PREPARATION OF (*E*)-1,2-BIS(2,2'-BITHIOPHENE-5-YL)ETHYLENE AND (*E*)-1,2-BIS(2,2':5',2"-TERTHIOPHENE-5-YL)ETHYLENE

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Abstract —— (*E*)-1,2-Bis(2,2'-bithiophene-5-yl)ethylene and (*E*)-1,2-bis(2,2':5',2"-terthiophene-5-yl)ethylene were synthesized by reductive coupling reaction of 2,2'-bithiophene-5-carbaldehyde and 2,2':5',2"-terthiophene-5-carbaldehyde, respectively, using a low-valent titanium reagent prepared from titanium(IV) chloride and zinc powder in tetrahydrofuran.

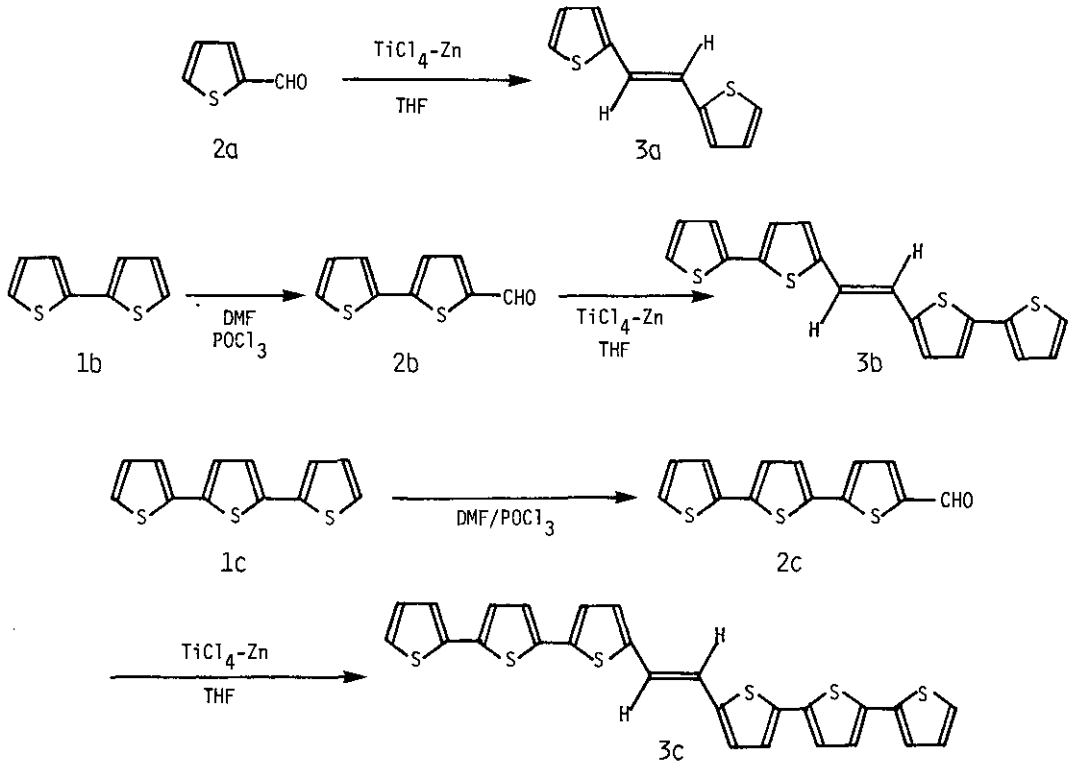
Bioactivities of bithiophenes and terthiophenes are recently receiving much attention. The most carefully scrutinized of these compounds is 2,2':5',2"-terthiophene (1c).[1] Furthermore it was recently reported that the doped polythiophene, prepared by electrochemical polymerization of 1c, is highly conductive.[2] Stimulated by these facts and also in our continuing synthetic study on polythiophenes, we planned the preparation of (*E*)-1,2-bis(2,2'-bithiophene-5-yl)ethylene (3b) and (*E*)-1,2-bis(2,2':5',2"-terthiophene-5-yl)-ethylene (3c) with expectation of obtaining biologically active thiophenes and also obtaining excellent materials for the preparation of organic conductors. These compounds are heterocyclic higher analogs of trans-stilbene and their two trans-substituted polythienyl groups are expected to conjugate through the central double bond, thus providing a long conjugated system. This property seems especially important in obtaining organic conductors and also bioactive thiophenes in that the bioactivities of 1c are strongly photoenhanced.[1]

