after 14 mos neat at ambient temperature afforded an unspecified yield of an impure amino diazo compound corresponding to **10**, along with a small amount of a 2:1 adduct. None of the triazoline was found.

Thus, azide-electron-deficient olefin dipolar cycloadditions, like many other pericyclic reactions,[5-9] are significantly accelerated by pressure. In view of the increasing availability of preparative high-pressure equipment, this methodology should prove to be synthetically useful in formation of various triazolines and aziridines in a reasonable time scale.

Experimental Section

General Procedure for High-Pressure Cycloadditions. A solution of 2.4 mmol of the azide and 2.7 mmol of the olefin in 1.1 mL of solvent was sealed in a 5-mL plastic Luerlok syringe and subjected to 12 kbar of pressure for 24 h at ambient temperature in a LECO Model PG-200-HPC apparatus.[10] The solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel eluting with ethyl acetate/hexanes (1:2), except for the methacrylamide products where pure ethyl acetate was used. Data for new compounds are listed below:

Triazoline **3** (EWG = CN, R = CH_2Ph): colorless oil; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.33 (m, 5 H), 4.84 (d, 1 H, J = 15.1 Hz), 4.77 (d, 1 H, J = 15.1 Hz), 3.36 (d, 1 H, J = 10.4 Hz), 2.97 (d, 1 H, $_J$ = 10.4 Hz), 1.59 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 134.2, 128.8, 128.6, 128.4, 128.2, 128.1, 118.6, 71.4, 54.6, 53.9, 22.6; IR (neat) 2235 cm^{-1}.

Triazoline **3** (EWG = CO_2Me, R = CH_2Ph): pale yellow oil; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.34 (m, 5 H), 4.91 (d, 1 H, J = 14.9 Hz), 4.72 (d, 1 H, J = 14.9 Hz), 3.77 (s, 3 H), 3.41 (d, 1 H, J = 10.0 Hz), 2.85 (d, 1 H, J = 10.0 Hz), 1.47 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 171.3, 135.4, 128.7, 128.4, 128.2, 128.1, 127.9, 83.7, 54.2, 53.3, 52.8, 21.8; IR (neat) 1735 cm^{-1}.

Triazoline **3** (EWG = COMe, R = CH_2Ph): pale yellow oil; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.25 (m, 5 H), 4.77 (d, 1 H, J = 14.8 Hz), 4.66 (d, 1 H, J = 14.8 Hz), 3.36 (d, 1 H, J = 10.1 Hz), 2.63 (d, 1 H, J = 10.1 Hz), 2.24 (s, 3 H), 1.34 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 205.3, 135.2, 128.5, 128.0, 127.7, 127.5, 126.8, 89.7, 54.0, 51.1, 25.6, 21.5; IR (neat) 1715 cm^{-1}.

Triazoline **3** (EWG = $CONH_2$, R = CH_2Ph): mp 114-115 °C; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.30 (m, 5 H), 6.76 (bs, 1 H), 6.71 (bs, 1 H), 4.84 (d, 1 H, J = 14.8 Hz), 4.67 (d, 1 H, J = 14.8 Hz), 3.33 (d, 1 H, J = 10.3 Hz), 2.87 (d, 1 H, J = 10.3 Hz), 1.45 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 175.4, 135.3, 128.8, 128.3, 128.2, 128.1, 128.0, 83.8, 54.3, 53.3, 23.3; IR (KBr) 3385, 3190, 1660 cm^{-1}.

Triazoline **6**: pale yellow oil; ^1H NMR $CDCl_3$, 360 (MHz) δ 7.34 (m, 5 H), 4.95 (d, 1 H, J = 15.1 Hz), 4.80 (d, 1 H, J = 15.1 Hz), 3.95 (d, 1 H, J = 10.0 Hz), 3.80 (s, 3 H), 3.75 (d, 1 H, J = 9.9 Hz), 3.57 (d, 1 H, J = 10.4 Hz), 3.25 (s, 3 H), 3.22 (d, 1 H, J = 10.4 Hz); ^{13}C NMR ($CDCl_3$) δ 169.2, 135.2, 128.8, 128.7, 128.3, 128.2, 128.1, 87.6, 68.1, 55.4, 54.1, 53.1, 48.8; IR (neat) 1735 cm^{-1}.

