi-heterocycles are commonly used as chelating agents, in coordination, organometallic and analytical chemistry. They have also been used as subunits in molecular hosts such as macrocycles and supermolecular species.[1] Moreover, some bi-heterocycles such as 2,2′-bi-1,3,4-thiadiazole derivatives exhibit interesting photoluminescence and electroluminescence and are used as thermotropic liquid crystals.[2,3] In addition, 3.3′-*bis*-1,2,4-triazoles have proved to possess bactericidal, fungicidal, and anthelmintic activities.[4]

In the course of our investigations, we have found that *bis*-hydrazonoyl chlorides **1a**,**b** are highly versatile and useful building blocks for the synthesis of a wide variety of bi-heterocyclic systems such as 3,3′-bi-1,2,4-triazole,[5,6] 3,3′-bipyrazole,[6–8] 2,2′-bi-1,3,4-thiadiazole,[9] and 2,2′-bi-1,3,4-selenadiazole[10] derivatives.

As part of our ongoing program to explore the utility of *bis*-hydrazonoyl chlorides **1** as reactive precursors in heterocyclic synthesis, we now report a convenient route to some 3,3′-bi-(1,2,4-triazolo[4,5-a]-benzimidazoles) **4**, 2,3-*bis*-arylhydrazonothiazolo-[3,2-a]benzimidazoles **8**, 5,5′-bi-1,3,4-thiadiazoles **15** and 2,3-*bis*-arylhydrazonothiazoles **18**.

Thus, when *bis*-hydrazonoyl chlorides **1** were allowed to react with 2-methyl-thiobenzimidazole (**2**) in 1:2 molar ratio in refluxing ethanol, in the presence of triethylamine, they furnished in each case, only one isolable product. The structure of the reaction products was established as 1,1′-diaryl-3,3′-bi-(1,2,4-triazolo[4,5-a]-benzimidazoles) **3** on the basis of their elemental and spectral analyses (Sch. 1).

On the other hand, when compound **1a** was treated with benzimidazole-2-thiol (**4**) in 1:2 molar ratio under the same experimental conditions, it afforded a high yield of an intense yellow product. Elemental analyses and spectral data showed that the reaction product is 1:1 instead of the expected 1:2 cyclocondensation product. This result was confirmed by carrying out the same reaction using 1:1 molar ratio of the starting substrates, where the same product was obtained. The structure of the isolated product was identified as 2,3-*bis*-phenylhydrazono-2,3,4,5-tetrahydrothiazolo[3,2-a]-benzimidazole (**5a**) (Sch. 1). The expected 1:2 adduct **3a**, which could be formed via loss of two molecules of hydrogen sulfide and hydrogen chloride, was not detected in the crude reaction product as examined by TLC. Similar results were obtained when compound **1b** was treated with benzimidazole-2-thiol (**4**) (see experimental part).

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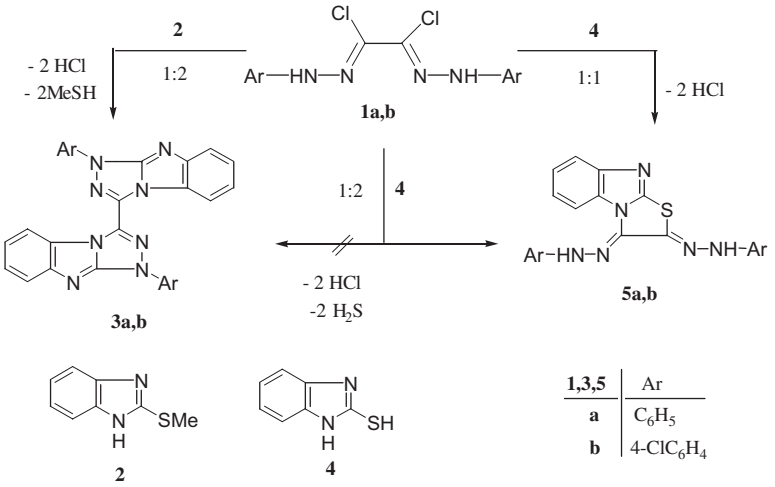

Scheme 1.

