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SYNTHESIS AND PROPERTIES OF ETHANEDIYLIDENE-2,2'-BIS(1,3-DITHIOLE)

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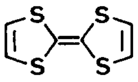
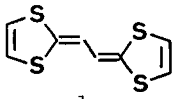
Summary: A new type of electron donors in the charge-transfer complex formation, ethanediylidene-2,2'-bis(1,3-dithiole)'s, have been synthesized by the reaction of (1,3-dithiolidene)phosphoranes with 2-formylmethylene-1,3-dithioles and their properties have been discussed.

Discoveries of the high electrical conductivity of the first organic metal, tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) complex,[1] and of organic super conductor, bis(tetramethyl tetraselenafulvalene) hexafluorophosphate,[2] have produced an important concept, from which we now know that highly conductive organic metals are formed from radical ions based on chalcogenfulvalenoids as the donor. Another concept for molecular design of organic metals is to minimize the Coulombic repulsion in the doubly ionized state[3,4] of the donor. Considering these points, we designed the novel π-donor, ethanediylidene-2,2'-bis(1,3-dithiole) (**1**) in which two 1,3-dithiole rings are connected with two sp^2 carbons. This new donor **1** can be expected to serve as more efficient donor than TTF from MINDO/3 ionization potentials. Here we report synthesis and properties of compounds **1**.



TTF



1a

The present synthesis is based on the Wittig-type reaction of (1,3-dithiolidene)phosphoranes (**2**) and 2-formylmethylene-1,3-dithioles (**3**) as

Scheme 1.

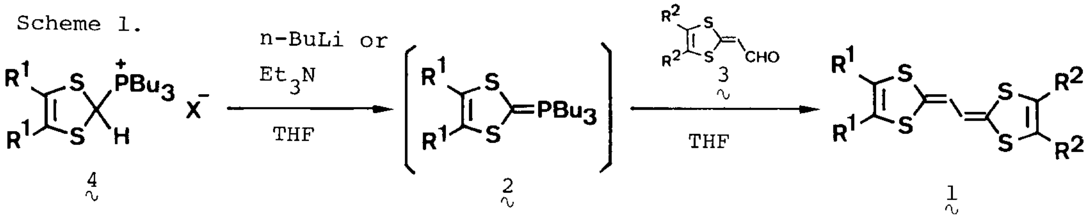


Table 1. Reactants and Products of Wittig Reaction

Phosphonium Salts (4)	Aldehydes (3)	Products (1)	Yield (%)
a(R^1=CO_2Me, X=BF_4)	a(R^2=CO_2Me)	b(R^1=R^2=CO_2Me)	73[b]
b(R^1=Me, X=ClO_4)	b(R^2=Me)	c(R^1=R^2=Me)	78[a]
c(R^1=-(CH=CH)$_2$-, X=BF_4)	c(R^2=-(CH=CH)$_2$-)	d(R^1=R^2=-(CH=CH)$_2$-)	80[a](30)[b]
a(R^1=CO_2Me, X=BF_4)	c(R^2=-(CH=CH)$_2$-)	e(R^1=CO_2Me, R^2=-(CH=CH)$_2$-)	46[b]

[a] n-BuLi was used as base. [b] Triethylamine was used as base.

shown in Scheme 1. To a solution of 4,5-dicarbomethoxy-1,3-dithiolyl-tributylphosphonium tetrafluoroborate (4a)[5] (507 mg, 1 mmol) and 2-formylmethylene-4,5-dicarbomethoxy-1,3-dithiole (3a)[6] (260 mg, 1 mmol) in 20 ml of tetrahydrofuran (THF) was added dropwise excess triethylamine (0.5 ml) at room temperature. After the reaction mixture was stirred for 1h and followed by subsequent concentration, the residue was chromatographed on silica gel with CH_2Cl_2 to afford purple crystals (1b) (337 mg, 73% yield). The reaction of 4a with 2-formylmethylene-(1,3-benzodithiole) (3c)[6] gave unsymmetrical derivative (1e) in 46% yield. Tetramethyl derivative (1c) was obtained in 78% yield by the reaction of phosphonium salt (4b)[7] with aldehyde (3b)[6] in the presence of n-BuLi. In the previous paper we reported the synthesis of dibenzo derivative (1d) via bis(1,3-dithiolylium) salt.[8] Similar Wittig-type reaction of 4c with 3c also gave 1d by the use of Et$_3$N or n-BuLi as base in 30 or 80% yield, respectively.

The carbomethoxy groups on the 1,3-dithiole rings of 1b and 1e were easily removed by LiBr·H_2O/HMPA treatment[9] to provide the title compound 1a (83% yield) and monobenzo derivative (1f) (37% yield), respectively (Scheme 2). The physical and spectral data for 1[10] are summarized in Table 2.

A cyclic voltammogram of 1a using the three-electrode technique in

Scheme 2.