Triazoline **7**: pale yellow oil; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.34 (m, 5 H), 4.90 (d, 1 H, J = 15.0 Hz), 4.83 (d, 1 H, J = 15.0 Hz), 3.81 (d, 1 H, J = 9.7 Hz), 3.79 (s, 3 H), 3.60 (d, 1 H, J = 9.7 Hz), 3.55 (d, 1 H, J = 10.4 Hz), 3.32 (s, 3 H), 3.23 (d, 1 H, J = 10.4 Hz); ^{13}C NMR ($CDCl_3$) δ 169.3, 135.2, 128.8, 128.7, 128.3, 128.2, 128.1, 87.8, 72.9, 59.5, 54.1, 53.1, 48.7; IR (neat) 1735 cm^{-1}.

Triazoline **9**: pale yellow oil; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.32 (m, 5 H), 4.84 (d, 1 H, J = 7.4 Hz), 4.47 (m, 1 H), 3.77 (s, 3 H), 1.29 (d, 3 H, J = 6.3 Hz).

Acknowledgment. We are grateful to the National Institutes of Health (GM-32299) for financial support of this work and thank Professor R. L. Funk for use of the high-pressure apparatus

Registry No. 1 (EWG = CN), 126-98-7; 1 (EWG = CO_2Me), 80-62-6; 1 (EWG = COMe), 814-78-8; 1 (EWG = $CONH_2$), 79-39-0; **2** (EWG = CN, R = Ph), 33708-57-5; **2** (EWG = CO_2Me, R = Ph), 4916-08-9; **2** (EWG = COMe, R = Ph), 33523-93-2; **2** (EWG = COMe, R = nBu), 33549-52-9; **2** (EWG = CO_2Me, R = $PhCH_2$), 136328-08-0; **2** (EWG = COMe, R = $PhCH_2$), 136328-09-1; **3** (EWG = CO_2Me, R = Ph), 136328-10-4; **3** (EWG = COMe, R = Ph), 136328-11-5; **3** (EWG = $CONH_2$, R = Ph), 136328-12-6; **3** (EWG = CN, R = nBu), 136328-13-7; **3** (EWG = CO_2Me, R = nBu), 136328-14-8; **3** (EWG = COMe, R = nBu), 33523-91-0; **3** (EWG = $CONH_2$, R = nBu), 136328-15-9; **3** (EWG = CN, R = $PhCH_2$), 136328-16-0; **3** (EWG = CO_2Me, R = $PhCH_2$), 136328-17-1; **3** (EWG = COMe, R = $PrCH_2$), 136328-18-2; **3** (EWG = $CONH_2$, R = $PhCH_2$), 136328-19-3; **3** (EWG = CN, R = Ph), 136328-20-6; **4** (EWG = CN, R = Ph), 33523-81-8; **4** (EWG = CO_2Me, R = Ph), 4916-07-8; **4** (EWG = COMe, R = Ph), 33549-51-8; **4** (EWG = $CONH_2$, R = Ph), 33523-85-2; **4** (EWG = CN, R = nBu), 33523-88-5; **4** (EWG = CO_2Me, R = nBu), 136328-21-7; **4** (EWG = COMe, R = nBu), 33523-87-4; **4** (EWG = $CONH_2$, R = nBu), 136328-22-8; **4** (EWG = CN, R = $PhCH_2$), 35303-38-9; **4** (EWG = CO_2Me, R = $PhCH_2$), 136328-23-9; **4** (EWG = COMe, R = $PhCH_2$), 136328-24-0; **4** (EWG = $CONH_2$, R = $PhCH_2$), 136328-25-1; **5**, 25328-81-8; **6**, 136328-26-2; **7**, 136328-27-3; **8**, 18707-60-3; **9**, 136328-28-4; **10**, 136328-29-5; $nBuN_3$, 7332-00-5; $PhCH_2N_3$, 622-79-7; PhN_3, 622-37-7.

