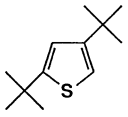
The First Synthesis and Properties of 2,3-Di-*t*-butylthiophene. Reaction of 3,4-Di-*t*-butyl-1,2-dithiete with Dimethyl Acetylenedicarboxylate

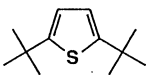
Juzo NAKAYAMA,* Keun Soo CHOI, Akihiko ISHII, and Masamatsu HOSHINO
Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338
(Received November 9, 1989)

Heating 3,4-di-*t*-butyl-1,2-dithiete (**5**) with dimethyl acetylenedicarboxylate (5 equiv) in refluxing *o*-dichlorobenzene affords dimethyl 2,5-di-*t*-butyl-3,4-thiophenedicarboxylate (**6**) (44%), dimethyl 2,3-di-*t*-butyl-4,5-thiophenedicarboxylate (**7**) (5%), tetramethyl 1,4-dithiin-2,3,5,6-tetracarboxylate (**8**) (4%), and tetramethyl 2,3,4,5-thiophenetetracarboxylate (**9**) (43%). Mechanism of the formation of these products is discussed. Treatment of the hindered ester **7** with lithium 1-propanethiolate affords 2,3-di-*t*-butyl-4,5-thiophenedicarboxylic acid (**13**) in 59% yield, which can be decarboxylated by treatment with copper powder to give 2,3-di-*t*-butylthiophene (**4**) in 88% yield. The thiophene **4** rearranges to 2,4-di-*t*-butylthiophene (**1**) on treatment with aluminum chloride. Oxidation with *m*-CPBA affords the corresponding sulfone (**23**). Electrophilic substitutions (bromination and nitration) of **4** occur exclusively at the less hindered and more electronically favored 5-position.

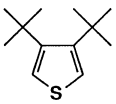
The five- and six-membered aromatic compounds having two *t*-butyl groups at the vicinal position constitute a body of overcrowded molecules. Their chemistry has been extensively investigated from interest in theories, syntheses, structures, and reactivities. Among the four di-*t*-butylthiophene isomers, 2,4- and 2,5-di-*t*-butylthiophenes (**1** and **2**) which are nearly free from steric strains are easily synthesized.[1] 3,4-Di-*t*-butylthiophene (**3**) having a large strain energy[2] was first synthesized in 1980 by Brandsma et al.[3] after many unsuccessful attempts by others.[4] We have also recently developed a convenient synthesis of **3** and investigated its reactivities.[5] The fourth isomer, 2,3-di-*t*-butylthiophene (**4**), has remained unknown[6] and is reported here. It is noteworthy that Krebs et al. have recently succeeded in the preparation of 2,3,4,5-tetra-*t*-butylthiophene.[7]