For the preparation of these compounds, we adopted the reductive coupling reaction of the corresponding formyl derivatives by use of a low-valent titanium reagent. Thus, first, the preparation of (*E*)-1,2-di(2-thienyl)ethylene (3a) from the commercially available thiophene-2-carbaldehyde (2a) was attempted by treat-

ment with a low-valent titanium reagent prepared from titanium(IV) chloride and zinc powder.[3] The reaction in boiling tetrahydrofuran for 4 h satisfactorily afforded 3a in 71% yield, the Z-isomer being formed in a trace amount.

2,2'-Bithiophene-5-carbaldehyde (2b) was thus prepared from 2,2'-bithiophene (1b) and subjected to the reductive coupling reaction using the foregoing low-valent titanium reagent. The reduction in refluxing tetrahydrofuran for 4 h afforded the desired (*E*)-1,2-bis(2,2'-bithiophene-5-yl)ethylene (3b) in 63% yield. Although the Z-isomer was formed in a small amount, it was easily removed by recrystallization to furnish pure 3b.

The Vilsmeier formylation of 1c with phosphorus oxychloride and dimethylformamide at 70 °C for 1 h provided 2,2':5',2"-terthiophene-5-carbaldehyde (2c) in 75% yield with 18% recovery of 1c. The reductive coupling reaction of 2c with the low-valent titanium reagent afforded (*E*)-1,2-bis(2,2':5',2"-terthiophene-5-yl)-ethylene (3c) in 68% yield.



The ethylene 3b is golden yellow crystals, while 3c is brick-red and has copper-like luster. Compound 3b is slightly soluble in organic solvents and 3c is hardly soluble in ordinary organic solvents at room temperature. Both compounds are strongly fluorescent both in a fluid dilute solution and in a rigid environment. The 400 MHz ^{1}H-NMR spectrum of 3b determined in $CDCl_3$ shows a singlet due to its olefinic protons at δ 6.96, the value which is reasonable as the olefinic proton of (*E*)-1,2-diarylethylene.[4] The low solubility of 3c made impossible to determine its ^{1}H-NMR spectrum. Figure 1 shows the UV spectra of compounds 3a-c determined in chloroform as solvent. The highest λ_{max} values of these compounds shift to longer wavelength and increase in intensities with the increase of the number of thiophene ring, thus suggesting that, as expected, two polythienyl groups fully conjugate through the central double bond.

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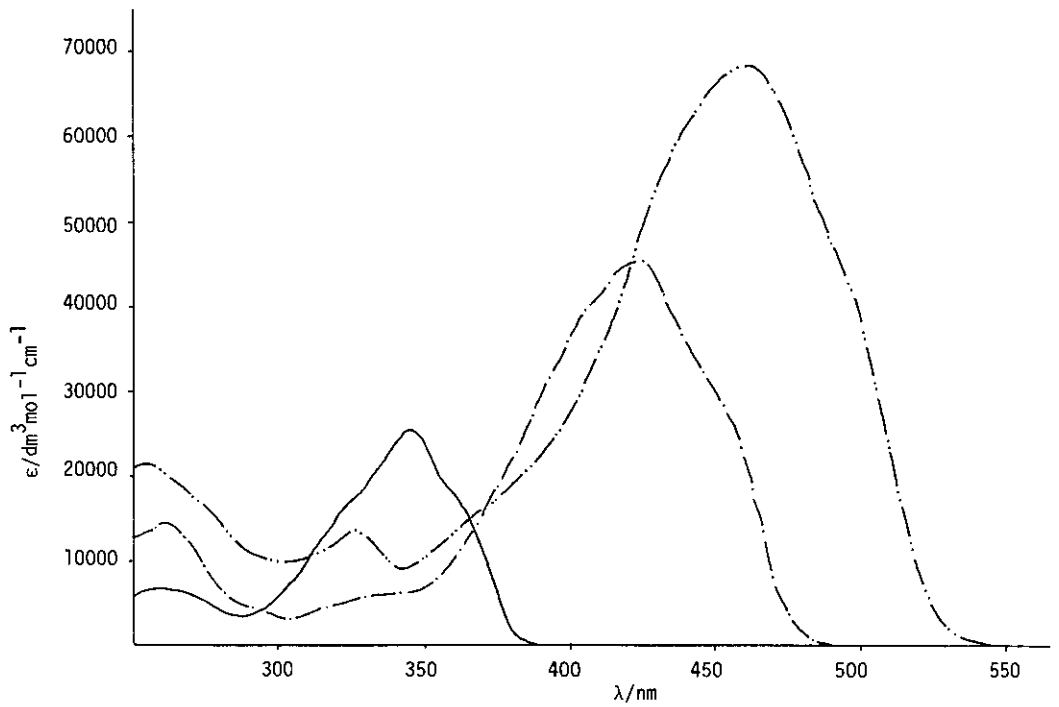

