

Unexpected rearrangement during the gas-phase dehalogenation approach to benzodithiophenes

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Experimental details

Products were vacuum distilled using a Buchi GKR-50 kugelrohr apparatus. NMR spectra were obtained at 300 MHz for ^1H and 75 MHz for ^{13}C on a Bruker instrument. All spectra were run in CDCl_3 with TMS as reference. Chemical shifts are reported in parts per million to high frequency of the reference and coupling constants J are in hertz. Mass spectra were recorded on a Finnigan Incos mass spectrometer using electron impact. GCMS was carried out on a Hewlett-Packard 5890A gas chromatograph coupled to a Finnigan Incos mass spectrometer with computerised data processing and library matching.

Preparation of Substituted Dichloromethylthiophenes

These were prepared from the corresponding thiophenecarbaldehydes by reaction with 1.2 equivalents of PCl_5 in CH_2Cl_2 either at 25 °C (Method A) or heated under reflux (Method B) for 2 h. Work up by washing with water, drying and evaporation was then followed in each case by kugelrohr distillation to give the product as follows. In common with previous workers,¹ we found these compounds to be unstable, undergoing darkening and polymerisation after a short time so they were used immediately for the pyrolysis studies.

2-Dichloromethylthiophene 1

Prepared from thiophene-2-carbaldehyde (Method A) as a colourless liquid (23.4 g, 70%), bp (oven temp.) 90 °C at 4 Torr (lit.,² 87 °C at 7–8 Torr); δ_{H} 6.92 (1 H, dd, J 5, 4), 6.98 (1 H, s), 7.21 (1 H, dd, J 4, 2) and 7.34 (1 H, dd, J 5, 2); δ_{C} 66.6 (CHCl_2), 126.4, 126.5, 127.8 and 143.7 (C-2).

3-Dichloromethylthiophene 3

Prepared from thiophene-3-carbaldehyde (Method A) as a colourless liquid (5.9 g, 79%), bp (oven temp.) 90 °C at 4 Torr (Found: $^{35}\text{Cl}_2\text{-M}^+$ 165.9412. $\text{C}_5\text{H}_4\text{Cl}_2\text{S}$ requires 165.9411); δ_{H} 6.80 (1 H, d, J 1), 7.28 (1 H, dd, J 5, 2), 7.36 (1 H, dd, J 5, 3) and 7.46 (1 H, ddd, J 3, 2, 1) [lit.,³ (CCl_4) 6.67 (1 H, s), 7.18 (1 H, m) and 7.30 (2 H, m)]; δ_{C} 66.8 (CHCl_2), 123.4, 125.6, 127.2 and 140.8 (C-3); m/z 170/168/166 (M^+ , 3/13/18%) and 133/131 ($\text{M}^+\text{-Cl}$, 38/100).

2-Dichloromethyl-5-methylthiophene 5

Prepared from 5-methylthiophene-2-carbaldehyde (Method A) as a pale yellow liquid (3.4 g, 80%), bp (oven temp.) 90 °C at 4 Torr (Found: $^{35}\text{Cl}_2\text{-M}^+$ 179.9566. $\text{C}_6\text{H}_6\text{Cl}_2\text{S}$ requires 179.9567); δ_{H} 2.45 (3 H, s), 6.62 (1 H, d, J 3), 6.95 (1 H, s) and 7.06 (1 H, d, J 3); δ_{C} 15.9 (Me), 67.5 (CHCl_2), 125.0, 127.1, 141.9 (4ry) and 143.6 (4ry); m/z 184/182/180 (M^+ , 6/32/62%), 165 (8), 145 (100), 125 (32), 109 (80), 95 (28), 69 (50) and 45 (65).

3-Bromo-2-dichloromethylthiophene 8

Prepared from 3-bromothiophene-2-carbaldehyde⁴ (Method B) as a colourless liquid (3.5 g, 90%), bp (oven temp.) 60 °C at 0.1 Torr (Found: $^{79}\text{Br}^{35}\text{Cl}_2\text{-M}^+$ 243.8523. $\text{C}_5\text{H}_3\text{BrCl}_2\text{S}$ requires 243.8516); δ_{H} 6.97 (1 H, d, J 6), 7.10 (1 H, s) and 7.44 (1 H, d, J 6); δ_{C} 65.2 (CHCl_2), 109.7 (C-3), 127.7, 129.3 and 138.8 (C-2); m/z 250/248/246/244 (M^+ , 1/3/9/5%), 213/211/209 ($\text{M}^+\text{-Cl}$, 21/80/62), 165 (4), 130 (8), 95 (12), 81 (12), 69 (12) and 45 (100).