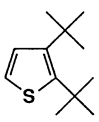
1



2



3



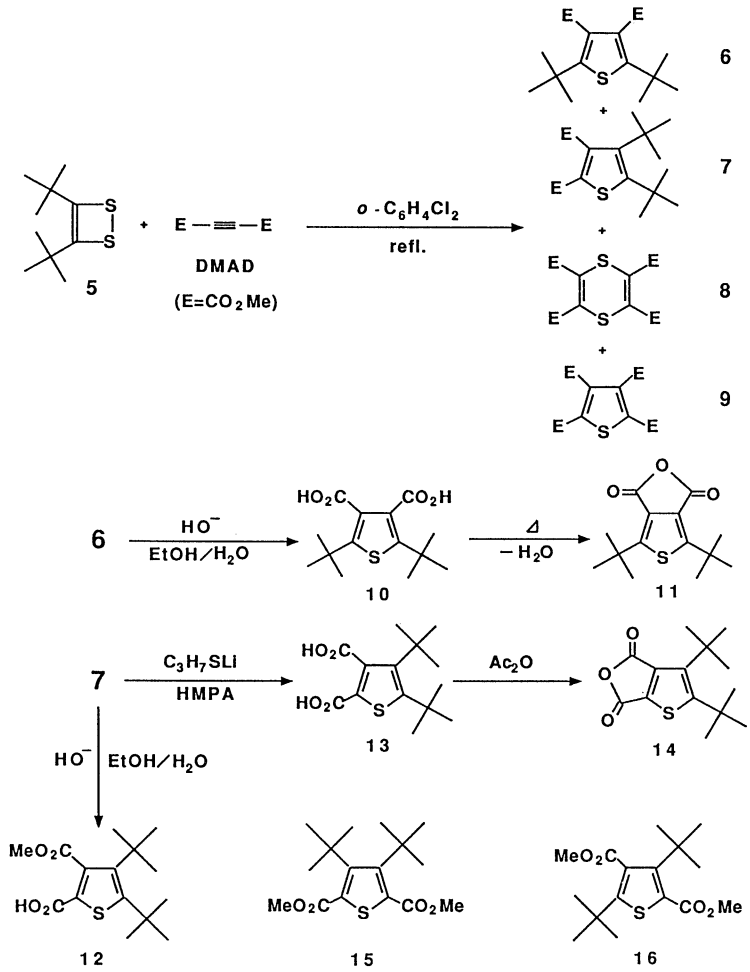
4

Results and Discussion

3,4-Di-*t*-butyl-1,2-dithiete (**5**),[8] which is one of a few isolable 1,2-dithietes[9] and posesses two *t*-butyl groups at the vicinal position in itself, was chosen as the starting material for the synthesis of **4**. Thus, a solution of **5** and dimethyl acetylenedicarboxylate (DMAD) (5 equiv) in *o*-dichlorobenzene was heated at reflux for 3 h. Chromatographic workup of the mixture afforded dimethyl 2,5-di-*t*-butyl-3,4-thiophenedicarboxylate (**6**)[10] (44%), dimethyl 2,3-di-*t*-butyl-4,5-thiophenedicarboxylate (**7**) (5%), and the known compounds tetramethyl 1,4-dithiin-2,3,5,6-tetracarboxylate (**8**)[11] (4%) and tetramethyl 2,3,4,5-thiophenetetracarboxylate (**9**)[12] (43%).

The molecular formula of **6** was determined to be $C_{16}H_{24}O_4S$ based on elemental analyses and MS. Both ^1H and ^{13}C NMR data showed that the compound has two equivalent *t*-butyl and methoxycarbonyl groups on the thiophene ring. Two isomeric thiophenes **6** and **15** are compatible with these NMR data. Therefore, the compound was hydrolyzed under alkaline conditions to give the dicarboxylic acid **10** in 97% yield. The diacid **10**, when heated above its melting point, smoothly eliminated water to give the corresponding acid anhydride **11** quantitatively. Thus, the structure of the compound was unambiguously determined to be **6**.

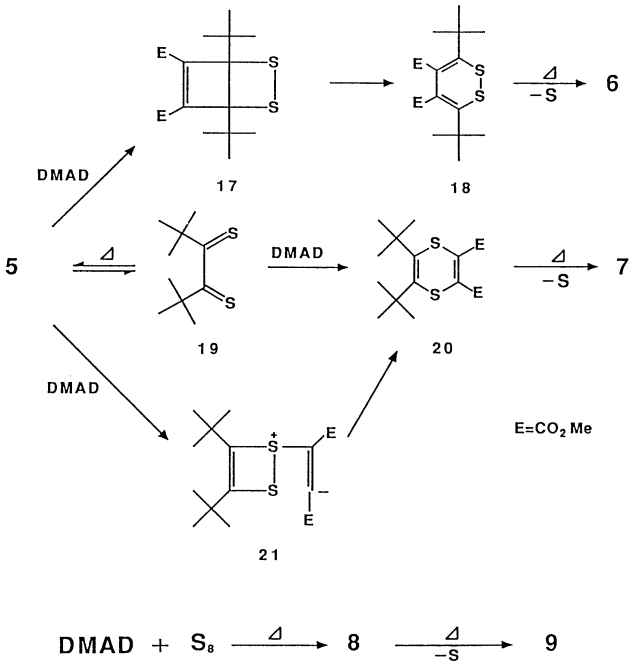
Compound **7** also has a molecular formula of $C_{16}H_{24}O_4S$. ^1H and ^{13}C NMR spectra revealed that the compound has two nonequivalent *t*-butyl and methoxycarbonyl groups on the thiophene ring. Two isomeric structures **7** and **16** are again in harmony with the observed NMR data. We then hydrolyzed the compound under the conditions which the hydrolysis of **6** was cleanly attained (potassium hydroxide in refluxing aqueous ethanol). The reaction afforded compound **12** as the sole product in which the more hindered ester group remained untouched. This ester was not hydrolyzed even on prolonged heating (42 h) with potassium hydroxide in boiling water. These results show that the ester carbonyl is highly sterically hindered and resists the usual based-catalyzed hydrolysis involving a tetrahedral intermediate. A number of procedures have been developed to overcome such difficulty. The use of lithium 1-propanethiolate in hexamethylphosphoric triamide (HMPA) is one of the excellent methods which can cleave the alkyl-oxygen bond of hindered



esters.[13] Application of this method to **7** satisfactorily afforded the dicarboxylic acid **13** in 59% yield. In contrast to the results with the diacid **10**, **13** did not lose water upon heating to give the corresponding acid anhydride **14**.[14] It could be converted to **14** in 72% yield by heating it with acetic anhydride. Thus, the structure of the compound was rigidly established to be **7**.

