

HETEROCYCLES, Vol. 65, No. 1, 2005, pp. 187 - 193

Received, 27th October, 2004, Accepted, 26th November, 2004, Published online, 26th November, 2004

A FACILE SYNTHESIS OF ASYMMETRICAL 2,3-DICYANO-SUBSTITUTED TETRATHIAFULVALENE DERIVATIVES

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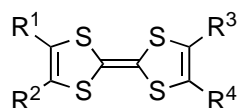
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Abstract – The cross-coupling reactions of 4,5-dicyano-1,3-dithiol-2-one (**3**) and 4,5-bis(alkylthio)- and 4,5-bis(methoxycarbonyl)-1,3-dithiole-2-thiones (**4a-e**) gave asymmetrical 2,3-dicyanotetrathiafulvalenes (**5a-e**) having electron-donating or electron-withdrawing substituents at the 6,7-positions under high dilution condition. A pyrrole-fused tetrathiafulvalene (**5f**) was also obtained. Their electrochemical behaviors were measured by means of cyclic voltammetry.

INTRODUCTION

Since the discovery of the first metallic charge-transfer tetrathiafulvalene (TTF) complex with tetracyano-*p*-benzoquinone,¹ the chemistry of tetrathiafulvalene and its derivatives has been intensively studied on account of their unique π -electron donating properties. The developments in synthesis and utility of TTF derivatives in the field of supramolecular chemistry have led to new elaborate TTF systems.²⁻⁴ A variety of electron-donating or electron-withdrawing substituents has been extensively introduced into the TTF skeleton. Of them, symmetrically and asymmetrically cyano-substituted tetrathiafulvalenes⁵ (**1a-c**) have been synthesized as compounds bearing strong electron-withdrawing substituents. Then, 4-cyanotetrathiafulvalene (**1a**) was used as a building block for the synthesis of new TTF derivatives with potentially interesting solid-state structures.⁵ These compounds (**1a-c**) were obtained by the introduction of the cyano substituents into the TTF itself by using *p*-toluenesulfonyl cyanide. The reactions were carried out under a very rigorous condition, namely, at -78 °C in the presence of lithium diisopropylamide (LDA). In addition, there is no systematic report on the synthesis of 2,3-dicyano-

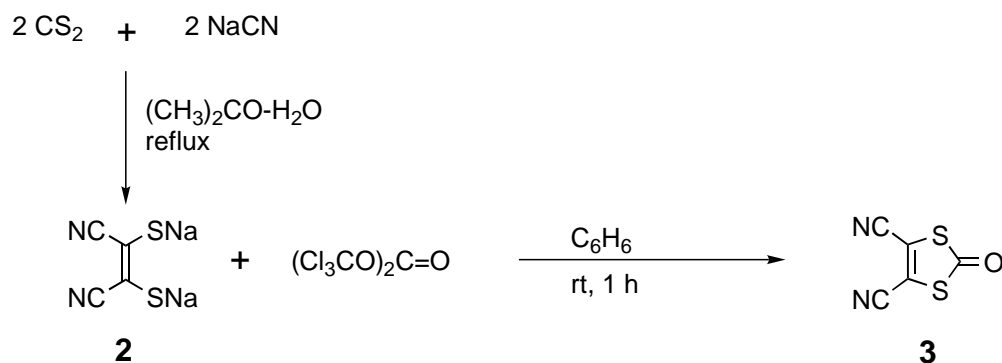
tetrathiafulvalene derivatives. In the present communication, we report the synthesis of these 2,3-dicyano-substituted TTF derivatives under the high dilution condition. Their oxidation potentials are also described on the basis of cyclic voltammetry measurements.