Next, the behavior of *bis*-hydrazonoyl chlorides **1** towards the reactive sulfur nucleophiles **7**, **10**, and **12** was investigated. Thus, when compounds **1a**,**b** were allowed to react with the nonisolable intermediate **7** (formed in situ from the reaction of 2-cyanomethybenzothiazole (**6**) with phenylisothiocyanate in the presence of potassium hydroxide), in each case, solely 1:2 cyclocondensation product was formed as evidenced by elemental analyses and mass spectrometry. Two possible isomeric structures **8** and **9** can be postulated for the reaction products (Sch. 2). The mass spectra of the isolated products displayed, in each case, a fragment ion corresponding to $M^+/2$ in addition to the molecular ion peak M^+. This finding provides a firm support for the 5,5′-bi-1,3,4-thiadiazole structure **8** rather than the other possible fused heterocyclic system **9**. The structures **11a**,**b** that can be formed via 1:1 cyclocondensation of **1a**,**b** with **7** were not detected in the crude reaction products.

However, compounds **8a**,**b** were obtained as minor products when the *bis*-hydrazonoyl chlorides **1a**,**b** were treated with the thioacetanilide derivative **10** in refluxing ethanol in the presence of triethylamine. The major products of this reaction were found to be 4,5-*bis*-arylhydrazonothiazole derivatives **11a**,**b** (Sch. 2). The structures of the latter products were established on the basis of their elemental analyses and spectral data (cf. Experimental part).

Most noteworthy is to report that, when the *bis*-hydrazonoyl chlorides **1a**,**b** were treated with the methyldithioacetal derivative **12**, in

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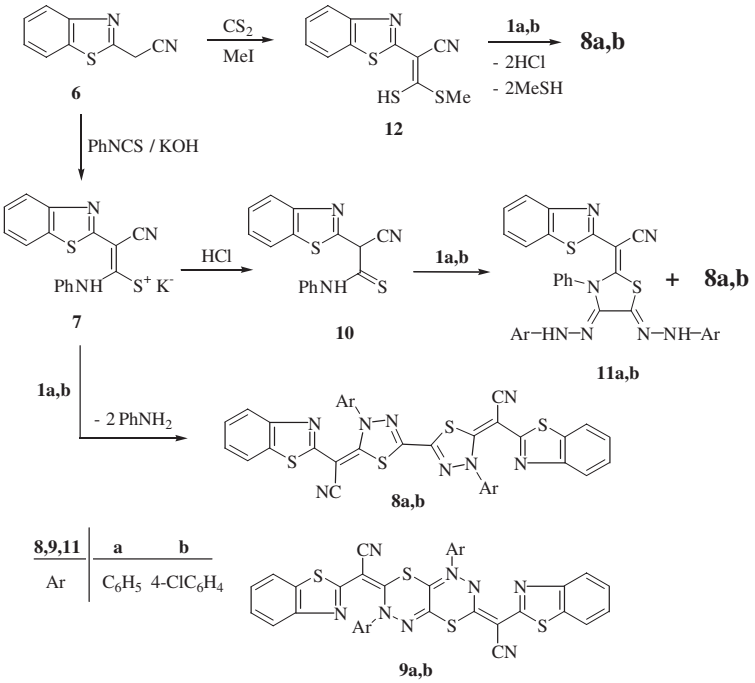

Scheme 2.

ethanolic triethylamine solution under reflux, they furnished products identical in all respects (TLC, m.p., mixed m.p., and spectral data) with compounds **8a**,**b**.

EXPERIMENTAL

Melting points were measured with a Gallenkamp apparatus and are uncorrected. Infrared spectra were recorded on Shimadzu FT-IR 8101 PC infrared spectrophotometer. The ^{1}H NMR spectra were determined in DMSO-d_6 at 300 MHz on a Varian Mercury VX 300 NMR spectrometer using TMS as an internal standard. Mass spectra were measured on a GCMS-QP1000 EX spectrometer at 70 eV. Elemental analyses were carried out at the Microanalytical center of Cairo University.