Supplementary Material Available: NMR spectra of new compounds (12 pages). Ordering information is given on any masthead page.

(10) Available from LECO Corporation, Bellefonte, PA.

Formation and Structure of a Spiro Dimer from Methyl 2,3-Bis(chloromethyl)thiophene-5-carboxylate by Treatment with NaI in DMF Solution

Michinori Takeshita, Masanori Koike, Shuntaro Mataka, and Masashi Tashiro*

Department of Molecular Science and Technology, Graduate School of Engineering Sciences and Institute of Advanced Material Study, Kyushu University, 6-1 Kasuga-koh-en, Kasuga-shi, Fukuoka 816, Japan

Received April 29, 1991

Recently, it was reported that 2,3-dihydro-2,3-dimethylenethiophene, a thiophene quinodimethane analogue, generated from the corresponding 2,3-bis(halomethyl)- or 2-methyl-3-(halomethyl)thiophene affords mainly the corresponding spiro dimer.[1-3] Unfortunately, it was not possible to determine the structure of the spiro dimer by means of its NMR, IR, or UV spectra. Furthermore, the compound is unstable and may be difficult to derivatize. Therefore, we synthesized a stable spiro dimer bearing an ester group and identified the structure by chemical conversions.

Results and Discussion

When methyl 2,3-bis(chloromethyl)thiophene-5-carboxylate (**1**)[4,5] was treated with NaI in DMF at 60 °C for 7 h, a mixture of spiro dimer **2** and cyclooctene derivative **3** was obtained. However, reaction for 24 h afforded **4**, which is an iodinated derivative of **2** as shown in Scheme I.

Since a distinction among the four possible structures for **2** (Chart I) was not possible from the available spectral data, chemical transformations were undertaken.

(1) He, C.; Wiseman, J. R. *Gaodeng Xuexiao Huaxue Xuebao* **1985** *6*(9), 813; *Chem. Abstr.* **1986**, *105*, 226237F.

(2) (a) Chauhan, P. M. S.; Jenkins, G.; Walker, S. M.; Storr, R. C. *Tetrahedron. Lett.* **1988**, *29*, 117. (b) van Leusen, A. M.; van den Berg, K. *Ibid.* **1988**, *29*, 2689.

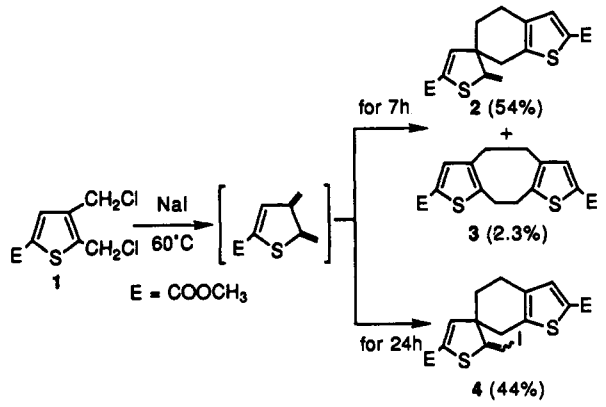
(3) Chadwick, D. J.; Plant, A. *Tetrahedron Lett.* **1987**, *28*, 6085.

(4) Zwanenbrug, D. J.; de Haan, H.; Wynberg, H. *J. Org. Chem.* **1966**, *31*, 3363.

(5) Cf. Takeshita, M.; Tashiro, M. *J. Org. Chem.* **1991**, *56*, 2837 for corresponding synthesis of ethyl ester.

