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A short and efficient synthesis of 5,5′-bi-1,2,3-dithiazoles

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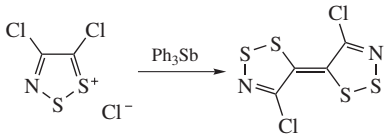
Reaction of 1-arylethanone oximes with S_2Cl_2 gives 4-aryl-5-chloro-1,2,3-dithiazol-1-ium chlorides, whose *in situ* treatment with copper powder affords 4,4′-diaryl-5,5′-bi-1,2,3-dithiazoles.

1,2,3-Dithiazoles have attracted much attention due to their wide spectrum of biological activity, unusual physical properties and diverse chemical transformations.[1–6] More recently, their potential utility in material science as new and efficient functional materials for electronics and spintronics has emerged.[7,8] Monocyclic 1,2,3-dithiazoles serve as precursors for stable radical species;[8–10] while fused derivatives have been studied as magnetic conductive materials.[8,11,12] A particular interest is drawn to 5,5′-linked bi-dithiazoles which could serve as templates for preparing conductive charge-transfer salts[13,14] and diradical species.[15] There is only one example of such diradical with two dithiazole rings bound by an exocyclic double bond C=C, namely, dichlorotetrathiadiazafulvalene **1a**, which was obtained by reduction of 4,5-dichloro-1,2,3-dithiazol-1-ium chloride (Appel's salt) **2a** with triphenylantimony in liquid sulfur dioxide at –70 °C in moderate yield (Scheme 1).[16] A series of 1:1 radical ion salts was prepared by electrooxidation of compound **1a** in the presence of tetrahedral counterions.[13] These stable radical cations can be used as potential building blocks for charge transfer conductors.



2a **1a**, 30%

Scheme 1

Herein we report short and convenient synthesis of substituted 5,5′-bi-1,2,3-dithiazoles **1a–e** which can be considered as precursors for the corresponding radical cations.

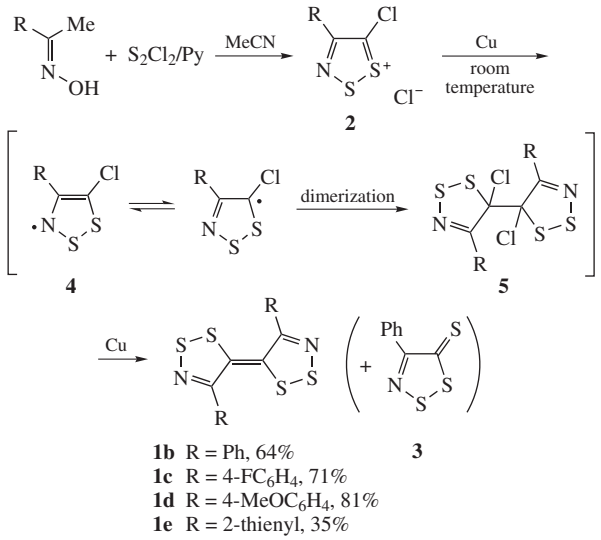
Surprisingly, apart from Appel's salt 4-substituted 1,2,3-dithiazolium chlorides, apparent precursors for **1a–e**, are hardly accessible. 4-Phenyl- and 4-(4-nitrophenyl)-1,2,3-dithiazolium chlorides have been prepared by the treament of acetophenone oxime and its 4-nitro derivative with sulfur monochloride.[17,18] These salts turned to be highly reactive and were converted to stable 5-arylimino derivatives by the reaction with primary aromatic amines. Recently an easy one-pot protocol for the preparation of 4-substituted 1,2,3-dithiazolium chlorides **2** from readily available acetoximes, sulfur monochloride, pyridine in MeCN has been developed. Further treatment of these salts with formic acid, thioacetamide or aniline afforded 5-oxo-, 5-thioxo- and 5-phenylimino-1,2,3-dithiazoles, respectively, in high to moderate yields.[19] To continue the investigation of the chemical utility of 4-substituted 1,2,3-dithiazolium chlorides **2**, we examined their reduction with a variety of metals (silver, zinc, iron and copper) and triphenylantimony. 4-Phenyl-1,2,3-dithiazolium chloride **1b**, prepared *in situ* from acetophenone oxime and sulfur monochloride, was subjected to reduction with triphenylantimony. Organic solvents (MeCN, benzene or CS_2), where Ph_3Sb was dissolved, were found ineffective for the synthesis of bi-dithiazole **1b**. In all cases 4-phenyl-5*H*-1,2,3-dithiazole-5-thione **3** formed in low yields (12, 20 and 36%, respectively). Similar results were obtained when iron or zinc powder were used as reducing agents, the yield of thione **3** was 38 and 34%, respectively. Silver powder was found inactive toward salt **2b**. The most successful procedure employed copper powder as a reductant at room temperature; the bi-dithiazole **1b** was isolated in 64% yield (Scheme 2).