As to the mechanism of the formation of **6**—**9**, the following seems probable. The unexpected formation of **6** may involve a stepwise [2+2]cycloaddition of DMAD to the double bond of **5** which is activated by large angle strains and electron-donating divalent sulfurs, though the process seems unfavorable sterically. The resulting **17** then undergoes ring opening to give the 1,2-dithiin **18** which loses sulfur to produce **6**. It is known that 1,2-dithiins thermally extrude sulfur to afford the corresponding thiophenes.[15]

The simplest explanation for the formation of **7** involves the valence tautomerization of **5** to the α-dithione **19**, which undergoes [4+2]cycloaddition with DMAD to give the 1,4-dithiin **20**.[16] Thermal sulfur extrusion of 1,4-dithiins yielding thiophenes is well documented[17] and hence **20** would give rise to **7** under the applied conditions. Although these are the very processes that we expected to occur at the beginning of the present study, currently we do not have any evidence for the presence of the dithiete-dithione tautomerization.[18] Therefore, an alternative path which involves electrophilic addition of DMAD to the

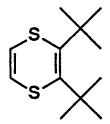


DMAD + S_8 → 8 → 9

sulfur of **5** followed by collapse of the resulting betaine **21** to **20** cannot be ruled out.

The straightforward explanation is available for the formation of **8** and **9**. Thermal sulfur extrusion of **8** yielding **9** is a known reaction.[11c] Also known is the formation of **9** by reaction of DMAD with elemental sulfur which probably involves **8** as the intermediate.[12] Therefore, in the present case, the sulfur extruded from **18** and **20** would react with DMAD to give **8**, which then loses sulfur to produce **9**.

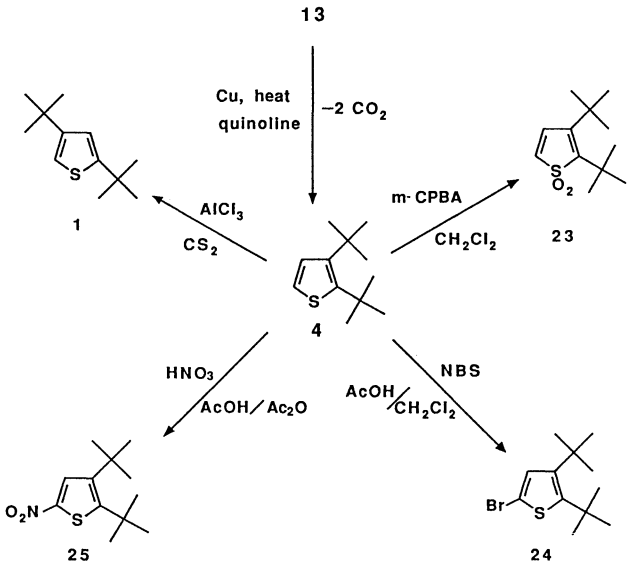
We have also examined the reaction of **5** with phenyl vinyl sulfoxide[19] at 180 °C using benzene as solvent in a stainless steel autoclave with expectation of obtaining the dithiin **22**. However, no reaction occurred with recovery of **5** in 87% yield. The dithiete **5** is also inactive toward benzyne generated by thermal decomposition of 2-carboxybenzenediazonium chloride in the presence of propylene oxide;[20] **5** was recovered in 86% yield. Irradiation of a solution of **5** in hexane containing excess DMAD with a 400-W medium-pressure mercury lamp afforded an intractable mixture;[18] no expected **20** was obtained.



22

Since we could obtain the dicarboxylic acid **13** though in low overall yield, its decarboxylation was attempted to prepare the parent 2,3-di-*t*-butylthiophene (**4**). Heating **13** with copper powder in refluxing quinoline cleanly afforded **4** in 88% yield as a colorless liquid. In the ^{1}H NMR spectrum, two nonequivalent *t*-butyls of **4** appear at δ 1.45 and 1.55 as sharp singlets indicating that the rotation about the thienyl-to-*t*-butyl bonds is fast on the ^{1}H NMR time scale at room temperature. The same conclusion is also reached by ^{13}C NMR spectrum in which each signal of two *t*-butyls consists of one singlet due to quaternary carbon and one quartet due to three equivalent methyl carbons. These NMR behaviors are analogous to those of **3**[5] and *o*-di-*t*-butylbenzene.[21] Meanwhile, the protons at C-4 and C-5 appear at δ 6.94 and 7.10, respectively, with J=5.4 Hz.[22] In the ^{13}C NMR, the signals due to C-4 and C-5 appear at δ 131.0 and 116.4, respectively, while those of two carbons carrying a *t*-butyl group appear at lower fields of δ 144.6 and 149.1.[23]