2-Chloro-3-dichloromethylthiophene 15

Prepared from 2-chlorothiophene-3-carbaldehyde⁵ (Method B) as a colourless liquid (2.8 g, 73%), bp (oven temp.) 55 °C at 0.1 Torr (Found: $^{35}\text{Cl}_2^{37}\text{Cl-M}^+$ 201.8984. $\text{C}_5\text{H}_3\text{Cl}_3\text{S}$ requires 201.8992); δ_{H} 6.94 (1 H, s) and 7.26 and 7.43 (2 H, AB pattern, J 6); δ_{C} 62.7 (CHCl_2), 123.2,

124.9, 125.6 (4ry) and 136.1 (4ry); m/z 200 ($^{35}\text{Cl}_3\text{-M}^+$, 10%), 167 (65), 165 (100), 131 (4), 103 (5), 95 (10), 79 (22), 69 (16) and 45 (42).

Pyrolysis of Substituted Dichloromethylthiophenes over Magnesium or Calcium

The procedure used was based on that reported previously.^{6,7} Using the standard apparatus for FVP,⁸ the required weight of magnesium turnings (or calcium chips) was placed at the centre of the furnace tube which was loosely packed with glass wool. The system was connected up to the vacuum pump with a stopper in place of the sample inlet, placed under vacuum, and heated to 700 °C (Mg) or 870 °C (Ca) resulting in the metal melting and subliming over the glass wool. The system was then isolated from the pump, cautiously refilled with nitrogen and after allowing the furnace to cool to the operating temperature (600 or 650 °C for Mg or 700 °C for Ca), the sample inlet tube was attached and the pyrolysis conducted as normal. The products in the cold trap were dissolved out while still cold using CDCl_3 and analysed using NMR and GCMS. Yields were determined by adding a known weight of an internal standard to the solution for ^1H NMR and comparing integrals and/or calibration of GC signals.

2-Dichloromethylthiophene 1

FVP of the title compound (0.61 g, 600 °C, 2.0×10^{-1} Torr, inlet 25 °C, 1.5 g magnesium) gave two fractions, a liquid and a solid. NMR and GCMS analysis showed the solid to consist mainly of (*E*)-1,2-di(2-thienyl)ethene (39%) [δ_{H} 7.05 (2 H, s) and 7.00–7.20 (6 H, m) (lit.,⁹ (CCl_4) 6.98 (2 H, s) and 7.20 (6 H, m)); δ_{C} 120.4, 123.2, 124.9, 126.6 and 141.3 (4ry); m/z 192] and (*Z*)-1,2-di(2-thienyl)ethene (4%) [δ_{H} 6.62 (2 H, s) and 7.00–7.20 (6 H, m) (lit.,⁹ (CCl_4) 6.54 (2 H, s) and 7.03 (6 H, m)); m/z 192] together with benzo[1,2-*b*:4,3-*b'*]dithiophene 2 (6%, confirmed with authentic sample) [m/z 190], while the liquid product consisted of a complex mixture of compounds including 2-methylthiophene (10%).

3-Dichloromethylthiophene 3

FVP of the title compound (0.61 g, 600 °C, 2.5×10^{-1} Torr, inlet 25 °C, 1.5 g magnesium) gave two fractions, a liquid and a solid. NMR and GCMS analysis showed the solid to consist mainly of (*E*)-1,2-di(3-thienyl)ethene (24%) [δ_{H} 7.05 (2 H, s) and 7.25–7.50 (6 H, m) (lit.,⁹ (CCl_4) 7.00 (2 H, s) and 7.28 (6 H, m)); δ_{C} 121.9, 122.9, 124.7, 126.1 and 140.0; m/z 192], (*Z*)-1,2-di(3-thienyl)ethene (7%) [δ_{H} 6.57 (2 H, s) and 7.25–7.50 (6 H, m) (lit.,⁹ (CCl_4) 6.43 (2 H, s) and 7.11 (6 H, m)); m/z 192] and benzo[2,1-*b*:3,4-*b'*]dithiophene 4 (8%) [m/z 190], while the liquid consisted mainly of 3-methylthiophene (5%) [δ_{H} 2.32 (3 H, s), 7.00–7.10 (1 H, m) and 7.25–7.50 (2 H, m); m/z 98],