0022-3263/91/1956-6948$02.50/0

Scheme I



Scheme II

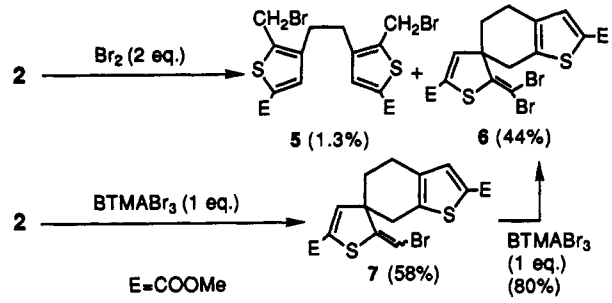
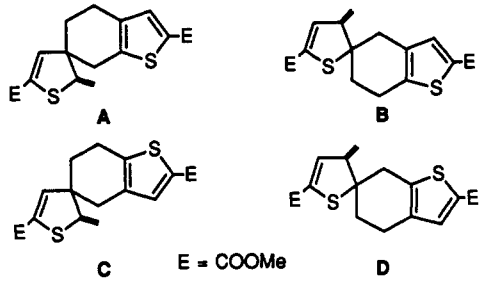


Chart I. Conceivable Structures of Spiro Compound 2

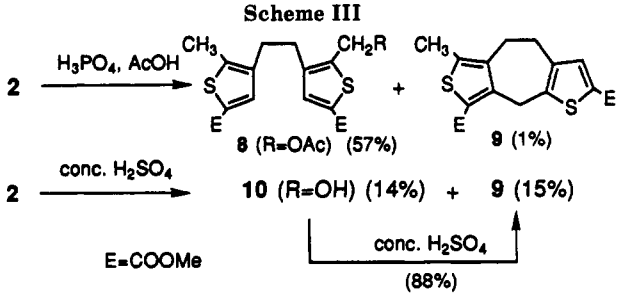


It was reported[6] that treatment of a similar spirodi-*o*-xylylene with bromine afforded the ring-opened product, 2,2′-bis(bromomethyl)bibenzyl. Thus, bromination of **2** was carried out under various conditions, and the results are summarized in Scheme II.

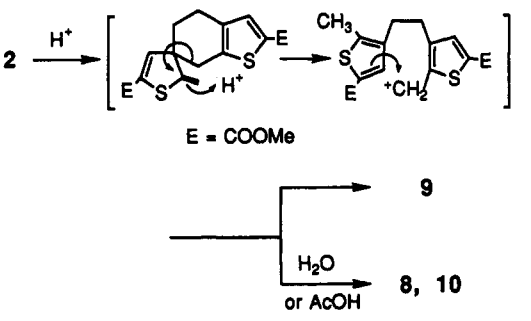
Bromination of **2** with 2 equiv of bromine afforded a small amount of the symmetrical bis(bromomethyl) compound **5**, along with dibromide **6**, the main product. Similar brominations with 2 equiv of NBS or $BTMABr_3$[7] (benzyltrimethylammonium tribromide) for 12 h at room temperature afforded **6** as the sole product, in 54 and 45% yield, respectively. Treatment of **2** with 1 equiv of $BTMABr_3$ afforded monobromide **7**, which is an intermediate in the formation of **6**. As expected, treatment of **7** with 1 equiv of $BTMABr_3$ afforded **6** in good yield. The formation of symmetrical **5** shows that the structure of **2** must correspond to A or B, since C and D would afford unsymmetrical bis(bromomethyl) products.

It is known that ring opening of spiro compounds also occurs by treatment with acids.[8] Treatment of **2** with acids such as concd H_2SO_4 and H_3PO_4 afforded ethane derivatives of **8** and **10**, and cycloheptene derivative **9** as shown in Scheme III. Compound **9** was also obtained from

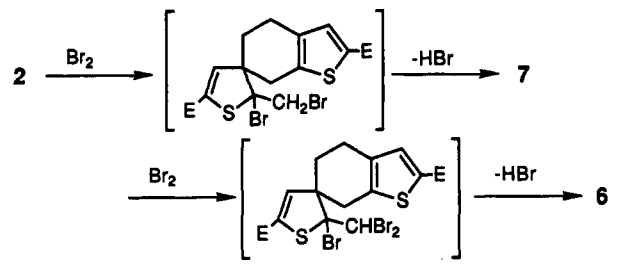
Scheme III



Scheme IV



Scheme V



10 by treatment with concd H_2SO_4.