Bis-hydrazonoyl chlorides **1a**,**b**,[8,9] 2-methylthiobenzimidazole (**2**),[11] benzimidazole-2-thiol (**4**),[12] and 2-cyanomethylbenzothiazole (**6**) and its derivatives **7**, **10** and **12**,[13] were prepared as reported in literature.

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Synthesis of 1,1′-Diaryl-3,3′-bi-(1,2,4-triazolo[4,5-a]benzimidazoles) 3a,b

A mixture of the appropriate *bis*-hydrazonoyl chloride **1a**,**b** (1 mmol) and 2-methylthiobenzimidazole (**2**) (2 mmol) in ethanol (20 mL) was refluxed for 1 h, then left to cool to room temperature. The brown-colored precipitate was filtered off, washed with ethanol and dried. Recrystallization from dimethylformamide (DMF) afforded the corresponding 3,3′-bi-1,2,4-triazolo[4,5-a]benzimidazoles **3a**,**b**.

1,1′-Diphenyl-3,3′-bi-(1,2,4-triazolo[4,5-a]benzimidazole) (3a). Yield 61%. M.p.: 298–300°C. IR (KBr): ν 1615 (C = N) cm^{-1}. ^{1}H NMR [DMSO-d_6] δ 7.12–8.23 (m, 14H, ArH), 8.3 (d, 2H, $J = 9.0$ Hz), 8.75 (d, 2H, $J = 8.1$ Hz). MS, m/z (%) 467 ($M^+ + 1$, 10.3), 466 (M^+, 19.8), 363 (14.4), 259 (16.4), 233 ($M^+/2$, 10.3), 207 (20.9), 77 (100). Calcd. for $C_{28}H_{18}N_8$: C, 72.09; H, 3.89; N, 24.02. Found: C, 71.83; H, 3.81;N, 23.77.

1,1′-Di-(4-chlorophenyl)-3,3′-bi-(1,2,4-triazolo[4,5-a]benzimidazole) (3b). Yield 74%. M.p. > 300°C. IR (KBr) ν 1627, 1608 (C = N) cm^{-1}. ^{1}H NMR [DMSO-d_6] δ 7.16–8.69 (m, ArH). MS, m/z (%) 537 (M^++3, 11.7), 536 ($M^+ + 2$, 26.9), 535 ($M^+ + 1$, 35.0), 534 (M^+, 46.4), 466 (38.0), 465 (40.3), 293 (20.3), 268 ($M^+ + 1/2$, 6.8), 267 ($M^+/2$, 7.4), 206 (39.4), 113 (37.4%), 111 (100), 75 (34.5). Calcd. for $C_{28}H_{16}Cl_2N_8$: C, 62.81; H, 3.01; N, 20.93. Found: C, 62.70; H, 3.19; N, 20.61.

2,3-*bis*-Arylhydrazono-2,3,4,5-tetrahydrothiazolo[3,2-a]-benzimidazoles 5a,b

These compounds were prepared by the same procedure used in the synthesis of compounds **3a**,**b** using benzimidazole-2-thiol (**4**) instead of 2-methylthiobenzimidazole (**2**).

2,3-*bis*-phenylhydrazono-2,3,4,5-tetrahydrothiazolo[3,2-a]benzimidazole (5a.) Yield 77%. M.p.: 253–255°C (DMF). IR (KBr): ν 3205, 3178 (2NH), 1598 (C = N)cm^{-1}. ^{1}H NMR [DMSO-d_6] δ 6.95 (t, 1H, $J = 7.2$ Hz), 7.03 (t, 1H, $J = 7.2$ Hz), 7.25–7.47 (m, 10H, ArH), 7.69 (d, 1H, $J = 7.2$ Hz), 8.12 (d, 1H, $J = 7.2$ Hz), 10.57 (s, 1H, NH), 11.03 (s, 1H, NH). MS, m/z (%) 385 ($M^+ + 1$, 8.6), 384 (M^+, 24.1), 293 (13.0), 186 (4.6), 143 (8.3), 105 (27.5), 92 (18.3), 77 (100). Calcd. for $C_{21}H_{16}N_6S$: C, 65.61; H, 4.19; N, 21.86; S, 8.34. Found: C, 65.77; H, 4.18; N, 21.58; S, 8.46.