Figure 1. UV Spectra of Ethylenes 3a (———), 3b (—·—), and 3c (—··—) Determined in $CHCl_3$ as Solvent

EXPERIMENTAL

(E)-1,2-Di(2-thienyl)ethylene (3a). To a solution of 1.12 g (10 mmol) of thiophene-2-carbaldehyde (2a) in 50 ml of anhydrous tetrahydrofuran was added 3.3 ml (30 mmol) of titanium(IV) chloride at -18 °C under nitrogen. The mixture was stirred for 0.5 h at -18 °C. To this mixture was added 4.0 g (61 mg-atoms) of zinc powder in small portions over a period of 10 min. The resulting mixture was stirred for 0.5 h at -18 °C, gradually warmed to room temperature, and then refluxed for 4 h. The mixture was cooled, poured onto ice-water, made alkaline by adding aqueous 10% sodium carbonate solution. To this was added ca. 200 ml of dichloromethane and the resulting two-phase mixture was stirred and then filtered through celite. The dichloromethane layer of the filtrate was separated, washed with water, dried over sodium sulfate, and evaporated. The residue was chromatographed on a column of silica gel. Elution with carbon tetrachloride gave 0.69 g (71%) of 3a contaminated with a trace amount of the cis-isomer. Recrystallization from hexane afforded pure 3a, mp 133 °C (lit.,[5] mp 133-134 °C).

2,2'-Bithiophene-5-carbaldehyde (2b). To ice-cooled and stirred 1.53 g (10 mmol) of phosphorus oxychloride was added 8 ml of dimethylformamide and the mixture was stirred for 0.5 h. To the resulting ice-cooled mixture was added dropwise a solution of 1.42 g (8.5 mmol) of 2,2'-bithiophene (1b) in 8 ml of dimethylformamide over a period of 0.5 h. After the completion of the addition, the mixture was gradually warmed to room temperature and then heated at 100 °C for 1 h. The mixture was cooled, poured onto ice-water, and extracted with ether. The ether extract was washed with water, dried over sodium sulfate, and evaporated. The residue was subjected to silica gel column chromatography. Elution with hexane gave 0.40 g (28% recovery) of 1b and then elution with benzene afforded 0.60 g (48%) of 2b, mp 58 °C (from hexane) (lit.,[6] mp 60 °C).

(E)-1,2-Bis(2,2'-bithiophene-5-yl)ethylene (3b). To a solution of 389 mg (2 mmol) of 2b in 20 ml of anhydrous tetrahydrofuran was added 0.66 ml (6 mmol) of titanium(IV) chloride at -18 °C under nitrogen. The mixture was stirred at -18 °C for 0.5 h. To this mixture was added 0.80 g (12 mg-atoms) of zinc powder in small portions over a period of 10 min. The resulting mixture was stirred at -18 °C for 0.5 h and at 0 °C for 1 h, gradually warmed to room temperature, and then refluxed for 4 h. The cooled reaction mixture was quenched by adding ice-water and the resulting precipitate (a mixture of organic and inorganic materials) was collected by filtration, washed with water, and air-dried thoroughly. Recrystallization of the precipitate from chlorobenzene afforded 225 mg (63%) of pure 3b as yellow crystals, mp 214-215 °C. ^{1}H-NMR anlaysis of the crystals abtainable from the mother liquor of the above recrystallization indicates that it contains a small amount of the cis-isomer whose olefinic protons appear at δ 6.50 as singlet ($CDCl_3$ as solvent). 3b: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 6.94 (2H, d, J=4 Hz), 6.96 (2H, s), 7.03