Finally reactivities of **4** were briefly examined. Treatment of **4** with aluminum chloride at room temperature caused a smooth rearrangement to the thermodynamically stable 2,4-isomer **1**. An analogous rearrangement to **1** has been observed with the 2,5- and 3,4-isomers **2**[1] and **3**.[5] Oxidation of **4** with excess *m*-chloroperbenzoic acid (*m*-CPBA) cleanly afforded 2,3-di-*t*-butylthiophene 1,1-dioxide (**23**) in 79% yield. This reactivity resembles that of the 3,4-



isomer **3**.[5] The oxidation of the 2,5-isomer with *m*-CPBA is known to give the first isolable thiophene sulfoxide, 2,5-di-*t*-butylthiophene 1,1-dioxide, though in low yield.[24] Electrophilic substitutions of **4**, as expected, exclusively occur at the less hindered and more electronically favored 5-position.[25] Thus, treatment of **4** with *N*-bromosuccinimide (NBS) afforded the bromide **24** in 79% yield. Nitration with fuming nitric acid in acetic acid produced the compound **25** quantitatively.

Experimental

General. Melting points were determined on a MEL-TEMP capillary tube apparatus and are uncorrected. Both ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q or a Bruker WM-400 spectrometer. Chemical shifts are expressed in parts per million from tetramethylsilane as an internal standard. Mass spectra were determined on a Shimadzu QP-1000 or a JEOL DX-303 spectrometer. High resolution mass spectra were determined on a JEOL DX-303 spectrometer. IR spectra were taken on a Hitachi 270-50 spectrometer.

Column chromatography was conducted using E. Merck silica gel 60 (70—230 mesh). 2,3-Di-*t*-butyl-1,2-dithiete (**5**) was prepared in the following way. *O*-(Methylsulfonyl)pivaloin prepared from pivaloin[26] and methanesulfonyl chloride, was treated with potassium thiocyanate in *N*,*N*-dimethylacetamide (DMA) to give 2,2,5,5-tetramethyl-4-thiocyanato-3-hexanone.[27] The cyanate was then treated with sodium hydroxide to give 2,2,5,5-tetramethyl-4-thioxo-3-hexanone,[8,27] which was sulfurized with freshly prepared Lawesson's reagent[28] to furnish **5**.[8] Dimethyl acetylenedicarboxylate (DMAD) was purified by distillation prior to use. 2-Carboxybenzenediazonium chloride was prepared according to the literature method.[20]

Reaction of 3,4-Di-*t*-butyl-1,2-dithiete (5) with DMAD. A solution of 1.07 g (5.3 mmol) of **5** and 3.76 g (26.5 mmol) of DMAD in 40 ml of *o*-dichlorobenzene was heated under reflux for 3 h. The dark brown mixture was evaporated under reduced pressure. The residue was chromato-

graphed on a column of silica gel (120 g). The column was first eluted with hexane to remove the remaining *o*-dichlorobenzene and then with benzene to give 1.13 g of dimethyl 2,5-di-*t*-butyl-3,4-thiophenedicarboxylate (**6**) contaminated with DMAD. Recrystallization of this material from hexane gave 0.73 g (44%) of pure **6**. Further elution of the column with benzene gave 0.13 g of crude dimethyl 2,3-di-*t*-butyl-4,5-thiophenedicarboxylate (**7**). Rechromatography of the above material gave 82 mg (5%) of pure **7**. The column was then eluted with dichloromethane to give 0.13 g of crude tetramethyl 1,4-dithiin-2,3,5,6-tetracarboxylate (**8**). Pure **8**, 80 mg (4%), was obtained by purifing the above material with rechromatography. Further elution of the original column with dichloromethane gave 0.72 g (43%) of tetramethyl 2,3,4,5-thiophenetetracarboxylate (**9**).

In a separate experiment, when **5** was allowed to react with a lesser amount of DMAD (1—3 equiv), elemental sulfur could be isolated in a considerable amount.