5-methyl-2-dichloromethylthiophene 5

FVP of the title compound (0.86 g, 600 °C, 4.0×10^{-1} Torr, inlet 25 °C, 1.5 g magnesium) gave a solid product and a polymeric material. The solid product was 1,2-bis(5-methyl-2-thienyl)ethene (0.20 g, 39%), mp 94–96 °C (lit.,⁹ 92–93 °C); δ_{H} 2.47 (6 H, s), 6.60 (2 H, d, *J* 3), 6.77 (2 H, d, *J* 3), and 6.83 (2 H, s) [lit.,⁹ (CCl_4) 2.46 (6 H, s), 6.60 (4 H, m) and 6.73 (2 H, s)]; δ_{C} 15.6, 120.7, 125.76, 125.83, 138.8 and 140.6; m/z 220. No analysis was carried out on the polymeric material as it was insoluble in any conventional solvents, however it is assumed to be poly(2,5-thienylenevinylene) 7.

3-Bromo-2-dichloromethylthiophene 8

FVP of the title compound (0.34 g, 600 °C, 3.8×10^{-2} Torr, inlet 25 °C, 0.5 g magnesium) gave a solid product. Analysis by GCMS and ^{13}C NMR showed this to consist of 1,2-bis(3-bromo-2-thienyl)ethene ((*E*)- and (*Z*)-, 9 and 10, 25 % and 4%), (*E*)-isomer; δ_{C} identical to authentic sample; m/z 352/350/348 (1:2:1), and chloro-1-(3-bromo-2-thienyl)-2-(2-thienyl)ethene 11 (13%); δ_{C} 115.3, 123.4, 123.6, 127.1, 127.8, 129.9, 130.2, 130.8, 132.0,

and 136.4; m/z 308/306/304 (1:4:3). Other compounds present included chloro-1,2-di(2-thienyl)ethene **12** (6%); m/z 224, 1,2-bis(3-bromo-2-thienyl)ethyne **13** (3%); δ_C 88.3 ($-\text{C}\equiv$); m/z 350/348/346 (1:2:1), with trace amounts of (*Z*)- and (*E*)-chloro-1,2-bis(3-bromo-2-thienyl)ethene and benzo[1,2-*b*:4,3-*b'*]dithiophene **2**; m/z 190.

Repeat pyrolysis under similar conditions but at a temperature of 650 °C, gave a product which consisted of 1,2-bis(3-bromo-2-thienyl)ethene ((*E*)- and (*Z*)-, **9** and **10**, 14% and 4%), chloro-1,2-di(2-thienyl)ethene **12** (12%), chloro-1-(3-bromo-2-thienyl)-2-(2-thienyl)ethene **11** (10%), benzo[1,2-*b*:4,3-*b'*]dithiophene **2** (8%), benzo[1,2-*b*:3,4-*b'*]dithiophene **14** (6%), and benzo[2,1-*b*:3,4-*b'*]dithiophene **4** (10%); each m/z 190. Trace amounts of 1,2-bis(3-bromo-2-thienyl)ethyne **13** and (*E*)- and (*Z*)-1-(3-bromo-2-thienyl)-2-(2-thienyl)ethene were also observed.

FVP of the title compound over calcium (0.34 g, 700 °C, 4×10^{-1} Torr, inlet 25 °C, 1.0 g calcium) gave a solid identified by ^{13}C NMR and GCMS as being three isomers of benzodithiophene, namely benzo[1,2-*b*:4,3-*b'*]dithiophene **2** (16%); δ_C identical to authentic sample; m/z 190, benzo[1,2-*b*:3,4-*b'*]dithiophene **14** (10%); δ_C identical to authentic sample; m/z 190 and benzo[2,1-*b*:3,4-*b'*]dithiophene **4** (16%); δ_C 122.9, 127.0, 127.1, 134.6 (4ry) and 138.5 (4ry); m/z 190. The other compounds present were chloro-1,2-di(2-thienyl)ethene **12** (8%); m/z 224, together with traces of naphthalene; m/z 128, benzothiophene; m/z 134, phenylthiophene; m/z 160 and 1,2-bis(3-bromo-2-thienyl)ethene **9/10**; m/z 350.