The formation of cycloheptadithiophene **9** shows that the structure of **2** is A, since from B [2.1]orthometacyclophane would be produced. The structural assignments for **4**, **6**, and **7** are based on the results described above.[9] The formation of cycloheptadithiophene **9** from **2** is proposed to occur as shown in Scheme IV.

A pathway leading to compounds **6** and **7** from **2** is given in Scheme V. Although bromination and iodination of **2** proceeded stereoselectively, the stereostructure (*E* or *Z*) of **4** and **7** was not determined.

Experimental Section

All melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 270 and 68 MHz.

Methyl 2,3-Bis(chloromethyl)thiophene-5-carboxylate (1).[4,5] A mixture of 40.0 g (0.28 mol) of methyl thiophene-2-carboxylate[10] and 113 g (1.4 mol) of chloromethyl methyl ether (1.4 mol) was stirred and cooled at 0 °C, as 80.0 g (0.42 mol) of $TiCl_4$ was added dropwise over 30 min. The mixture was stirred for 1 h at 0 °C and poured into the ice–water. The organic products were extracted with $CHCl_3$. The extract was washed with brine, dried ($MgSO_4$), and evaporated in vacuo. Recrystallization of the residue afforded 59 g (87%) of **1**: colorless needles (hexane); mp 71 °C (lit.[4] 72–72.5 °C).

Treatment of 1 with NaI in DMF for 7 h. A solution of 10 g (42 mmol) of **1** and 33 g (210 mmol) of NaI in 120 mL of dry DMF was stirred at 60 °C for 7 h under N_2. The mixture was poured into water, and the organic products were extracted with $CHCl_3$. The extract was washed with aqueous $Na_2S_2O_3$ and brine,

(6) Errede, L. A. *J. Am. Chem. Soc.* **1961**, *83*, 949.
(7) For example: Kajigaeshi, S.; Kakinami, T.; Tokiyama, H.; Hirakawa, T.; Okamoto, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2667.
(8) Tashiro, M.; Yamato, T. *Chem. Lett.* **1982**, 61.
(9) One of the reviewers informed us that the same structure for **2** (E = H) was established through ^1H NMR spectra of two different deuteriated derivatives of **2** (E = H) in two different research groups.
(10) Weinstein, B. *J. Am. Chem. Soc.* **1955**, *77*, 6709.

dried ($MgSO_4$), and evaporated in vacuo. The residue was subjected to column chromatography (silica gel; eluent, benzene). Recrystallization of the first eluate afforded 3.8 g (54%) of **2**. Recrystallization of the second eluate afforded 160 mg (2.3%) of **3**.

Dimethyl 4,5-dihydro-2′-methylenespiro[benzo[*b*]thiophene-6(7*H*),3′(2′*H*)-thiophene]-2,5′-dicarboxylate (2): colorless plates (EtOH); mp 154.0–155.0 °C; IR (KBr) ν (cm^{-1}) 2950, 2842, 1710, 1622, 1297, 1074, 745; ^1H NMR ($CDCl_3$) δ (ppm) 1.82–1.93 (1 H, m), 2.06–2.13 (1 H, m), 2.69–2.92 (2 H, m), 2.98 and 3.04 (2 H, AB d, J = 17 Hz), 3.79 (3 H, s), 3.86 (3 H, s), 5.14 (1 H, d, J = 2 Hz), 5.24 (1 H, dd, J = 2, 1 Hz), 6.51 (1 H, d, J = 1 Hz), 7.52 (1 H, s); ^{13}C NMR ($CDCl_3$) δ (ppm) 23.0, 33.9, 37.5, 52.1, 52.5, 56.9, 105.4, 130.6, 131.5, 133.6, 134.9, 137.9, 141.2, 153.6, 162.2, 162.7; MS m/e 336 (M^+). Anal. Calcd for $C_{16}H_{16}O_4S_2$: C, 57.12; H, 4.79. Found: C, 56.85; H, 4.89.