**1a-c****1a** R¹ = CN, R² = R³ = R⁴ = H**1b** R¹ = R² = CN, R³ = R⁴ = H**1c** R¹ = R² = R³ = R⁴ = CN**Figure 1**

RESULTS AND DISCUSSION

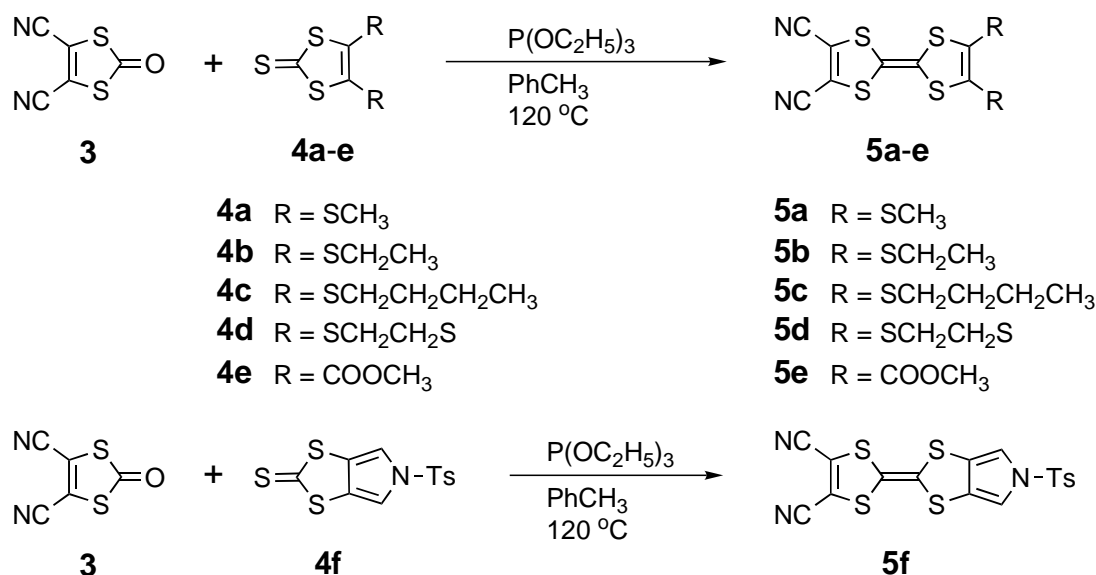
Preparation of 4,5-Dicyano-1,3-dithiol-2-one (3)

Previously, it was reported that 4,5-dicyano-1,3-dithiol-2-one (**3**) was prepared by passing phosgene into the solution of disodium dimercaptomaleonitrile (**2**).⁶ In the present work, we obtained 4,5-dicyano-1,3-dithiol-2-one (**3**) by using solid phosgene, bis(trichloromethyl) carbonate, instead of gaseous phosgene. A mixture of disodium dimercaptomaleonitrile (**2**) and a third equivalent of bis(trichloromethyl) carbonate in benzene was stirred for 15 min at 0 °C and for additional 1 h at room temperature to give 4,5-dicyano-1,3-dithiol-2-one (**3**) in 50% yield. On the other hand, 4,5-bis(alkylthio)-1,3-dithiole-2-thiones (**4a-d**) were prepared according to the literature.⁷ Compound (**4c**) was newly obtained in the present work. Bis(methoxycarbonyl)-substituted and pyrrole-fused 1,3-dithiole-2-thiones (**4e⁸,f⁹**) were previously reported.

**Scheme 1**

Synthesis of Tetrathiafulvalenes (5a-f)

In general, TTF derivatives have been prepared by the self-coupling or cross-coupling reactions of appropriate 1,3-dithiole-2-thione or 1,3-dithiol-2-one in the presence of trialkyl phosphite. However, this method could not be directly applied to the synthesis of asymmetrical tetrathiafulvalenes which have two cyano groups in a 1,3-dithiole ring and other two substituents in another ring. After trying a variety of reactions, we developed a cross-coupling reaction under high dilution condition. The reactions of 4,5-dicyano-1,3-dithiol-2-one (**3**) (0.5 mmol) with compounds (**4a-f**) (0.5 mmol) were carried out in the presence of triethyl phosphite (4 mL) in 110 mL of toluene (310 mL for **5f**) at refluxing temperature and resulted in 2,3-dicyano-6,7-bis(alkylthio)tetrathiafulvalenes (**5a-d**) and 6,7-bis(methoxycarbonyl)-substituted tetrathiafulvalene (**5e**) in 10-47% yields. In a similar manner, a pyrrole-fused tetrathiafulvalene (**5f**) was obtained in 21% yield.



Scheme 2

Electrochemical Behavior of Compounds (5a-f)

It is well-known that TTF is a stable and reversible two-electron donor. Thus, oxidations to the cation radical and dication occur sequentially and at relatively low potentials, $E_{1/2}^1 = 0.34$ V and $E_{1/2}^2 = 0.73$ V vs Ag/AgCl in acetonitrile.⁹ The oxidation potentials of 2,3-dicyano-6,7-bis(alkylthio)tetrathiafulvalenes (**5a-d**) and related compounds (**5e,f**) were obtained in dichloromethane-acetonitrile (1:1) by cyclic voltammetry and are summarized in Table 1. Compounds (**5a-d**) contain electron-withdrawing cyano groups and electron-donating alkylthio groups. Their oxidation potentials were observed between the values for tetracyanothiafulvalene ($E_{1/2}^1 = + 1.12$ V and $E_{1/2}^2 = + 1.22$ V)¹⁰ and that for tetrakis-(methylthio)tetrathiafulvalene ($E_{1/2}^1 = + 0.51$ V).¹¹ The oxidation potentials of 2,3-dicyano-6,7-