2-Chloro-3-dichloromethylthiophene **15**

FVP of the title compound (0.70 g, 600 °C, 3.5×10^{-2} Torr, inlet 30–40 °C, 1.7 g magnesium) gave a solid product. GCMS showed that it consisted mainly of 1,2-bis(2-chloro-3-thienyl)ethene ((*E*)- and (*Z*)-, **16** and **17**, 28% and 10%); m/z 260, and chloro-1,2-bis(2-chloro-3-thienyl)ethene ((*Z*)- and (*E*)-, **19** and **20**, 18% and 10%); m/z 296. Also present were small amounts of chloro-1,2-di(3-thienyl)ethene (*Z*:*E*-, 1% and 4%); m/z 226, 1,2-di(2-chloro-3-thienyl)ethyne **18** (6%); m/z 258, benzo[1,2-*b*:3,4-*b'*]dithiophene **14** (2%), benzo[2,1-*b*:3,4-*b'*]dithiophene **4** (2%); each m/z 190, and 1,2-di(3-thienyl)ethene (<1%); m/z 192.

Repeat pyrolysis under similar conditions at 650 °C gave a product which consisted mainly of 1,2-bis(2-chloro-3-thienyl)ethene **16/17** (24%/8%), benzo[1,2-*b*:3,4-*b'*]dithiophene **14** (6%) and benzo[2,1-*b*:3,4-*b'*]dithiophene **4** (2%). There were also traces (<1%) of benzothiophene; m/z 134, phenylthiophene; m/z 160, 1,2-dithienylethene; m/z 192, chloro-1,2-dithienylethene; m/z 226 and 1,2-bis(2-chloro-3-thienyl)ethyne **18**; m/z 258.

FVP of the title compound over calcium (0.38 g, 700 °C, 5.6×10^{-1} Torr, inlet 25 °C, 1.0 g calcium) gave a similar mixture of compounds namely 1,2-bis(2-chloro-3-thienyl)ethene ((*E*)- and (*Z*)-, **16** and **17**, 21% and 3%), 1,2-bis(2-chloro-3-thienyl)ethyne **18** (12%), chloro-1,2-bis(2-chloro-3-thienyl)ethene ((*Z*)- and (*E*)-, **19** and **20**, 9% and 3%), benzo[1,2-*b*:3,4-*b'*]dithiophene **14** (9%) and benzo[2,1-*b*:3,4-*b'*]dithiophene **4** (3%).

Preparation of Authentic Samples of Benzodithiophenes

Benzo[1,2-*b*:4,3-*b'*]dithiophene **2**

Following the published method,¹⁰ Wittig reaction using the phosphonium salt derived from 3-bromo-2-chloromethylthiophene (11.4 g, 24 mmol), sodium ethoxide in DMF, and 3-bromothiophene-2-carbaldehyde (4.5 g, 24 mmol) followed by flash chromatography column (SiO_2 , hexane) gave a liquid which partly crystallised with time. The yellow crystals of (*E*)-1,2-bis(3-bromo-2-thienyl)ethene were filtered off; δ_H 7.07 and 7.28 (4 H, AB pattern, *J* 4) and 7.25 (2 H, s); δ_C 111.5 (C-3), 121.3, 124.5, 130.9 and 136.5 (C-2); m/z 352/350/348 (1:2:1), while the major (*Z*)-isomer **21** (7.0 g, 83%) remained as a liquid; δ_H 6.70 (2 H, s) and 6.90 and 7.10 (4 H, AB pattern, *J* 3).

Cyclisation of (*Z*)-1,2-bis(3-bromo-2-thienyl)ethene (5.0 g, 14 mmol) **21** by treatment with butyllithium (30 mmol) followed by anhydrous cupric chloride (4.0 g, 30 mmol) gave a solid product, which was recrystallised (70% aq. ethanol) to give the title compound **2** (1.86 g, 70%) as a light green solid, mp 118 °C (lit.,¹⁰ 117 °C); δ_{H} 7.65 and 7.81 (4 H, AB pattern, *J* 4) and 7.93 (2 H, s); δ_{C} 118.7, 121.9, 126.4, 134.6 (4ry) and 136.4 (4ry) (lit.,¹⁰ 118.6, 121.7, 126.3, 134.4 and 136.2).

