BIS(BENZO-1,3-DITHIAFULVENYL)

Tokuzo Kawase, Hiroshi Awaji, Shigeo Yoneda and Zen-ichi Yoshida*
Department of Synthetic Chemistry, Kyoto University, Yoshida
Kyoto 606, Japan

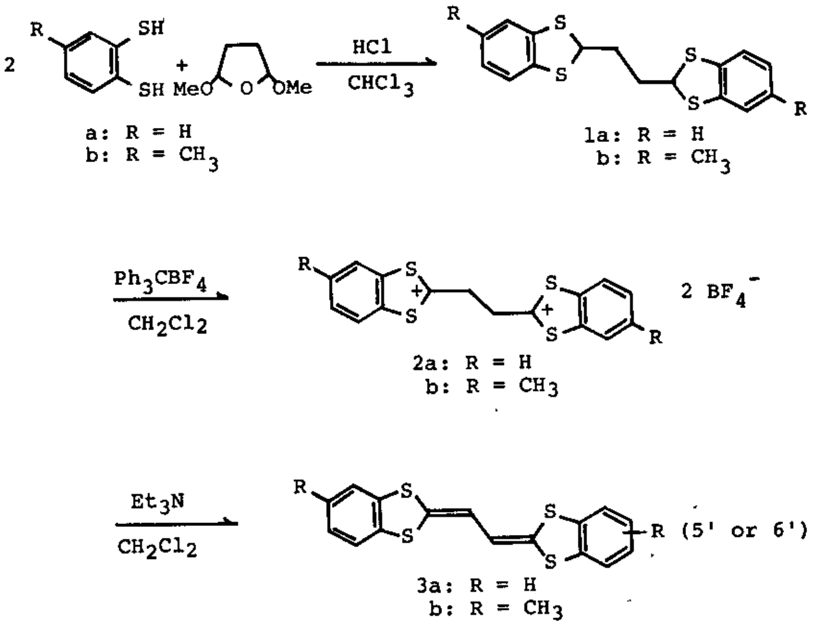
Abstract — Bis(benzo-1,3-dithiafulvenyl) (**3**) is newly prepared in three steps from o-benzenedithiol and 2,5-dimethoxytetrahydrofuran, and the cyclic voltammogram shows the excellent electron-donating property of **3**.

The discovery of the high electrical conductivity of the charge-transfer complex of TTF-TCNQ[1] has given impetus to the syntheses of a variety of new "synthetic metals". Moreover, the recent discovery of the super conductivity of $(TMTSeF)_2PF_6$[2] has strongly directed the attention toward the synthesis of new donors possessing 1,3-dithiole rings.[3]

We now report the synthesis of a novel donor, bis(benzo-1,3-dithiafulvenyl) (**3**). o-Benzenedithiols were reacted with 2,5-dimethoxytetrahydrofuran in the presence of hydrogen chloride to give bisdithioacetals (**1**) : **1a** (75%), m.p. 130-131 °C, and **1b** (94%), m.p. 118.5-119.5 °C. Treatment of **1** with 2 equiv of triphenylmethyl fluoroborate in CH_2Cl_2 gave bis(benzo-1,3-dithiolium) fluoroborate (**2**) almost in quantitative yield. Deprotonation of **2** by excess of Et_3N proceeded cleanly to afford **3** : **3a** (48%), m.p. 220 °C (decomp.) and **3b** (57%), m.p. 258-260 °C (decomp.).

Compounds, **3a** and **3b**, gave C, H, and S analyses within 0.3% of the calculated values. Their i.r. spectra exhibited C=C bands in the regions 1505-1515 and 800-805 cm^{-1}. The n.m.r. spectrum of **3a** in $CDCl_3$ consisted of peaks at δ 5.99 2H, s, exo-olefin) and 7.12 (8H, br s, aromatic).[†] The n.m.r. spectrum of **3b** showed peaks at δ 2.27 (6H, s, $C\underline{H}_3$), 5.94 (2H, s, exo-olefin) and 6.9∿7.1 (6H, m, aromatic). The electronic spectra were measured in $CHCl_3$: **3a**, λ_{max} (logε); 376 (4.55), 394 (4.53), and **3b**; 379 (4.64), 398 (4.63).

The cyclic voltammogram of **3a** displays two clear reversible one-electron oxi-



a: R = H
b: R = CH_3

1a: R = H
b: R = CH_3

2a: R = H
b: R = CH_3

3a: R = H
b: R = CH_3

dation waves at $E_{\frac{1}{2}}^{1} = 0.47$ and $E_{\frac{1}{2}}^{2} = 0.64$ V (vs. Ag|AgCl, 0.1M Et_4NClO_4, CH_3CN, Pt electrode, room temperature). The fact that the values of oxidation potentials of **3a** are smaller than those of dibenzo TTF [$E_{\frac{1}{2}}^{1} = 0.61$ and $E_{\frac{1}{2}}^{2} = 0.93$ V] clearly indicates bis(1,3-dithiafulvenyl) system is superior as a donor to TTF one. In fact, **3a** instantly afforded dark purple charge-transfer salt (**4a**) with DDQ in a ratio 1 : 1. Furthermore, **3a** was readily converted to the cation radical salt (**5a**), $(\mathbf{3a})_x(BF_4)_y$, by the method of Hünig et al.[4] as purple crystals.‡

References

1. A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, 1974, **7**, 218 and references cited therein.
2. D. Jérome, A. Mazaud, M. Ribault and K. Bechgraard, *J. de Physique Letters*, 1980, **41**, L 95; K. Bechgaard, C. S. Jacobsen, K. Mortensen, H. J. Pedersen and N. Thorup, *Solid State Commun.*, 1980, **33**, 1119.
3. M. Narita and C. U. Pittman, Jr., *Synthesis*, 1976, 486; Y. Ueno, M. Bahry and M. Okawara, *Tetrahedron Lett.*, 1977, 4607; M. V. Lakshmikantham and M. P. Cava, *J. Org. Chem.*, 1978, **43**, 82; M. Sato, M. V. Lakshmikantham, M. P. Cava and A. F. Garito, *ibid.*, 1978, **43**, 2085; N. C. Gonnella and M. P. Cava, *ibid.*, 1978, **43**, 369; J. M. Fabre, E. Torreilles and L. Giral, *Tetrahedron Lett.*, 1978, 3703.
4. S. Hünig, G. Kiesslich, H. Quast and D. Scheutzow, *Justus Liebigs Ann. Chem.*, 1973, 41.

†: The n.m.r. spectra of **3** were recorded on JEOL FX-90Q using FT technique because of poor solubility (*ca.* 1 mg/ml $CDCl_3$). Since the position (5' or 6') of methyl group in **3b** is difficult to determine by the usual spectral data, X-ray crystallographic study of **3b** is now under way.

‡: Several values of the ratio (x to y) are obtained through the reaction conditions.

Received, 28th September, 1981