6: Mp 93—93.5 °C (hexane); ^{1}H NMR ($CDCl_3$) δ=1.40 (18H, s, *t*-butyl), 3.77 (6H, s, CO_2Me); ^{13}C NMR ($CDCl_3$) δ=31.17 (q), 35.12 (s), 51.81 (q), 128.84 (s), 152.41 (s), 166.17 (s); IR (KBr) 1270, 1728 cm^{-1} (ester); MS *m/z* 312 (M^+), 281, 265 (base), 233. Anal. ($C_{16}H_{24}O_4S$) C, H.

7: Viscous oil; ^{1}H NMR ($CDCl_3$) δ=1.48 (9H, s, *t*-butyl), 1.58 (9H, s, *t*-butyl), 3.77 (3H, s, CO_2Me), 3.85 (3H, s, CO_2Me); ^{13}C NMR ($CDCl_3$) δ=32.96 (q), 33.82 (q), 36.05 (s), 37.18 (s), 51.92 (q), 52.37 (q), 123.92 (s), 142.44 (s), 144.23 (s), 157.77 (s), 161.35 (s), 168.77 (s); MS *m/z* 312 (M^+), 281, 265 (base); IR (film) 1214, 1734 cm^{-1} (with two shoulders) (ester). HRMS Found: *m/z* 312.1375. Calcd for $C_{16}H_{24}O_4S$: M, 312.1395.

8: Mp 123—123.5 °C (lit,[11a] mp 126—127 °C); ^{1}H NMR ($CDCl_3$) δ=3.82 (s); ^{13}C NMR ($CDCl_3$) δ=53.49 (q), 134.59 (s), 161.62 (s).

9: Mp 125—126.5 °C (lit,[12c] mp 125—126 °C); ^{1}H NMR ($CDCl_3$) δ=3.88 (s); ^{13}C NMR ($CDCl_3$) δ=52.83 (q), 53.00 (q), 135.94 (s), 136.86 (s), 160.05 (s), 162.60 (s).

Conversion of 6 to 2,5-Di-*t*-butyl-3,4-thiophenedicarboxylic Anhydride (11). A mixture of 0.50 g of potassium hydroxide, 100 mg (0.32 mmol) of **6**, 2 ml of water, and 8 ml of ethanol was heated under reflux for 24 h. The resulting clear solution was evaporated under reduced pressure and the residue was dissolved in 5 ml of water and acidified with 12 M hydrochloric acid (1 M=1 mol dm^{-3}). The resulting white crystalline material was extracted with dichloromethane. The extracts were washed with water, dried over anhydrous sodium sulfate, and evaporated to give 88 mg (97%) of 2,5-di-*t*-butyl-3,4-thiophenedicarboxylic acid (**10**): mp 188—190 °C (from benzene); ^{1}H NMR ($CDCl_3$) δ=1.43 (18H, s, *t*-butyl), 11.00 (2H, broad s, CO_2H); IR (KBr) 1698 cm^{-1} (CO_2H).

Heating the diacid **10** at its melting point for a few minutes in a small test tube afforded the anhydride **11** quantitatively: mp 129.5—130 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ=1.50 (s); ^{13}C NMR ($CDCl_3$) δ=30.25 (q), 35.72 (s), 128.63 (s), 157.07 (s), 160.05 (s); IR (KBr) 1820, 1768 cm^{-1}. Anal. ($C_{14}H_{18}O_3S$) C, H.

Conversion of 7 to 2,3-Di-*t*-butyl-4,5-thiophenedicarboxylic Anhydride (14). To a stirred solution of 560 mg (7.4 mmol) of 1-propanethiol in 8 ml of hexamethylphosphoric triamide (HMPA) was added dropwise 2.7 ml of a 1.5 M solution of butyllithium in hexane at 0 °C. The mixture was stirred for 0.3 h at room temperature and then cooled to 0 °C. To this mixture a solution of 209 mg (0.67 mmol) of **7** in 2 ml of HMPA was added under ice-cooling. The mixture was slowly warmed to room temperature and stirred for 7 h. The resulting mixture was acidified with 1 M hydrochloric acid and was extracted with ether. The extracts were shaken with 2 M sodium hydroxide (2×10 ml). The alkaline layers were washed with ether and then acidified with 1 M hydrochloric acid. The mixture was extracted with ether. The ether extracts were washed with water, dried over anhydrous sodium sulfate, and evaporated. The residue (129 mg) was triturated with hexane to give 112 mg (59%) of pure 2,3-di-*t*-butyl-4,5-thiophenedicarboxylic acid (**13**): mp 246—249 °C; ^{1}H NMR (DMSO-d_6) δ=1.48 (9H, s, *t*-butyl), 1.56 (9H, s, *t*-butyl), 13.0 (2H, broad s, CO_2H); ^{13}C NMR (DMSO-d_6) δ=32.75 (q), 33.49 (q), 35.74 (s), 36.67 (s), 123.82 (s), 143.46 (s), 143.51 (s), 155.89 (s), 161.71 (s), 168.93 (s). HRMS Found: *m/z* 284.1089. Calcd for $C_{14}H_{20}O_4S$: M, 284.1083.

