Tetrahedron Letters,Vol.24,No.33,pp 3473-3476,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

SYNTHESIS AND PROPERTIES OF 1,4-BUTENEDIYLIDENE-2,2'-BIS(1,3-DITHIOLE)

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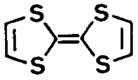
Summary: A new type of π-donor, 1,4-butenediylidene-2,2'-bis(1,3-dithiole)'s have been synthesized by two routes and their electrochemical properties have been discussed.

In the preceeding paper,[1] we have reported that introduction of two sp^2 carbons between both 1,3-dithiole rings of tetrathiafulvalene (TTF, **1**) led to the formation of more powerful π-donor ethanediylidene-2,2'-bis(1,3-dithiole (EDBDT, **2**) than TTF.[2] Based on this result, we designed the new type of π-donor, 1,4-butenediylidene-2,2'-bis(1,3-dithiole) (BDBDT, **3**) in which four sp^2 carbon atoms are inserted. The MINDO/3 calculation suggests that the ionization potential decreases in the order of TTF > EDBDT > BDBDT. In this paper, we wish to report the synthesis of BDBDT, **3** and its derivatives and their characteristic electrochemical properties.



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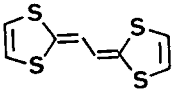

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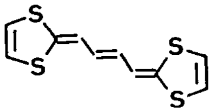

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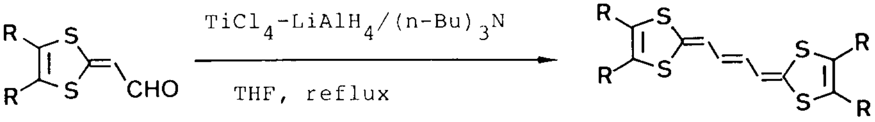
The following two methods are applied to synthesize BDBDT's. Method A: reductive coupling of aldehydes by $TiCl_4$-$LiAlH_4$ (Scheme 1) and Method B: desurfulization coupling of thioaldehydes and subsequent demethoxycarbonylation (Scheme 2).

Method A. Dibenzo derivative (**5**) was synthesized by the reductive coupling of aldehyde (**4**),[3] prepared from glyoxal and 1,3-benzodithiolyltributylphosphonium tetrafluoroborate in THF in the presence of Et_3N. To a solution of $TiCl_4$ (0.34 ml) and $LiAlH_4$ (3 mg) in dry THF (6 ml)[4] was added a solution of aldehyde 4 (120 mg) and $(n\text{-}Bu)_3N$ (0.15 ml) in dry THF (4 ml) under reflux. After being refluxed for additional 3 hr, the reaction mixture was treated with 20% aq. K_2CO_3 and then filtered. The filtrate was extracted with benzene and the extract was washed with water and dried over Na_2SO_4. Column chromatography on silica gel with benzene gave 5 in 69% yield as yellow crystals.[5]

Scheme 1.



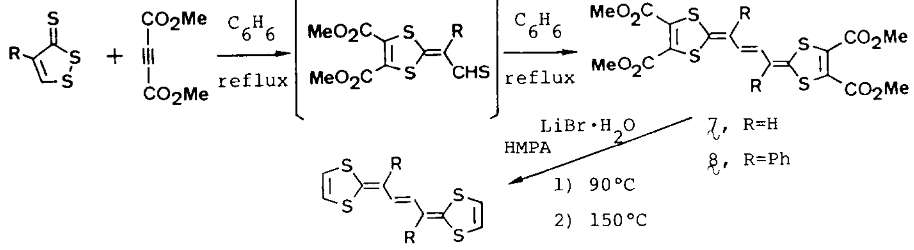
4, R=-(CH=CH)$_2$-
6, R=H

5, R=-(CH=CH)$_2$-, 69%
3, R=H, 55%

The parent compound 3 could not be obtained by the method via the reductive coupling of 2-formylmethylene-4,5-dicarbomethoxy-1,3-dithiole,[6] but could be obtained by the reductive coupling of 2-formylmethylene-1,3-dithiole[7] in 55% yield (Scheme 1). Also the compound 3 could be synthesized by demethoxycarbonylation[8] of tetraester derivative (7) prepared by the desulfurization coupling reaction of thioaldehydes[9] as follows (Method B).

Method B. A mixture of tetraester 7[9] (97 mg) and $LiBr \cdot H_2O$ (0.40 g) in HMPA (5 ml) was heated at 90°C for 1h and then at 150°C for 15 min under argon atomosphere. The reaction mixture was poured into water, extracted with ether, dried over Na_2SO_4 and concentrated. The residue was chromatographed on silica gel with benzene to afford 3 in 31% yield as orange crystals. Diphenyl derivative (9) was similarly obtained from (8)[9] in 45% yield. The physical and spectral data are shown in Table I.