2,3-*bis*-(4-chlorophenylhydrazono)-2,3,4,5-tetrahydrothiazolo[3,2-a]-benzimidazole (5b). Yield 90%. M.p.: 266–268°C (DMF). IR (KBr): ν 3215, 3180 (2NH), 1601 (C = N) cm^{-1}. ^{1}H NMR [DMSO-d_6] δ 7.27–7.48 (m, 10H, ArH), 7.68 (d, 1H, $J = 7.2$ Hz), 8.10 (d, 1H, $J = 7.2$ Hz), 10.66

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(s, 1H, NH), 10.97 (s, 1H, NH). MS, *m*/*z* (%) 454 ($M^+ + 2$, 13.6), 453 ($M^+ + 1$, 18.8), 452 (M^+, 22.4), 327 (30.4), 326 (32.4), 186 (8.1), 175 (14.9), 139 (47.9), 126 (28.4), 111 (100), 90 (29.3), 75 (31.6). Calcd. for $C_{21}H_{14}Cl_2N_6S$: C, 55.64; H, 3.11; N, 18.54; S, 7.07. Found: C, 55.72; H, 3.05; N, 18.29; S, 7.25.

5,5′-Bi-[3-Aryl-2-(benzothiazol-2-yl)cyanomethylene-2,3-dihydro-1,3,4-thiadiazoles] 8a,b

Method A. To a stirred solution of potassium hydroxide (0.11 g, 2 mmol) in DMF (20 mL) was added 2-benzothiazoleacetonitrile (**6**) (0.348 g, 2 mmol). The mixture was stirred for 30 min, then phenylisothiocyanate (0.27 g, 2 mmol) was added, and the stirring was continued for 6 h. The appropriate *bis*-hydrazonoyl chloride **1a**,**b** (1 mmol) was added portion wise and the resulting reaction mixture was stirred for further 12 h, during which the *bis*-hydrazonoyl chlorides **1** dissolved and an orange-red product precipitated. The solid product was filtered off, washed with water and ethanol, dried and finally recrystallized from DMF to afford the corresponding 5,5′-bi-1,3,4-thiadiazole derivatives **8a**,**b** in 66 and 71% yields, respectively.

Method B. A mixture of the appropriate *bis*-hydrazonoyl chloride **1a**,**b** (1 mmol) and 2-(benzothiazol-2-yl)cyanothioacetanilide (**10**) (0.618 g, 2 mmol) in ethanol (20 mL), in the presence of triethylamine, was refluxed for 1 h, during which the starting materials were dissolved and a heavy solid product was precipitated. TLC proved that the reaction affords in all cases a mixture of two products. The so-formed precipitate was filtered off, washed with ethanol, and dried. Partial crystallization from DMF afforded compounds **8a**,**b** in 35 and 27% yields, respectively. Dilution of the mother-liquor with water resulted in the formation of solid preciptate which was filtered off, dried and recrystallized from DMF/water to give the 3,4-*bis*-arylhydrazonothiazole derivatives **11a**,**b** in 45 and 60% yields, respectively.

Method C. A procedure similar to that in method **B** using the methyl dithioacetal derivative **12** instead of thioacetanilde derivative **10** was conducted. 5,5′-bi-1,3,4-thiadiazoles **8a**,**b** were obtained in 83 and 90% yields, respectively.