The diacid **13** (10.3 mg) was heated in refluxing acetic anhydride (0.5 ml) for 3 h. The mixture was evaporated under reduced pressure and the residual solid was purified by sublimation to provide 6.9 mg (72%) of the anhydride **14**: mp 114—116 °C; ^{1}H NMR ($CDCl_3$), δ=1.60 (9H, s, *t*-butyl), 1.63 (9H, s, *t*-butyl); IR (KBr) 1832, 1772 cm^{-1}; MS *m/z* 266 (M^+), 251, 233. HRMS Found: *m/z* 266.0980. Calcd for $C_{14}H_{18}O_3S$: M, 266.0977.

Alkaline Hydrolysis of 7. A mixture of 82 mg (0.26 mmol) of **7** and 330 mg of potassium hydroxide in 1.7 ml of water and 6.5 ml of ethanol was heated under reflux for 23 h. The mixture was evaporated under reduced pressure and the residue was dissolved in 5 ml of water. The solution was acidified with 12 M hydrochloric acid. The mixture was extracted with ether. The ether extracts were washed with water, dried over anhydrous sodium sulfate, and evaporated to give 61 mg (79%) of the half ester **12**: mp 208—211 °C; ^{1}H NMR ($CDCl_3$) δ=1.50 (9H, s, *t*-butyl), 1.60 (9H, s, *t*-butyl), 3.83 (3H, s, CO_2Me), 9.38 (1H, broad s, CO_2H).

Heating **12** with potassium hydroxide in boiling water for 42 h resulted in the quantitative recovery of **12**.

2,3-Di-*t*-butylthiophene (4). A mixture of 92 mg (0.32 mmol) of the dicarboxylic acid **13** and 0.5 g of copper powder in 1.5 ml of quinoline was refluxed for 3 h. The mixture was placed on a column of silica gel (50 g). The column was eluted with pentane to give 56 mg (88%) of **4** as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ=1.45 (9H, s, *t*-butyl), 1.55 (9H, s, *t*-butyl), 6.92 (1H, d, *J*=5.4 Hz, ring proton at C-4), 7.10 (1H, d, *J*=5.4 Hz, ring proton at C-5); ^{13}C NMR ($CDCl_3$) δ=33.68 (q), 33.92 (q), 34.85 (s), 35.61 (s), 116.38 (d), 131.01 (d), 144.63 (s), 149.07 (s); MS, *m/z* 196 (M^+), 181 (base). HRMS Found: *m/z* 196.1285. Calcd for $C_{12}H_{20}S$: M, 196.1285.

Isomerization of 4 to 2,4-Di-*t*-butylthiophene (1). A mixture of 10 mg (0.05 mmol) of **4** and 8 mg of aluminum chloride in 1.5 ml of carbon disulfide was stirred for 3.5 h at room temperature. The mixture was evaporated and the residue was made alkaline by adding 2 M potassium hydroxide (2 ml) and extracted with ether. The extract was washed with water, dried over anhydrous sodium sulfate, and evaporated. The residue was passed through a short column of silica gel using hexane as solvent to give 7.4 mg (74%) of **1**, whose ^{1}H and ^{13}C NMR spectra agreed with those synthesized independently.[1]

2,3-Di-*t*-butylthiophene 1,1-Dioxide (23). To a stirred solution of 10 mg (0.05 mmol) of **4** in 1.5 ml of dichloromethane, 27 mg (0.16 mmol) of *m*-CPBA was added in small portions. The mixture was stirred for 17 h at room temperature. The mixture was diluted with 10 ml of dichloromethane, washed with aqueous sodium carbonate, dried over anhydrous sodium sulfate, and evaporated. The residue was passed through a short column of silica gel using benzene as eluent to give 9.7 mg (79%) of **23**: mp 89—90 °C; ^{1}H NMR ($CDCl_3$) δ=1.37 (9H, s), 1.58 (9H, s), 6.48 (1H, d, J=7.1 Hz), 7.01 (1H, d, J=7.1 Hz); ^{13}C NMR ($CDCl_3$) δ=31.17 (q), 31.72 (q), 34.50 (s), 35.18 (s), 126.29 (d), 133.66 (d), 141.47 (s), 144.71 (s); IR (KBr) 1134, 1280 cm^{-1} (SO_2). HRMS Found: m/z 228.1221. Calcd for $C_{12}H_{20}O_2S$: M, 228.1184.