Benzo[1,2-*b*:3,4-*b'*]dithiophene 14¹¹

Wittig reaction using the 2-thienylmethyltriphenylphosphonium bromide (10.0 g, 22 mmol), butyllithium (23 mmol) and thiophene-3-carbaldehyde (2.0 g, 18 mmol) followed by kugelrohr distillation (160 °C at 0.5 Torr) gave a mixture of (*Z*)- and (*E*)-isomers of 1-(2'-thienyl)-2-(3'-thienyl)ethene as a colourless solid (2.8 g, 82%); *m/z* 192. Photolysis of this (2.0 g, 10 mmol) with iodine (0.13 g, 0.5 mmol) in toluene (500 cm³) followed by kugelrohr distillation gave the title compound **14** (0.82 g, 41%) as colourless crystals, mp 41 °C (lit.,¹⁰ 40–41 °C); δ_{H} 7.18 and 7.22 (2 H, AB pattern, *J* 2), 7.30 and 7.36 (4 H, AB pattern, *J* 4) and 7.55 and 7.65 (4 H, AB pattern, *J* 6); δ_{C} 118.6, 119.8, 121.3, 123.8, 124.3, 126.8 (all CH), 133.3, 134.1, 135.9 and 136.5 (all 4ry) [lit.,¹⁰ (CD₃COCD₃) 119.5, 120.8, 122.0, 125.1, 125.3, 128.2, 134.2, 134.9, 136.8 and 137.7].

Pyrolysis of Benzodithiophenes and Bis(bromothieryl)ethenes

Benzo[1,2-*b*:4,3-*b'*]dithiophene 2

FVP of the title compound (0.42 g, 650 °C, 5.8×10^{-2} Torr, inlet 85–90 °C, 1.5 g magnesium) gave unchanged starting material.

Benzo[1,2-*b*:3,4-*b'*]dithiophene 14

FVP of the title compound (0.33 g, 650 °C, 4.0×10^{-2} Torr, inlet 85–90 °C, 1.5 g magnesium) gave unchanged starting material.

1,2-bis(3-Bromo-2-thienyl)ethene 21

FVP of the title compound (0.65 g, 650 °C, 2×10^{-2} Torr, inlet 130–135 °C, 1.5 g magnesium) gave a solid product which by GCMS and GC comparison with authentic samples was shown to consist of benzo[1,2-*b*:3,4-*b'*]dithiophene **14** (29% composition), benzo[1,2-*b*:4,3-*b'*]dithiophene **2** (69% composition) and a further isomer, possibly benzo[2,1-*b*:3,4-*b'*] dithiophene **4** (2% composition).

1-(3-Bromo-2-thienyl)-2-(2'-bromo-3'-thienyl)ethene 22

The required 1-(3-bromo-2-thienyl)-2-(2-bromo-3-thienyl)ethene **22** was prepared by Wittig reaction of the phosphonium salt derived from 3-bromo-2-chloromethylthiophene with 2-bromothiophene-3-carbaldehyde as colourless crystals, mp 144–146 °C (lit.,¹⁰ 148–149 °C); δ_{H} 6.95 (2 H, m), 7.20 (2 H, m), and 7.25 (2 H, m); δ_{C} 111.2 and 112.0 (2 C-Br), 121.8, 122.4, 124.3, 124.6, 126.3, 130.9, 136.8 (4ry), and 137.6 (4ry).

FVP of the title compound (0.55 g, 650 °C, 4.0×10^{-2} Torr, inlet 130–135 °C, 1.5 g magnesium) gave a product which consisted mainly of benzo[1,2-*b*:3,4-*b'*]dithiophene **14** (92% composition) together with benzo[1,2-*b*:4,3-*b'*]dithiophene **2** (3% composition), benzo[2,1-*b*:3,4-*b'*]dithiophene **4** (<1%) and a further unidentified isomer of benzodithiophene (4.5% composition).

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