Dimethyl [2.2](2,3)(2,3)thiophenophane-5,12-dicarboxylate (dimethyl 2,3,7,8-tetrahydrocycloocta[1,2-*d*:5,6-*b*]dithiophene-5,10-dicarboxylate) (3): colorless needles (EtOH); mp 197.0–198.0 °C; IR (KBr) ν (cm^{-1}) 1707, 1463, 1298, 1262, 1083, 753; ^1H NMR ($CDCl_3$) δ (ppm) 3.06 (4 H, s), 3.30 (4 H, s), 3.81 (6 H, s), 7.37 (2 H, s); MS m/e 336 (M^+). Anal. Calcd for $C_{16}H_{16}O_4S_2$: C, 57.12; H, 4.79. Found: C, 57.30; H, 4.91.

Treatment of 1 with NaI in DMF for 24 h. A solution of 2.0 g (42 mmol) of **1** and 9.0 g (58 mmol) of NaI in 30 mL of dry DMF was stirred for 24 h at 60 °C under N_2. The mixture was poured into water, and the organics were extracted with $CHCl_3$. The extract was washed with aqueous $Na_2S_2O_3$ and brine, dried ($MgSO_4$), and evaporated in vacuo. The residue was subjected to column chromatography (silica gel; eluent, benzene). Recrystallization of the eluate afforded 840 mg (44%) of **4**.

Dimethyl 4,5-dihydro-2′-(iodomethylene)spiro[benzo[*b*]thiophene-6(7*H*),3′(2′*H*)-thiophene]-2,5′-dicarboxylate (4): colorless needles (ethanol); mp 177 °C dec; IR (KBr) ν (cm^{-1}) 2946, 1694, 1612, 1468, 1254, 1076, 739; ^1H NMR ($CDCl_3$) δ (ppm) 1.86–1.96 (1 H, m), 2.06–2.15 (1 H, m), 2.69–2.96 (2 H, m), 2.97 and 3.07 (2 H, AB d, J = 17 Hz), 3.81 (3 H, s), 3.87 (3 H, s), 6.20 (1 H, s), 6.87 (1 H, s), 7.52 (1 H,s); MS m/e 462 (M^+). Anal. Calcd for $C_{16}H_{15}IO_4S_2$: C, 41.57; H, 3.27. Found: C, 41.87; H, 3.38.

Treatment of 2 with Br_2. To a solution of 500 mg (1.3 mmol) of **2** in 25 mL of CH_2Cl_2 was added 480 mg (3.0 mmol) of Br_2 and the mixture was stirred at rt for 17 h. The mixture was poured into water, and the organic phase was separated and washed with $NaHCO_3$(aq) and brine. After drying ($MgSO_4$), the solvent was removed by evaporation. The residue was subjected to column chromatography (silica gel; eluent, benzene). Recrystallization of the first eluate afforded 323 mg (44%) of **6**, and recrystallization of the second eluate afforded 10 mg (1.3%) of **5**.

1,2-Bis(2-(bromomethyl)-5-(methoxycarbonyl)-3-thienyl)ethane (5): colorless plates (hexane/$CHCl_3$); mp 180.0–181.0 °C; IR (KBr) ν (cm^{-1}) 1703, 1257, 756, 590; ^1H NMR ($CDCl_3$) δ (ppm) 2.93 (4 H, s), 3.88 (6 H, s), 4.54 (4 H, s), 7.52 (2 H, s); ^{13}C NMR ($CDCl_3$) δ (ppm) 23.7, 28.6, 52.4, 132.6, 134.8, 140.9, 141.4, 162.2; MS m/e 494, 496, 498 (M^+). Anal. Calcd for $C_{16}H_{16}Br_2O_4S_2$: C, 38.73; H, 3.25. Found: C, 39.10; H, 3.45.