5-Bromo-2,3-di-*t*-butylthiophene (24). To a stirred solution of 10.7 mg (0.055 mmol) of **4** in 1 ml of acetic acid and 1 ml of dichloromethane, 11 mg (0.062 mmol) of *N*-bromosuccinimide was added. The mixture was stirred for 2 h at room temperature. The resulting mixture was diluted with 10 ml of dichloromethane, washed with water, dried over anhydrous sodium sulfate, and evaporated. The residue was passed through a short column of silica gel using hexane as eluent to give 12 mg (79%) of **24** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ=1.41 (9H, s), 1.51 (9H, s), 7.00 (1H, s); ^{13}C NMR ($CDCl_3$) δ=33.51 (q), 33.62 (q), 35.07 (s), 36.25 (s), 104.95 (s), 133.64 (d), 145.81 (s), 151.13 (s); MS m/z 276 (M^+, ^{81}Br), 274 (M^+, ^{79}Br), 261 (base), 259, 205, 203. HRMS Found: m/z 274.0368. Calcd for $C_{12}H_{19}BrS$: M, 274.0391.

2,3-Di-*t*-butyl-5-nitrothiophene (25). Fuming nitric acid (3.5 mg, 0.05 mmol) was dissolved in 0.5 ml of acetic acid. To this solution, a solution of 9 mg (0.046 mmol) of **4** in 1 ml of acetic anhydride was added at 0 °C. The mixture was slowly warmed to room temperature and stirred for 8 h. The reaction was quenched by adding ice (ca. 5 g). The mixture was extracted with ether. The extract was washed with aqueous sodium carbonate and then with water, dried over anhydrous sodium sulfate, and evaporated. The residue was passed through a short column of silica gel using carbon tetrachloride as eluent to give 11 mg (99%) of **25** as pale yellow solid: mp 75—76 °C; ^{1}H NMR ($CDCl_3$) δ=1.47 (9H, s), 1.58 (9H, s), 7.95 (1H, s); ^{13}C NMR ($CDCl_3$) δ=33.33 (q), 33.35 (q), 35.55 (s), 37.25 (s), 132.39 (d), 146.51 (s), 159.94 (s); MS m/z 241 (M^+), 226, 184. HRMS Found: m/z 241.1128. Calcd for $C_{12}H_{19}NO_2S$: M, 241.1136.

Elemental analyses were performed by the Analytical Center of Saitama University, for which we thank Professor M. Sato and his staff.

References

1) H. Wynberg and U. E. Wiersum, *J. Org. Chem.*, **30**, 1058 (1965).

2) E. H. Wiebenga and H. Bouwhuis, *Tetrahedron*, **25**, 453 (1969).

3) L. Brandsma, J. Meijer, H. D. Verkruijsse, G. Bokkers, A. J. M. Duisenberg, and J. Kroon, *J. Chem. Soc., Chem. Commun.*, **1980**, 922. For X-ray crystal structure analysis of **3**, see G. Bokkers, A. J. M. Duisenberg, J. Kroon, and L. Brandsma, *Cryst. Struct. Chem.*, **10**, 361 (1981).

4) H. Wynberg, *Acc. Chem. Res.*, **4**, 65 (1971).

5) J. Nakayama, S. Yamaoka, and M. Hoshino, *Tetrahedron Lett.*, **29**, 1161 (1988).

6) R. M. Kellogg, "Comprehensive Heterocyclic Chemistry," ed by C. W. Bird and G. W. H. Cheeseman, Pergamon Press, Oxford (1984), Vol. 4, p. 721.

7) We thank Professor A. Krebs of University of Hamburg for informing us of this successful synthesis prior to the publication.

8) B. Köpke and J. Voss, *J. Chem. Res. (S)*, **1982**, 314.

9) C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Am. Chem. Soc.*, **82**, 1515 (1960); C. G. Krespan, *ibid.*, **83**, 3434 (1961); J. Hencher, Q. Shen, and D. G. Tuck, *ibid.*, **98**, 899 (1976); A. Krebs, H. Colberg, U. Höpfner, H. Kimling, and J. Odenthal, *Heterocycles*, **12**, 1153 (1979); R. B. Boar, D. W. Hawkins, J. F. McGhie, S. C. Misra, D. H. R. Barton, M. F. C. Ladd, and D. C. Povey, *J. Chem. Soc., Chem. Commun.*, **1975**, 756; W. Küsters and P. de Mayo, *J. Am. Chem. Soc.*, **95**, 2383 (1974); M. Breitenstein, R. Schulz, and A. Schweig, *J. Org. Chem.*, **47**, 1979 (1982).