To evaluate the scope of the reaction, substrates **2c–e** were converted into products **1c–e** in high to moderate yields (see Scheme 2).[†] Apparently, the yield of fulvalenes **1** depended on the amount of the salt **2** formed in the reaction of substituted

[†] *General procedure for the reaction of 1-(het)arylethanone oximes with S_2Cl_2.* Pyridine (0.96 ml, 6 mmol) was added dropwise to a stirred solution of ethanone oxime (2 mmol) and sulfur monochloride (0.64 ml, 4 mmol) in acetonitrile (15 ml) at –5–0 °C under atmosphere of argon. The mixture was stirred at –2–0 °C for 15 min. Then copper powder (192 mg, 3 mmol) was added, the mixture was stirred at room temperature for 1.5 h and poured into ice water (100 ml). The precipitate was filtered, washed with water, dried and extracted with CH_2Cl_2 (3×15 ml). The combined extracts were dried with $CaCl_2$ and solvents were evaporated under reduced pressure. The residue was rapidly separated by flash chromatography (Silica gel Merck 60, light petroleum and then light petroleum–CH_2Cl_2 mixtures).

4,4′-Diphenyl-5,5′-bi-1,2,3-dithiazole **1b**. Dark-violet crystals, yield 64%, mp 167–168 °C. ^{1}H NMR ($CDCl_3$) δ: 7.52 (m, 8H, Ar), 8.03 (d, 2H, Ar, J 7.6 Hz). ^{13}C NMR ($CDCl_3$) δ: 127.3, 129.2, 130.2 (3CH, Ph), 132.9, 156.1, 161.1 (3 sp^2 tertiary C). IR (KBr, ν/cm^{-1}): 1684, 1652, 1616, 1456, 1440, 1424, 1340, 1280, 1172, 1064, 1020, 804, 764, 732, 688. UV ($CHCl_3$, λ/nm): 333 (3.7), 586 (3.5). MS (EI, 70 eV), *m/z* (%): 358 (M^+, 5), 326 (5), 294 (40), 191 (47). HRMS (ESI), *m/z*: 357.9713 $[M+H]^+$ (calc. for $C_{16}H_{10}N_2S_4$, *m/z*: 357.9721). Found (%): C, 53.83; H, 2.93; N, 7.95. Calc. for $C_{16}H_{10}N_2S_4$ (%): C, 53.60; H, 2.81; N, 7.81.

4,4′-Bis(4-fluorophenyl)-5,5′-bi-1,2,3-dithiazole **1c**. Black crystals, yield 71%, mp 147–148 °C. ^{1}H NMR ($CDCl_3$) δ: 7.24 (m, 4H, Ar), 8.00 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$) δ: 116.4 (d, 4CH, Ar, J 22.0 Hz), 129.3 (d, 4CH, Ar, J 8.6 Hz), 129.1, 155.1, 162.7 and 163.9 (d, J 248 Hz) (8 sp^2 tertiary C). IR (KBr, ν/cm^{-1}): 2920 (C–H), 1508, 1432, 1412, 1284, 1228, 1156, 1048, 840, 808, 720. UV ($CHCl_3$, λ/nm): 347 (3.6), 590 (3.29). MS (EI, 70 eV), *m/z* (%): 394 (M^+, 7), 362 (5), 330 (27), 229 (25). HRMS (ESI), *m/z*: 393.9531 $[M]^+$ (calc. for $C_{16}H_8F_2N_2S_4$, *m/z*: 393.9533). Found (%): C, 48.89; H, 2.08; N, 6.97. Calc. for $C_{16}H_8F_2N_2S_4$ (%): C, 48.71; H, 2.04; N, 7.10.



Scheme 2

acetoxime with sulfur monochloride at the first step. When Appel's salt **2a** was treated with copper in acetonitrile at room temperature, dichlorotetrathiadiazafulvalene **1a** was obtained in practically quantitative yield (98%). The procedure is superior to the known method[16] by the yield of bi-dithiazole **1a** and by avoiding the use of awkward sulfur dioxide and low reaction temperature.