5,5′-Bi-[3-phenyl-2-(benzothiazol-2-yl)cyanomethylene-2,3-dihydro-1,3,4-thiadiazole] (8a). Yield 83%. M.p.: >300°C. IR (KBr): ν 2192 (C≡N), 1622, 1593 (2C=N) cm^{-1}. ^{1}H NMR [DMSO-d_6] δ 7.21–8.55 (m, ArH). MS, *m*/*z* (%) 666 (M^+, 8.4), 611 (4.3), 586 (14.3), 536 (3.3), 509 (100), 450 (6.0), 393 (6.3), 359 (44.6), 307 (40.4), 248 (13.2), 135

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(33.8), 91 (47.8), 77 (89.7). Calcd. for $C_{34}H_{18}N_8S_4$: C, 61.24; H, 2.72; N, 16.81; S, 19.23. Found: C, 61.39; H, 2.66; N, 16.63; S, 19.27.

5,5′-Bi-[3-(4-chlorophenyl)-2-(benzothiazol-2-yl)cyanomethylene-2,3-dihydro-1,3,4-thiadiazole] (8b). Yield 90%. M.p.: >300°C. IR (KBr): ν 2195 (C≡N), 1624, 1585 (2C=N) cm^{-1}. ^{1}H NMR. Insoluble in the common solvents. MS, m/z (%) 736 ($M^+ + 2$, 4.8), 735 ($M^+ + 1$, 6.9), 734 (M^+, 13.2), 521 (2.4), 520 (15.3), 394 (100), 393 (51.3), 367 (4.6), 307 (65.9), 271 (28.3), 204 (22.6), 160 (64.2), 127 (81.0), 111 (64.4), 90 (34.3), 75 (81.0). Calcd. for $C_{34}H_{16}Cl_2N_8S_4$: C, 55.51; H, 2.19; N, 15.23; S, 17.43. Found: C, 55.42; H, 2.26; N, 14.97; S, 17.28.

4,5-Di-(phenylhydrazono)-2-(benzothiazol-2-yl)cyanomethylene-3-phenyl-2,3,4,5-tetrahydrothiazole (11a). Yield 45%. M.p.: 238–240°C. IR (KBr): ν 3228 (br., 2NH), 2193 (C≡N), 1599 (C=N) cm^{-1}. ^{1}H NMR [DMSO-d_6] δ 7.15–8.23 (m, 19H, ArH), 9.07 (br. s, 1H, NH), 10.92 (br. s, 1H, NH). MS, m/z (%) 544 ($M^+ + 1$, 13.3), 543 (M^+, 18.5), 478 (23.1), 359 (37.6), 307 (27.6), 275 (17.8), 178 (12.5), 146 (12.4), 109 (13.0), 77 (100). Calcd. for $C_{30}H_{21}N_7S_2$: C, 66.28; H, 3.89; N, 18.03; S, 11.80; Found: C, 66.04; H, 3.81; N, 17.78; S, 11.83.

4,5-Di-(4-chlorophenylhydrazono)-2-(benzothiazol-2-yl)cyanomethylene-3-phenyl-2,3,4,5-tetrahydrothiazole (11b). Yield (60%). M.p.: 259–261°C. IR (KBr): ν 3230, 3159 (2NH), 2194 (C≡N), 1602 (C=N) cm^{-1}. ^{1}H NMR [DMSO-d_6] δ 7.12–8.33 (m, 17H, ArH), 10.71 (br., s, 1H, NH), 11.20 (br., s, 1H, NH). MS, m/z (%) 614 ($M^+ + 2$, 10.3), 613 ($M^+ + 1$, 18.5), 612 (M^+, 27.2), 486 (23.7), 343 (26.3), 275 (14.2), 204 (12.5), 160 (12.4), 126 (28.0), 111 (100), 77 (63.6). Calcd. for $C_{30}H_{19}Cl_2N_7S_2$: C, 58.82; H, 3.13; N, 16.01; S, 10.47. Found: C, 58.61; H, 3.45; N, 16.33; S, 10.41.

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