Dimethyl 4,5-dihydro-2′-(dibromomethylene)spiro[benzo[*b*]thiophene-6(7*H*),3′(2′*H*)-thiophene]-2,5′-dicarboxylate (6): colorless needles (ethanol) mp 165.0–168.0 °C; IR (KBr) ν (cm^{-1}) 1711, 1469, 1252, 746; ^1H NMR ($CDCl_3$) δ (ppm) 2.05 (1 H, dd, J = 6, 13 Hz), 2.60–2.78 (1 H, m), 2.82–3.03 (3 H, m), 3.79 (3 H, s), 3.87 (3 H, s), 4.02 (1 H, dd, J = 2, 1 Hz), 6.63 (1 H, s), 7.52 (1 H, s); ^{13}C NMR ($CDCl_3$) δ (ppm) 23.1, 27.7, 31.2, 52.2, 52.7, 58.2, 74.2, 129.2, 130.9, 133.6, 134.5, 138.8, 140.4, 149.0, 161.5, 162.6; MS m/e 492, 494, 496 (M^+). Anal. Calcd for $C_{16}H_{14}Br_2O_4S_2$: C, 38.88; H, 2.86. Found: C, 38.56; H, 3.17.

Treatment of 2 with 1 equiv of $BTMABr_3$. A solution of 500 mg (1.3 mmol) of **2** and 586 mg (1.5 mmol) of $BTMABr_3$[7] in 25 mL of CH_2Cl_2 was stirred at rt for 17 h. The reaction mixture was poured into water, and the organic phase was washed with $NaHCO_3$ and brine. After the organic phase was dried ($MgSO_4$), the solvent was removed by evaporation. The residue was subjected to column chromatography (silica gel; eluent, benzene). Recrystallization of the eluate afforded 363 mg of **7** in 58% yield.

Dimethyl 4,5-dihydro-2′-(bromomethylene)spiro[benzo[*b*]thiophene-6(7*H*),3′(2′*H*)-thiophene]-2,5′-dicarboxylate (7): colorless needles (ethanol); mp 174.0–177.0 °C; IR (KBr) ν (cm^{-1}) 2946, 1693, 1469, 1295, 736; ^1H NMR ($CDCl_3$) δ (ppm) 1.85–1.96 (1 H, m), 2.08–2.17 (1 H, m), 2.70–2.96 (2 H, m), 3.03 (2 H, AB dd, J = 17 Hz), 3.81 (3 H, s), 3.87 (3 H, s), 6.11 (1 H, s), 6.67 (1 H, s), 7.52 (1 H, s); MS m/e 414, 416 (M^+). Anal. Calcd for $C_{16}H_{15}BrO_4S_2$: C, 46.27; H, 3.64. Found: C, 46.56; H, 3.88.

Treatment of 2 with H_3PO_4 in AcOH. A solution of 100 mg (0.30 mmol) of **2** and 1.0 mL of H_3PO_4 in 10 mL of AcOH was stirred at 75 °C for 12 h. The reaction mixture was poured into water, and the precipitate was extracted with CH_2Cl_2. The organic layer was washed with $NaHCO_3$(aq) and brine, dried ($MgSO_4$), and evaporated in vacuo. The residue was subjected to column chromatography (silica gel; eluent, benzene). Recrystallization of the first eluate afforded 1.0 mg (1%) of **9**. Recrystallization of the second eluate afforded 68 mg (57%) of **8**.

1-(2-(Methoxycarbonyl)-5-methyl-4-thienyl)-2-(2-(acetoxymethyl)-5-(methoxycarbonyl)-3-thienyl)ethane (8): colorless needles (hexane/benzene); mp 85.0–87.0 °C; IR (KBr) ν (cm^{-1}) 2954, 1722, 1459, 1251, 1062, 753; ^1H NMR ($CDCl_3$) δ (ppm) 2.07 (3 H, s), 2.22 (3 H, s), 2.74–2.89 (4 H, m), 3.85 (3 H, s), 3.87 (3 H, s), 4.99 (2 H, s), 7.49 (1 H, s), 7.51 (1 H, s); ^{13}C NMR ($CDCl_3$) δ (ppm) 13.3, 20.8, 29.0, 29.2, 52.0, 52.2, 58.1, 128.9, 132.5, 134.7, 135.0, 137.6, 139.7, 140.7, 142.4, 162.4, 162.6, 170.4; MS m/e 396 (M^+). Anal. Caldc for $C_{18}H_{20}O_6S_2$: C, 54.53; H, 5.08. Found: C, 54.81; H, 5.16.