Bi-1,2,3-dithiazoles **1** synthesized are unstable in light and in air but can be stored in dark bottles in a refrigerator under inert gas. All bi-dithiazoles **1** are dark-blue to black crystals; they were characterized by UV spectral data: λ = 586–590 nm with lgε from 3.29 to 3.5.

4,4'-Bis(4-methoxyphenyl)-5,5'-bi-1,2,3-dithiazole **1d**. Black crystals, yield 81%, mp 211–212 °C. ^{1}H NMR ($CDCl_3$) δ: 3.90 (s, 6H, OMe), 7.06 (d, 4H, Ar, *J* 8.6 Hz), 7.93 (d, 4H, Ar, *J* 8.6 Hz). ^{13}C NMR ($CDCl_3$) δ: 114.6, 128.8 (2CH, Ph), 129.5, 155.9, 161.1, 168.4 (4 sp^2 tertiary C). IR (KBr, ν/cm^{-1}): 1604, 1544, 1504, 1480, 1460, 1428, 1416, 1304, 1248, 1176, 1024, 832. UV ($CHCl_3$, λ/nm): 345 (3.5), 588 (3.4). MS (EI, 70 eV), *m/z* (%): 418 (M^+, 90), 386 (19), 354 (95), 253 (38), 165 (27). HRMS (ESI), *m/z*: 417.9926 $[M]^+$ (calc. for $C_{18}H_{14}N_2O_2S_4$, *m/z*: 417.9933). Found (%): C, 51.92; H, 3.31; N, 6.48. Calc. for $C_{18}H_{14}N_2O_2S_4$ (%): C, 51.65; H, 3.37; N, 6.69.

4,4'-Di(2-thienyl)-5,5'-bi-1,2,3-dithiazole **1e**. Dark-blue crystals, yield 35%, mp 142–143 °C. ^{1}H NMR ($CDCl_3$) δ: 7.25 (m, 1H, Ar), 7.65 (d, 1H, Ar, *J* 4.7 Hz), 7.93 (d, 1H, Ar, *J* 4.8 Hz). IR (KBr, ν/cm^{-1}): 2920 (C–H), 2856, 1652, 1536, 1448, 1424, 1344, 1256, 1224, 1048, 852, 800, 760, 704, 680, 664, 624. UV ($CHCl_3$, λ/nm): 352 (3.8), 589 (3.45). MS (EI, 70 eV), *m/z* (%): 418 (M^+, 90), 386 (19), 354 (95), 253 (38), 165 (27). HRMS (ESI), *m/z*: 369.8841 $[M+H]^+$ (calc. for $C_{12}H_6N_2S_6$, *m/z*: 369.8850). Found (%): C, 38.73; H, 1.62; N, 7.82. Calc. for $C_{12}H_6N_2S_6$ (%): C, 38.89; H, 1.63; N, 7.56.

4,4'-Dichloro-5,5'-bi-1,2,3-dithiazole **1a**. Copper powder (256 mg, 4 mmol) was added to a slurry of 4,5-dichloro-1,2,3-dithiazol-1-ium chloride **2a** (416 mg, 2 mmol) in acetonitrile (10 ml). The mixture was stirred at room temperature for 1 h, poured into ice water (100 ml), the precipitate was filtered, washed thoroughly with water (2×10 ml), MeCN (2×5 ml), CH_2Cl_2 (2×5 ml) and dried to afford black crystals of compound **1a**, yield 98%, mp 144–145 °C (lit.,[13] mp 120–121 °C). The IR, UV and mass spectra are similar to those of the sample prepared by the literature method.[13]

The most plausible mechanism for the formation of bi-dithiazoles **1** is given in Scheme 2. The key steps are assumed with the formation of unstable 1,2,3-dithiazolium radical **4** which would dimerize by carbon atoms to bi-dithiazole **5** followed by dechlorination with copper to produce the final fulvalene **1**.

The structure of diphenyltetrathiadiazafulvalene **1b** was explicitly confirmed by X-ray analysis, which will be published elsewhere.

In conclusion, a short and convenient method for the synthesis of 5,5′-bi-1,2,3-dithiazoles has been elaborated. The preparation of radical cations from bi-dithiazoles **1** is under investigation.

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