bis(methoxycarbonyl)tetrathiafulvalene (**5e**) resulted in the highest values. This is caused by the additional electron-withdrawing methoxycarbonyl substituents. Compound (**5f**) also exhibited higher oxidation potentials. In this compound, the annelation of a pyrrole unit to the TTF framework might decrease the electron-donating ability, besides the electron-withdrawing effect of the tosyl group.

Table 1 Oxidation Potentials $E_{1/2}$ for Tetrathiafulvalenes (**5a-f**)^a

Compound	$E_{1/2}^1$ (V)	$E_{1/2}^2$ (V)	E_p (V)
5a	1.01	1.26	0.25
5b	1.02	1.29	0.27
5c	1.02	1.28	0.26
5d^b	1.01	1.32	0.31
5e	1.20	1.44	0.24
5f	1.15	1.40	0.25

a $c = 10^{-3}$ M; 0.1 M Bu_4NPF_6 ; scan rate 100 mv/s.

b **5d** did not completely dissolve under the same condition.

CONCLUSION

A series of asymmetrical 2,3-dicyanotetrathiafulvalene derivatives (**5a-f**) was synthesized under the high dilution condition. Their oxidation potentials were found to be $E_{1/2}^1 = 1.01\text{-}1.20$ V and $E_{1/2}^2 = 1.26\text{-}1.44$ V by means of cyclic voltammetry measurements.

EXPERIMENTAL

The melting points were determined by a Buchi apparatus and are uncorrected. The IR spectra were taken on a Varian FT-IR 1730 spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AV-300 spectrometer. The MS spectral data were obtained by a Hewlett Packard 1100-HPLC/MSD instrument. The cyclic voltammetry were carried out on a Potentiostat/Galvanostat 273A instrument employing 0.1 M $\text{Bu}_4\text{N}_4\text{PF}_6$ as supporting electrode in dichloromethane-acetonitrile (1:1) with a

sweep rate of 100 mv/s. Counter and working electrodes were made of platinum and platinum-carbon, respectively, and the reference electrode was Ag/AgCl. All reagents were obtained from ACROS and used without further purification. All solvents were purified and dried by standard methods, unless otherwise stated. Silica gel (100-200 mesh) was purchased from Qing Dao Hai Yang Chemical Factory. All the reactions were carried out under dry argon atmosphere. Disodium dimercaptomaleonitrile (**2**) was prepared according to the literature.⁶

4,5-Dicyano-1,3-dithiol-2-one (3). A solution of bis(trichloromethyl) carbonate (3.75 g, 0.013 mol) in benzene (35 mL) was added to a suspension of disodium dimercaptomaleonitrile (**2**) (7.05 g, 0.04 mol) in benzene (70 mL) in a period of 15 min under ice cooling. The mixture was stirred for 1 h at rt, filtered, and evaporated. The crude product was purified by chromatography on a silica gel column with petroleum ether-ethyl acetate (10:1) as eluent. The second fraction was collected and recrystallized from carbon tetrachloride to give 4,5-dicyano-1,3-dithiol-2-one (**3**) as colorless needles, yield: 1.57 g (50%), mp 121-123 °C (lit.,¹² 123-124 °C).

4,5-Bis(butylthio)-1,3-dithiole-2-thione (4c). To a solution of bis(tetraethylammonium) bis(2-thioxo-1,3-dithiole-4,5-dithiolato)zincate (2.17 g, 3.0 mmol) in acetonitrile (60 mL) was added 1-bromobutane (2.48 g, 18 mmol). The solution was refluxed for 6 h. The evaporation residue was chromatographed on a silica gel column with petroleum ether-dichloromethane (1:1) to give **4c** as a orange yellow oil; yield 1.69 g (91%), ¹H NMR (CDCl₃): δ 0.96 (6H, t, *J* = 7.5 Hz, CH₃ x 2), 1.50 (4H, m, CH₂CH₃ x 2), 1.66 (4H, m, SCH₂CH₂ x 2), 2.89 (4H, t, *J* = 7.5 Hz, SCH₂ x 2); MS (APCI): *m/z* 311 ([M+1]⁺). *Anal.* Calcd for C₁₁H₁₈S₅: C, 42.54; H, 5.84. Found: C, 42.89; H, 5.65.

