GENERATION OF NEW DITHIA DICATIONS FROM STERICALLY CONGESTED 1,9-DITHIODIBENZOTHIOPHENES AND THEIR MONOOXIDES IN CONCENTRATED SULFURIC ACID

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Abstract: 1,9-Dithiodibenzothiophenes 2 were prepared by ring contraction of 4,6-dithiothianthrene-5-oxides with n-butyllithium. Both compounds 2 and their monooxides 3 upon dissolution in conc. H_2SO_4 afforded the corresponding new dithia dications. Electrochemical oxidation of 2 provides the evidence for the neighboring group interaction between the two 1,9-sulfenyl sulfur atoms.

Sterically congested 1,9-dithiodibenzothiophenes 2 were readily prepared by coupling reactions of the corresponding 4,6-dithiosubstituted thianthrene-5-oxides $1.^1$ Since compounds 2a,b have two closely located sulfur atoms of the 1,9 positions, they should provide a new dicationic S-S σ -bond on oxidation.^{2,3} This paper reports the formation of new dithia dications by treatment of 2 and 3 in conc. H₂SO₄ together with electrochemical oxidation of **2**.

Dibenzothiophenes 2a,b were prepared by the reactions of 1 with n-butyllithium in THF at -78 °C in 22% and 65% yields respectively. Upon oxidation with an equimolar of m-chloroperbenzoic acid (mCPBA) of 2a,b afforded the corresponding monosulfoxides 3a,b in 92% and 78% yields (Scheme 1).⁴

The formation of dication from 2a and 3a was confirmed by the following experiments. Namely, in the ¹H NMR spectrometry of 3a in conc. D_2SO_4 , the two methyl protons observed at δ 2.79 (SOCH₃) and 2.33



(SCH₃) ppm in CDCl₃ shifted to downfield and coalesced to a singlet at δ 3.04 ppm. Then the solution was treated with ice-water to give the sulfoxide 3a in 56% yield together with a trace amount of the demethylated disulfide 6. Furthermore, when the deuterated sulfoxide 4 (D-content > 96%), prepared by H-D exchange reaction of 3a with D₂O-THF and NaOD in 95% yield, was dissolved in conc. H₂SO₄ and after treatment of the solution with ice-water, a 1:1 mixture of 4 and 5 was obtained in 63% yield (Scheme 1). ¹⁸O labeled sulfoxide of 3a (¹⁸O content > 98%) prepared from 2a was treated similarly as described above to give non labeled sulfoxide 3a in 70% yield.⁵ These results demonstrate clearly that a new dithia dication 7 is formed as an intermediate in the deoxygenation reaction by the neighboring group participation of the sulferyl sulfur atom. In the reaction of 3a in conc. H₂SO₄, 1,9-bis(methylthio)dibenzothiophene-5-oxide was not obtained at all demonstrating that dication should be localized on the two outer sulfur atoms. The ¹H NMR spectrum of 2a in conc. D₂SO₄ displayed the same with that of the sulfoxide 3a, suggesting again that the dication 7 is formed from the oxidation of the sulfide 2a. Indeed, when 2a was treated with NOBF4, its dicationic salt was isolated as hygroscopic white powder.⁶ On the other hand, the ¹H and ¹³C NMR spectra of 3b measured in conc. D₂SO₄ suggest the formation of dication.⁷ After treating the solution with ice-water, the starting sulfoxide **3b** was obtained in 89% yield. Measurement of cyclic voltammetry for all compounds was carried out using Pt electrode and Ag/(0.01 M)AgNO₃ as a reference electrode (scan rate: 200 mV/s) at 25 °C in acetonitrile. The cyclic voltammograms of 2a,b revealed three irreversible oxidation peaks. Interestingly, the first peak potentials of 2a (0.76 V) and 2b (0.86 V) were considerably lower than 1-(methylthio)- 8a (1.02 V), 1-(phenylthio)- 8b (1.12 V), 2,8-bis(methylthio)dibenzothiophene 9 (0.96 V) and diphenyl sulfide (1.21 V). The cyclic voltammetric results provide also the evidence for the neighboring group interaction between the two outer sulfur atoms on electrochemical oxidation.²

Acknowledgement: This work was supported by the Grant-in-Aid for Scientific Research on Priority Area of Organic Unusual Valency from the Ministry of Education, Science, and Culture of Japan (No. 03233101).

References and Notes

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- 2) Fujihara, H.; Furukawa, N. J. Mol. Struct. (Theochem), 1989, 186, 261; and references cited therein.
- 3) Kimura, T.; Horie, Y.; Ogawa, S.; Furukawa, N. Heterocycles, in press.
- 4) 2a: mp. 147.5-148 °C; ¹H NMR (CDCl₃) δ 7.83-6.99 (m, 6H, Ar-H), 2.40 (s, 6H, CH₃); MS (m/z) 276 (M⁺); Anal. Calcd for C₁₄H₁₂S₃: C, 60.83; H, 4.38. Found; C, 60.83; H, 4.37; 3a: mp 158-160 °C; ¹H NMR (CDCl₃) δ 8.47-8.46 (m, 1H, Ar-H), 8.10-7.18 (m, 5H, Ar-H), 2.79 (s, 3H, SOCH₃), 2.33 (s, 3H, SCH₃); FT IR (KBr) 1021 cm⁻¹; MS (m/z) 292 (M⁺); Anal. Calcd for C₁₄H₁₂OS₃: C, 57.50; H, 4.14. Found: C, 57.65; H, 4.11.
- 5) Okuruszek, A. J. Labelled Compd. Radiopharm., 1983, 20, 724.
- 6) Dicationic salt: mp 113 °C (decomposition); ¹H NMR (500 MHz, CD₃CN, TMS) δ 8.50 (d, J=7.9 Hz, 2H, Ar-H), 8.38 (d, J=7.9 Hz, 2H, Ar-H), 8.04 (t, J=7.9 Hz, 2H, Ar-H), 3.37 (s, 6H, CH₃).
- 7) ¹H NMR (500 MHz, D₂SO₄, DSS) δ 8.11 (d, J=8.0 Hz, 2H), 7.64-7.56 (m, 2H), 7.48 (t, J=8.0 Hz, 2H), 7.26 (d, J=8.0 Hz, 2H), 7.24-7.07 (m, 4H), 6.94 (brs, 2H), 5.90 (brs, 2H); ¹³C NMR (125 MHz, D₂SO₄, DSS) δ 148.2, 146.4, 140.8, 136.1, 135.7, 134.0, 133.9, 130.8, 122.4, 112.2.