(2H, d/d, J=5 and 4 Hz), 7.07 (2H, d, J=4 Hz), 7.13 (2H, d/d, J=4 and 1 Hz), 7.22 (2H, d/d, J=5 and 1 Hz); UV $\lambda_{max}^{CHCl_3}$ 423 nm (ε 45100); IR (KBr) 3064, 1510, 1464, 1428, 1240, 1056, 1048, 928, 840, 798, 688 cm^{-1}. Anal. Calcd for $C_{18}H_{12}S_4$: C, 60.64; H, 3.39; S, 35.97%. Found: C, 60.60; H, 3.39; S, 35.08%.

2,2':5',2"-Terthiophene-5-carbaldehyde (2c). To ice-cooled and stirred 3.22 g (21 mmol) of phosphorus oxychloride was added 20 ml of dimethylformamide and the mixture was stirred for 15 min. To this was added dropwise a solution of 4.96 g (20 mmol) of 2,2':5',2"-terthiophene (1c) in 20 ml of dimethylformamide over a period of 0.5 h at 0 °C. The mixture was gradually warmed to room temperature and then heated at 70 °C for 1 h. The mixture was cooled and poured onto ice-water. The resulting crystalline precipitate was collected by filtration, washed with water, air-dried, and chromatographed on a column of silica gel. Elution with carbon tetrachloride gave 0.90 g (18% recovery) of 1c) and then elution with benzene afforded 4.13 g (75%) of 2c, mp 140-141 °C (from carbon tetrachloride), whose spectroscopic data (^{1}H-NMR, IR, and UV) agreed with those of naturally occurring 2c, mp 135-136 °C.[7]

(E)-1,2-Bis(2,2':5',2"-terthiophene-5-yl)ethylene (3c). To a stirred and cooled solution of 558 mg (2 mmol) of 2c in 40 ml of anhydrous tetrahydrofuran was added 0.66 ml (6 mmol) of titanium(IV) chloride at -18 °C under nitrogen over a period of 15 min. The mixture was stirred for 15 min at -18 °C. To this mixture was added 0.80 g (12 mg-atoms) of zinc powder at -18 °C over a period of 15 min. The resulting mixture was stirred for 0.5 h at -18 °C, waremd to room temperature, and refluxed. On heating the crystals of 3c precipitate from the reaction mixture. After refluxing for 6 h, the mixture was cooled and quenched by adding ice-water. The precipitate (a mixture of 3c and inorganic materials) was collected by filtration, washed with water, and air-dried thoroughly. Recrystallization of the precipitate from boiling o-dichlorobenzene afforded 356 mg (68%) of 3c as brick-red crystals with copper-like luster, mp 291-294 °C. MS m/z 520 (M^+, 100%), 260 (M^{2+}, 27%); IR (KBr) 3064, 1504, 1421, 1226, 1066, 940, 836, 798, 690 cm^{-1}; UV $\lambda_{max}^{CHCl_3}$ 324 (ε 13400), 460 nm (68400). Anal. Calcd for $C_{26}H_{16}S_6$: C, 59.96; H, 3.10; S, 36.94%. Found: C, 59.64; H, 3.05; S, 36.42%.

REFERENCES

1. J. Kagan and S. K. Arora, J. Org. Chem., 1983, 48, 4317 and references cited therein.
2. Y. Yumoto and S. Yoshimura, Synthetic Metals, 1986, 13, 185.
3. T. Mukaiyama, T. Sato, and J. Hanna, Chem. Lett., 1973, 1041.
4. W. Brügel, 'Handbook of NMR Spectral Parameters,' Heydon, London, 1979, Vol. 2, p. 377.
5. R. M. Lellogg, M. B. Groen, and H. Wynberg, J. Org. Chem., 1967, 32, 3093.
6. R. E. Atkinson and F. E. Hardy, J. Chem. Soc. (B), 1971, 357.
7. F. Bohlmann and C. Zdero, Chem. Ber., 1970, 103, 834.

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