2,3-Dicyano-6,7-bis(alkylthio)tetrathiafulvalenes (5a-e). General Procedure: A solution of 4,5-dicyano-1,3-dithiol-2-one (**3**) (84 mg, 0.50 mmol) and 4,5-bis(alkylthio)-1,3-dithiole-2-thione (**4a-d**) (0.5 mmol) in toluene (10 mL) was added dropwise to a solution of triethyl phosphite (4 mL, 23 mmol) in toluene (100 mL) under argon atmosphere. When the solution was heated at refluxing temperature, a color of the solution changed to dark purple after 10-15 min. The mixture was stirred for an additional 4-5 h and then allowed to cool to rt. The toluene was removed in vacuo. After adding methanol (40 mL), a purple precipitate was collected, washed with methanol, and dried in vacuo. The product was chromatographed on a silica gel column with petroleum ether-dichloromethane (3:1) as eluent to give 2,3-dicyano-6,7-bis(alkylthio)tetrathiafulvalenes (**5a-e**).

2,3-Dicyano-6,7-bis(methylthio)tetrathiafulvalene (5a). This compound was obtained from the reaction with 4,5-bis(methylthio)-1,3-dithiole-2-thione (**4a**)¹³ under heating for 5.5 h as purple flakes (from hexane-benzene); yield 17 mg (10%), mp 164-165 °C; IR (KBr): ν 2360 (CN); ¹H NMR (CDCl₃): δ 2.46 (6H, s, CH₃ x 2); ¹³C NMR (CDCl₃): δ 20.72, 100.90, 109.03, 118.71, 123.39, 127.99;

MS (APCI): m/z 347 ($[M+1]^+$). *Anal.* Calcd for $C_{10}H_6N_2S_6$: C, 34.66; H, 1.75; N, 8.08. Found: C, 34.48; H, 1.71; N, 7.83.

2,3-Dicyano-6,7-bis(ethylthio)tetrathiafulvalene (5b). This compound was obtained from the reaction with 4,5-bis(ethylthio)-1,3-dithiole-2-thione (**4b**)⁷ under heating for 3.5 h as purple plates (from hexane); yield 41 mg (22%), mp 150-152 °C; IR (KBr): ν 2360 (CN); ¹H NMR (CDCl₃): δ 1.34 (6H, t, $J = 7.4$ Hz, CH₃ x 2), 2.88 (4H, q, $J = 7.4$ Hz, CH₂ x 2); ¹³C NMR (CDCl₃): δ 15.00, 30.81, 109.05, 118.77, 123.26, 128.30; MS (APCI): m/z 375 ($[M+1]^+$). *Anal.* Calcd for $C_{12}H_{10}N_2S_6$: C, 38.47; H, 2.69; N, 7.48. Found: C, 38.35; H, 2.84; N, 7.43.

2,3-Dicyano-6,7-bis(butylthio)tetrathiafulvalene (5c). This compound was obtained from the reaction with 4,5-bis(butylthio)-1,3-dithiole-2-thione (**4c**) under heating for 4 h as purple flakes (from hexane); yield 87 mg (36%), mp 105-107 °C; IR (KBr): ν 2360 (CN); ¹H NMR (CDCl₃): δ 0.95 (6H, t, $J = 7.3$ Hz, CH₃ x 2), 1.37-1.60 (4H, m, CH₂CH₃ x 2), 1.60-1.74 (4H, m, SCH₂CH₂ x 2), 2.85 (4H, t, $J = 7.2$ Hz, SCH₂ x 2); ¹³C NMR (CDCl₃): δ 13.54, 21.59, 31.71, 36.30, 100.01, 109.07, 118.76, 123.26, 128.26; MS (APCI): m/z 431 ($[M+1]^+$). *Anal.* Calcd for $C_{16}H_{18}N_2S_6$: C, 44.62; H, 4.21; N, 6.50. Found: C, 44.46; H, 3.88; N, 6.30.

2,3-Dicyano-6,7-(ethylenedithio)tetrathiafulvalene (5d).¹⁴ This compound was obtained from the reaction with 4,5-bis(ethylenedithio)-1,3-dithiole-2-thione (**4d**)⁷ under heating for 10 h. Methanol (40 mL) was added to the reaction mixture to precipitate purple solid, which was collected and washed with methanol to give **5d** as purple crystals (from chlorobenzene); yield 81 mg (47%), mp 236-238 °C; MS (APCI): m/z 345 ($[M+1]^+$).

