CHEMISTRY LETTERS, pp. 1827-1828, 1994.

Convenient Synthesis of Bis-1,3-dithiolium Salts by One-electron Oxidation of Tetrathiafulvalene with Oxoaminium Salts

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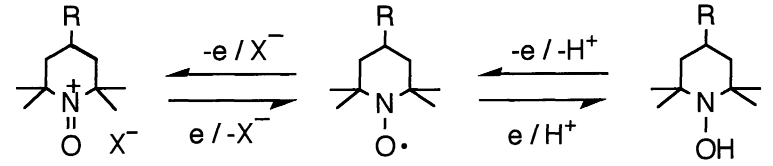
Several bis-1,3-dithiolium salts, radical cation salts of tetrathiafulvalene were synthesized in quantitative yields by oxidation of tetrathiafulvalene with oxoaminium salts for 1min at room temperature.

Oxoaminium salt (**1**) forms the following reversible redox system together with the corresponding nitroxyl radical (**2**) and hydroxyl amine (**3**), and serves as a mild and selective oxidant for a few organic substances such as alcohols.1-3) The oxidations are usually performed by one or two electron transfer to **1** from substrates,4) depending on the structure of the substrates.



1 **2** **3**

Several amines including phenothiazines are quantitatively oxidized by **1** to the corresponding radical cations via one-electron transfer process.5) Similarly, carbon-oxygen bond cleavage of benzyl ethers with **1** selectively undergoes via initial one-electron oxidation with **1**.6) Meanwhile, selective and efficient synthesis of bis-1,3-dithiolium salt (**5**) is a recent topic in the field of organic solid conductors, because bis-1,3-dithiolium chloride (**5**, X = Cl) is known as an excellent organic semiconductor.7) Synthesis of **5** by oxidation of TTF with chlorine has been reported by Wudl *et al.*,8) but overoxidation to dication (**6**) has remained as problem. In this paper, convenient and selective synthesis of **5** by the oxidation of bis-1,3-dithiol (**4**) with **1** is disclosed.

The oxidation of **4** with 1 equiv. of **1a** (X = SbF_6) was carried out in acetonitrile at room temperature for 1min. Bis-1,3-dithiolium hexafluoroantimonate (**5a**, X = SbF_6) was isolated in 94% yield, mp 216.5 °C (decomp); IR (KBr, cm^{-1}) 3237, 3105, 1506, 1476, 1351, 1263, 1236, 1073, 919, 831, 824, 707, 672; UV

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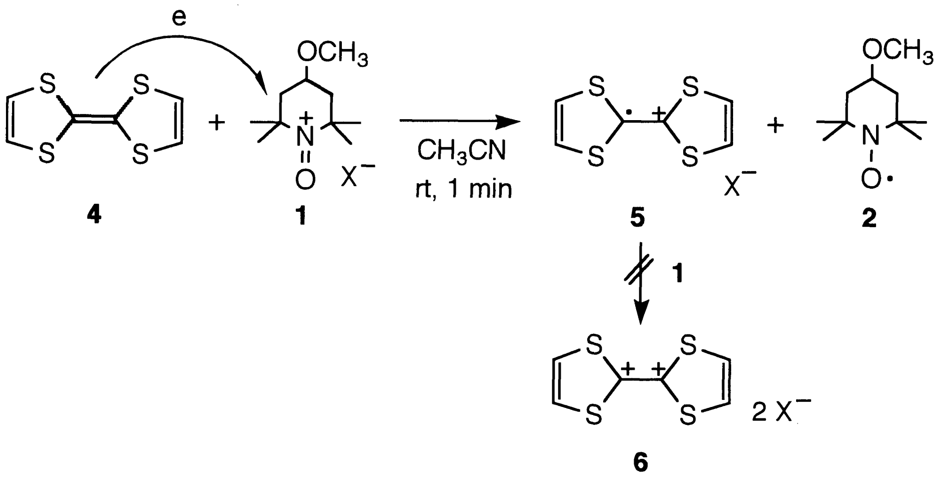
(H_2O, λmax, nm) 197.2, 215.6 (sh), 338.4, 405.2 (sh), 434.0, 580.0; ESR (EtOH, -50 ℃) H = 1.24 ± 0.02 G, g = 2.0075]. These physical and spectral data well agreed with those of Wudl's previously reported.[8] Since the yield of **5a** was quantitative and **2** was obtained in 93% yield in the oxidation, it is obvious that this oxidation involves a complete one-electron transfer from **4** to **1a**. When **4** was oxidized with 2 equiv. of **1a** under the same conditions, the product obtained was identified as **5a** but not the corresponding dication (**6a**), suggesting that no overoxidation from **5a** to **6a** with **1a** occurred in the oxidation. Furthermore, both **4** and **5a** did not react with **2** at all. Therefore, the oxidation-reduction potentials of these compounds are suggested to follow the order; **2**/**3** < **5**/**4** < **1**/**2** < **6**/**5**, in accordance with the reported potentials.[9-11] The oxidations of **4** with **1b**-**1e** having counter anions ClO_4^- (**b**), BF_4^- (**c**), NO_3^- (**d**), or Cl^- (**e**) also afforded the corresponding **5b**-**5e** in high yields; **5b**; 92%, mp 210.3-210.5 ℃ (decomp), **5c**; 95%, mp 211.5-211.8 ℃ (decomp), **5d**; 93%, mp 150.0-150.3 ℃ (decomp.), **5e**; 89%, mp 173.4-174.3 ℃ (decomp). All these compounds showed UV and ESR spectra (g = 2.0073-2.0095 and ^aH = 1.24 ± 0.2 G) similar to those of **5a**. **5d** and **5e** were insoluble in acetonitrile, whereas **5a**-**5c** were readily soluble in acetonitrile.



References

1) J. M. Bobbitt and M. C. L. Flores, *Heterocycles*, **27**, 509 (1988).

2) T. Miyazawa, T. Endo, S. Shiihashi, and M. Okawara, *J. Org. Chem.*, **50**, 1332 (1985).

3) E. Yoshida, T. Takata, and T. Endo, *Makromol. Chem.*, **194**, 1307 (1993).

4) M. F. Semmelhack, C. R. Schmid, and D. A. Cortes, *Tetrahedron Lett.*, **27**, 1119 (1986).

5) Y. C. Liu, Z. L. Liu, L. M. Wu, and P. Chen, *Tetrahedron Lett.*, **26**, 4201 (1985).

6) E. Yoshida, T. Takata, and T. Endo, *Macromolecules*, **26**, 554 (1993).

7) F. Wudl, D. Wobschall, and E. J. Hufnagel, *J. Am. Chem. Soc.*, **94**, 670 (1972).

8) F. Wudl, G. M. Smith, and E. J. Hufnagel, *J. Chem. Soc., Chem. Commun.*, **1970**, 1453.

9) D. L. Coffen, J. Q. Chambers, D. R. Williams, P. E. Garrett, and N. D. Canfield, *J. Am. Chem. Soc.*, **93**, 2259 (1971).

10) E. M. Engler, F. B. Kaufman, D. C. Green, C. E. Klots, and R. N. Compton, *J. Am. Chem. Soc.*, **97**, 2922 (1975).

11) T. Endo, T. Miyazawa, S. Shiihashi, and M. Okawara, *J. Am. Chem. Soc.*, **106**, 3877 (1984).

(Received June 27, 1994)