Dimethyl 1-methylcyclohepta[1,2-*c*:4,5-*b*′]dithiophene-3,6-dicarboxylate (9): colorless needles (hexane); mp 171.0–173.0 °C; IR (KBr) ν (cm^{-1}) 2946, 1710, 1462, 1254, 754; ^1H NMR ($CDCl_3$) δ (ppm) 2.41 (3 H, s), 2.87–3.01 (4 H, m), 3.83 (3 H, s), 3.84 (3 H, s), 4.60 (2 H, s), 7.41 (1 H, s); ^{13}C NMR ($CDCl_3$) δ (ppm) 13.4, 24.1, 26.9, 28.9, 51.8, 52.0, 121.9, 128.4, 136.6, 136.8, 139.0, 139.4, 140.7, 146.8, 162.7, 163.0; MS m/e 336 (M^+). Anal. Calcd for $C_{16}H_{16}O_4S_2$: C, 57.12; H, 4.79. Found: C, 56.96; H, 5.10.

Treatment of 2 with H_2SO_4. A solution of 500 mg of **2** and 5.0 mL of H_2SO_4 in 50 mL of dioxane was stirred at rt for 140 h. This mixture was poured into water, and the organic products were extracted with CH_2Cl_2. The extract was washed with aqueous $NaHCO_3$ and brine and dried ($MgSO_4$). The solvent was removed by evaporation, and the residue was subjected to column chromatography (silica gel; eluent, benzene and $CHCl_3$). Recrystallization of the benzene eluate afforded 76 mg (15%) of **8**. Recrystallization of the chloroform eluate afforded 77 mg (14%) of **10**.

1-(2-(Methoxycarbonyl)-5-methyl-4-thienyl)-2-(2-(hydroxymethyl)-5-(methoxycarbonyl)-3-thienyl)ethane (10): colorless prisms (hexane/AcOEt); mp 140.0–141.0 °C; IR(KBr) ν (cm^{-1}) 3426, 1712, 1681, 1452, 1263, 882, 753; ^1H NMR ($CDCl_3$) δ (ppm) 2.22 (3 H, s), 2.42 (1 H, br s), 2.72–2.84 (4 H, m), 3.84 (3 H, s), 3.86 (3 H, s), 7.48 (1 H, s), 7.53 (1 H, s); MS m/e 354 (M^+). Anal. Calcd for $C_{16}H_{18}O_5S_2$: C, 54.22; H, 5.12. Found: C, 54.39; H, 5.24.

Registry No. 1, 7353-89-1; 2, 136629-85-1; 3, 136629-86-2; 4, 136629-87-3; 5, 136629-88-4; 6, 136629-89-5; 7, 136629-90-8; 8, 136629-91-9; 9, 136629-92-0; 10, 136629-93-1; methyl 2-thiophenecarboxylate, 5380-42-7; chloromethyl methyl ether, 107-30-2.

Titration of Organolithiums and Grignards with 1-Pyreneacetic Acid

Harri Kiljunen and T. A. Hase*

Department of Chemistry, University of Helsinki, Vuorikatu 20, Helsinki 10, Finland

Received June 3, 1991

Many of the more convenient alkyllithium titration methods[1] utilize the simple titration technique where the addition of an alkyllithium causes a titration reagent to lose a proton, usually from a hydroxy group, in a stoichiometric reaction. After the first equivalent has reacted,

(1) For reviews, see: Wakefield, B. J. *Organolithium Methods*; Academic Press: London, 1988; p 16; *Aldrichimica Acta* 1988, *21*, 14.

0022-3263/91/1956-6950$02.50/0