2,3-Dicyano-6,7-bis(methoxycarbonyl)tetrathiafulvalene (5e). This compound was obtained from the reaction with 4,5-bis(methoxycarbonyl)-1,3-dithiole-2-thione (**4e**)⁸ under heating for 6.5 h and the chromatography was performed using petroleum ether-dichloromethane (2:1) as eluent to give as brown needles (from hexane); yield 39 mg (21%), mp 193-194 °C; IR (KBr): ν 2340 (CN); ¹H NMR (CDCl₃): δ 3.87 (6H, s, CH₃ x 2); ¹³C NMR (CDCl₃): δ 53.75, 102.39, 108.79, 118.68, 131.72, 159.04; MS (APCI): m/z 371 ($[M+1]^+$). *Anal.* Calcd for $C_{12}H_6N_2O_4S_4$: C, 38.91; H, 1.63; N, 7.56. Found: C, 38.66; H, 1.54; N, 7.69.

***N*-Tosyl-2-[4,5-dicyano-1,3-dithiole-2-ylidene]-(1,3)-dithiolo[4,5-*c*]pyrrole (5f).** The reaction of *N*-tosyl-(1,3)-dithiolo[4,5-*c*]pyrrole-2-thione (**4f**)⁹ (163 mg, 0.5 mmol) was carried out in the thrice amounts of toluene (300 mL) under heating for 5 h. The product was chromatographed on a silica gel column with petroleum ether-dichloromethane (2:1) as eluent to give **5f** as brown microcrystals (from hexane-toluene); yield 55 mg (25%), mp 270 °C (decomp); IR (KBr): ν 2360 (CN); ¹H NMR (CDCl₃):

δ 2.45 (3H, s, 4'-CH₃), 6.59 (2H, s, =CH x 2), 7.34 (2H, d, $J = 8.3$ Hz, 3'-,5'-H), 7.78 (2H, d, $J = 8.3$ Hz, 2'-,6'-H); ¹³C NMR (CDCl₃): δ 21.69, 108.89, 111.80, 125.10, 127.09, 130.27, 135.07, 145.86; MS (APCI): m/z 448 ([M+1]⁺). *Anal.* Calcd for C₁₇H₉N₃O₂S₅: C, 45.62; H, 2.03; N, 9.39. Found: C, 45.77; H, 2.11; N, 9.69.

ACKNOWLEDGMENT

We are grateful to the National Science Foundation of China for the financial support (No. 20462001).

REFERENCES

- 1 J. P. Ferraris, D. O. Cowan, V. Walatka, and J. H. Perlstein, *J. Am. Chem. Soc.*, 1973, **95**, 948.
- 2 M. B. Nielsen and J. Becher, *Liebigs Ann. /Recueil*, 1997, 2177.
- 3 M. B. Nielsen, C. Lomholt, and J. Becher, *Chem. Soc. Rev.*, 2000, **29**, 153.
- 4 J. L. Segura and N. Martin, *Angew. Chem., Int. Ed.*, 2001, **40**, 1372.
- 5 G. Cook, A. K. Powell, and S. L. Heath, *Synthesis*, 1995, 1411.
- 6 E. Ciganek and C. G. Krespan, *J. Org. Chem.*, 1968, **33**, 541.
- 7 K. B. Simonsen, N. Svenstrup, J. Lau, O. Simonsen, P. Mork, G. J. Kristensen, and J. Becher, *Synthesis*, 1996, 407.
- 8 L. R. Melby, H. D. Hartzler, and W. A. Sheppard, *J. Org. Chem.*, 1974, **39**, 2456.
- 9 J. O. Jeppesen, K. Takimiya, F. Jensen, T. Brimert, K. Nielsen, N. Thorup, and J. Becher, *J. Org. Chem.*, 2000, **65**, 5794.
- 10 M. G. Miles, J. D. Wilson, D. J. Dahm, and J. H. Wagenknecht, *J. Chem. Soc., Chem. Commun.*, 1974, 751.
- 11 M. B. Nielsen, J. O. Jeppesen, J. Lau, C. Lomholt, D. Damgaard, J. P. Jacobsen, J. Becher, and J. F. Stoddart, *J. Org. Chem.*, 2001, **66**, 3559.
- 12 E. Klingsberg, *J. Am. Chem. Soc.*, 1964, **86**, 5290.
- 13 K. Hartke and H. Hoppe, *Chem. Ber.*, 1974, **107**, 3121.
- 14 Z.-J. Zhong, X.-Z. You, and K. Yu, *Acta Crystallgr., C*, 1996, **52**, 449.