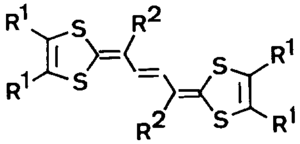
Scheme 2.



7, R=H
8, R=Ph

3, R=H, 31%
9, R=Ph, 45%

Table I. 1,4-Butenediylidene-2,2'-bis(1,3-dithiole)'s



Compounds	R^1	R^2	mp, °C	Yield, %	^1H-NMR($CDCl_3$), δ, ppm
3	H	H	118-120 (dec.)	31[a] (55[b])	5.29(d,2H,J=3Hz), 5.87(d,2H, J=3Hz), 6.21(s,4H)
9	H	Ph	171-172	45[a]	5.30(s,2H), 6.36(s,4H), 7.36(s,10H)
5	$-(CH=CH)_2-$	H	225-227 (dec.)	32[b]	5.30(d,2H,J=3Hz), 6.03(d,2H, J=3Hz), 7.1-7.3(m,8H)

[a] based on tetraester. [b] based on aldehyde.

The oxidation potentials of BDBDT's (3, 5, and 9) obtained by cyclic voltammetry measurements[11] are summarized in Table II together with those of TTF's and EDBDT's. All BDBDT's, interestingly, have only one reversible oxidation-reduction process at +0.22∿+0.47 V which are attributed to one step two-electron oxidation, though TTF and EDBDT show two clear oxidation processes.

Table II. Cyclic Volammetry Oxidation Potentials[a] at Room Temperature (V vs.|Ag AgCl)

Compounds	E_1	E_m[b]	E_2	E_2-E_1
3		+0.22		
9		+0.28		
5		+0.47		
1	+0.34		+0.71	+0.37
Dibenzo TTF	+0.61		+0.93	+0.32
2	+0.20		+0.36	+0.16
Dibenzo EDBDT	+0.47		+0.64	+0.17

[a] Solvent, CH_3CN; supporting electrolyte, 0.1M Et_4NClO_4; indicating electrode, Pt; reference electrode, Ag|AgCl; scan rate, 43mV/s.

[b] $E_m=(E_1+E_2)/2$.

The similar one step two-electron oxidation is reported for the vinylogous redox system.[12] The peak separation could not be observed for BDBDT's even at -50°C. The two-electron oxidation was confirmed by Coulometric analysis of 3. This result could be explained in terms of a larger decrease of Coulombic repulsion of doubly ionized state of 3 than TTF and/or EDBDT by introducing four sp^2 carbon atoms between two 1,3-dithiole rings.

References and Notes

1. Published in this issue.
2. F. Wudl, G. M. Smith, and E. J. Hufnagel, *J. Chem. Soc., Chem. Commun.*, 1453 (1970).
3. Aldehyde 4 was synthesized as follows: 1,3-benzodithiolyl-tributylphosphonium tetrafluoroborate was reacted with 2 equiv. of glyoxal (40% aq. solution) in THF at room temperature in the presence of Et_3N to give 4 in 88% yield. 4: yellow needles (from CH_2Cl_2-hexane); 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}, mass m/e 194(M^+).
4. A. Ishida and T. Mukaiyama, *Chemistry Lett.*, 1127 (1976).
5. The products obtained from reductive coupling by $TiCl_4$-$LiAlH_4$ are reported to be trans form with regard to the central double bond.[4] Therefore the compound 5 is considered to be trans form.
6. 2-Formylmethylene-4,5-dicarbomethoxy-1,3-dithiole is described in the preceeding paper.[1]
7. 2-Formylmethylene-1,3-dithiole was prepared as follows: 1,3-dithiolyl-tributylphosphonium tetrafluoroborate was reacted with two equivalent of glyoxal (40% aq. solution) in THF at room temperature in the presence of triethylamine to give 2-formylmethylene-1,3-dithiole in 71% yield; orange needles (from hexane); mp 81-82°C; ^{1}H-NMR($CDCl_3$) δ 6.77(d, 1H, J=2Hz), 6.87(s, 2H), 9.40(d, 1H, J=2Hz); IR(KBr) 3100, 3070, 2840, 2790, 1613, 1594, 1452, 750, 670 cm^{-1}; mass m/e 144 (M^+).
8. S. Yoneda, T. Kawase, Y. Yasuda, and Z. Yoshida, *J. Org. Chem.*, **44**, 1728 (1979).
9. D. M. Mckinnon and J. M. Buchshriber, *Can. J. Chem.*, 49, 3299 (1971).
10. All new compounds have been fully characterized by spectra (IR, NMR and Mass). Also, satisfactory elemental analyses were obtained.
11. Cyclic voltammograms of TTF's, EDBDT's, and BDBDT's were measured on a Yanaco Voltammetric Analyzer P-1000 under the same conditions.
12. S. Hunig and H. Ch. Steinmetzer, *Liebigs Ann. Chem.*, 1060 (1976).

(Received in Japan 22 April 1983)