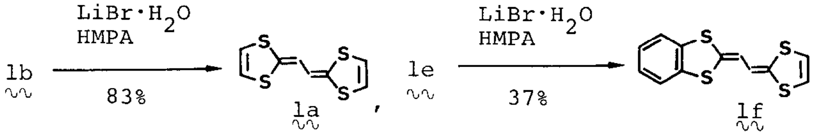
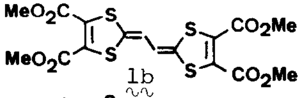
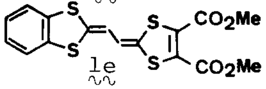
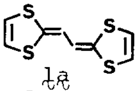
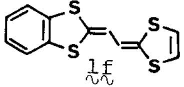
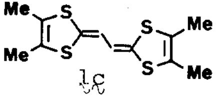


Table 2. Physical and Spectral Data for Ethanediylidene-2,2-Bis-(1,3-Dithiole)'s

Compounds	mp, °C	^{1}H-NMR(CDCl$_3$), δ	Visible(CHCl$_3$) λ$_{max}$ nm(log ε)
 **1b**	184-185	3.88(s, 12H), 5.75(s, 2H)	374(4.45) 389(4.42)
 **1e**	134-135	3.87(s, 6H), 5.87(s, 2H) 7.00(s, 4H)	374(4.56) 393(4.53)
 **1a**	164-165 (dec.)	5.88(s, 2H), 6.23(s, 4H)	387(4.31) 406(4.33)
 **1f**	126-127	5.90(s, 2H), 6.21(s, 2H) 7.11(s, 4H)	380(4.19) 400(4.14)
 **1c**	220-222 (dec.)	1.92(s, 12H), 5.97(s, 2H)	394(4.45) 415(4.47)

acetonitrile solution containing 0.1M Et$_4$NClO$_4$ as the supporting electrolyte at room temperature exhibits two oxidative waves, at E$_1$ +0.20 and E$_2$ +0.36V vs. Ag|AgCl, which are electrochemically reversible.[11] The fact that the two oxidation potentials of **1a** are smaller than those of TTF (E$_1$ +0.34 and E$_2$ +0.71V vs. Ag|AgCl)[11] obviously demonstrates that **1a** is more efficient donor than TTF as expected from the calculated ionization potentials. In fact, **1a** is readily oxidized to the corresponding radical cation, which was confirmed by esr spectroscopy.[12] Another interesting point is that the value of E$_2$-E$_1$ of **1a** is smaller than that of TTF, which clearly indicates that Coulombic repulsion of **1a** dication has decreased compared with that of TTF dication.

The electrical conductivity of charge transfer complexes between **1** with electron acceptors (eg. TCNQ) and of the complex radical cation salts (eg. [(**1**)$_n$**1**$^{+\cdot}$]X$^-$) will be reported soon.

References and Notes

1. (a) J. P. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, *J. Am. Chem. Soc.*, 95, 948 (1973); (b) L. B. Colemen, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. G. Heeger, *Solid State Commun.*, 12, 1125 (1973).
2. (a) K. Bechgaard, C. S. Jacobsen, K. Mortensen, H. J. Pedersen, and N. Thorup, *Solid State Commun.*, 33, 1119 (1980). (b) D. Jerome, A. Mazaud, M. Ribault, K. Bechgaard, *J. Phys. Lett.*, 41, L95 (1980), (c) K. Andres, F. Wudl, D. B. McWhan, G. A. Thomas, D. Nalewajek, and A. L. Stevens, *Phys. Rev. Lett.*, 45, 1449 (1980).
3. (a) Y. Ueno, M. Bahry, and M. Okawara, *Tetrahedron Lett.*, 4607 (1977); (b) M. Sato, M. V. Lakshmikantham, M. P. Cava, and A. F. Garito, *J. Org. Chem.*, 43, 2084 (1978); (c) Y. Ueno, A. Nakayama, and M. Okawara, *J. Chem. Soc., Chem. Commun.*, 74 (1978).
4. (a) R. R. Schumaker, and E. M. Engler, *J. Am. Chem. Soc.*, 99, 5521 (1977); (b) *idem.*, *ibid.*, 102, 6651 (1980).
5. M. Sato, N. C. Gonnella, and M. P. Cava, *J. Org. Chem.*, 44, 930 (1979).
6. The compounds **3a-c** were newly prepared as follows. Phosphonium salt, **4a**, **4b** or **4c** was reacted with 2 equiv. of glyoxal (40% aq. solution) in THF at room temperature in the presence of triethylamine to give **3a**, **3b**, and **3c** in 70, 83 and 88% yield, respectively. **3a**:yellow needles; mp 111-115°C; ^{1}H-NMR (CDCl$_3$) δ 3.93 (s, 6H), 6.68 (d, 1H, J=3H), 9.48 (d, 1H, J=3Hz); IR (KBr) 2720, 1730, 1700, 1630 cm^{-1}. **3b**:orange plates; mp 51-52°C; ^{1}H-NMR (CDCl$_3$) δ 2.15 (s, 6H), 6.60 (d, 1H, J=3Hz), 9.90 (d, 1H, J=3Hz); IR (KBr) 2900, 1618, 1465, 1380, 1280, 1060 cm^{-1}. **3c**:yellow needles; mp 93-94°C; ^{1}H-NMR(CDCl$_3$) δ 6.70 (d, 1H,J=3Hz), 7.2-7.7 (m, 4H), 9.57 (d, 1H, J=3Hz); IR(KBr) 2770, 2700, 1625, 1470, 1040, 760 cm^{-1}.
7. K. Ishikawa, K. Akiba, and N. Inamoto, *Tetrahedron Lett.*, 3695 (1976).
8. T. Kawase, H. Awaji, S. Yoneda, and Z. Yoshida, *Heterocycles*, 18, 123 (1982).
9. S. Yoneda, T. Kawase, Y. Yasuda, and Z. Yoshida, *J. Org. Chem.*, 44, 1728 (1979).
10. All new compounds have been fully characterized (IR, NMR and MS). Also, satisfactory elemental analyses were obtained.
11. Cyclic voltammograms of **1a** and TTF were measured on a Yanaco Voltammetric Analyzer P-100 under the same conditions.
12. The detailed esr investigation of the radical cation will be reported elsewhere.

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