10) Although the formation of **6** was previously reported, its properties were not given in detail: J. Buter, S. Wassenaar, and R. M. Kellogg, *J. Org. Chem.*, **37**, 4045 (1972).

11) a) O. Scherer and F. Kluge, *Chem. Ber.*, **99**, 1973 (1966); b) W. Ried and W. Ochs, *ibid.*, **105**, 1093 (1972); c) S. C. Olsen and J. P. Snyder, *Acta. Chem. Scand., Sect. B*, **32**, 152 (1978).

12) a) A. Michael, *Ber.*, **28**, 1633 (1895); b) H. Hopff and J. von der Crone, *Chimia*, **13**, 107 (1959); c) T. Sone, Y. Abe, and T. Oikawa, *Nippon Kagaku Zasshi*, **92**, 1193 (1971); d) J. Nakayama, M. Kashiwagi, R. Yomoda, and M. Hoshino, *Nippon Kagaku Kaishi*, **1987**, 1414.

13) P. A. Bartlett and W. S. Johnson, *Tetrahedron Lett.*, **1970**, 4459.

14) In the parent thiophene, the bond angle HC(3)C(4) (123°36′) is smaller than the bond angles HC(2)C(3) (128°41′) and C(2)C(3)H (124°17′): B. Back, D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectrosc.*, **7**, 58 (1961). This, along with symmetrical structure of **10**, should make the formation of **11** easier.

15) F. Bohlmann and K.-M. Kleine, *Chem. Ber.*, **98**, 3081 (1965); W. Schroth, F. Billing, and G. Reinhold, *Angew. Chem., Int. Ed. Engl.*, **6**, 698 (1967).

16) P. de Mayo and A. C. Weedon, *J. Org. Chem.*, **44**, 1977 (1979).

17) W. H. Parham and V. J. Traynelis, *J. Am. Chem. Soc.*, **76**, 4960 (1954); R. Grigg, R. Hayes, and J. Jackson, *J. Chem. Soc., Chem. Commun.*, **1969**, 1167; K. Kobayashi, K. Mutai, and H. Kobayashi, *Tetrahedron Lett.*, **1979**, 5003; J. Nakayama, M. Shimomura, M. Iwamoto, and M. Hoshino, *Heterocycles*, **23**, 1907 (1985).

18) Semiempirical SCF-MO calculations show that the conversion of an α-dithione to a 1,2-dithiete is allowed photochemically; the thermal processes, both forward and reverse, are forbidden: J. P. Snyder, "Organic Sulphur Chemistry," ed by C. J. M. Stirling, Butterworths, London (1975), p. 307.

19) L. A. Paquette, R. E. Moerck, B. Harirchian, and P. D. Magnus, *J. Am. Chem. Soc.*, **100**, 1597 (1978).

20) B. H. Klanderman and T. R. Criswell, *J. Org. Chem.*, **34**, 3426 (1969).

21) W. A. Gibbons and V. M. S. Gil, *Mol. Phys.*, **9**, 163 (1965).

22) $J_{2,3}$ ($J_{4,5}$) of thiophenes has an average value of 4.90—5.80: see Ref. 6, p. 730.
23) In the thiophene **3**, the signal due to C-2 (C-5) appears at δ 122.3 and that due to C-3 (C-4) at 150.6 (Ref. 5).
24) W. L. Mock, *J. Am. Chem. Soc.*, **92**, 7610 (1970).
25) S. Rajappa, "Comprehensive Heterocyclic Chemistry," ed by C. W. Bird and G. W. H. Cheeseman, Pergamon Press, Oxford (1984), Vol. 4, p. 741; G. R. Newkome and W. W. Paudler, "Contemporary Heterocyclic Chemistry," John Wiley, New York (1982), p. 92.
26) J. M. Snell and S. M. McElvain, *Org. Synth.*, II, 114 (1943).
27) N. J. Jacobson, P. de Mayo, and A. C. Weedon, *Nouv. J. Chim.*, **2**, 331 (1978).
28) B. S. Pedersen, S. Scheibye, N. H. Hilsson, and S.-O. Lawesson, *Bull. Soc. Chim. Belg.*, **87**, 223 (1978).