

## Metal-assisted Reactions. Part 18.<sup>1</sup> Reaction of Titanium Tetrachloride with Cyclic Sulphides: Novel Bicyclic Disulphur Compounds

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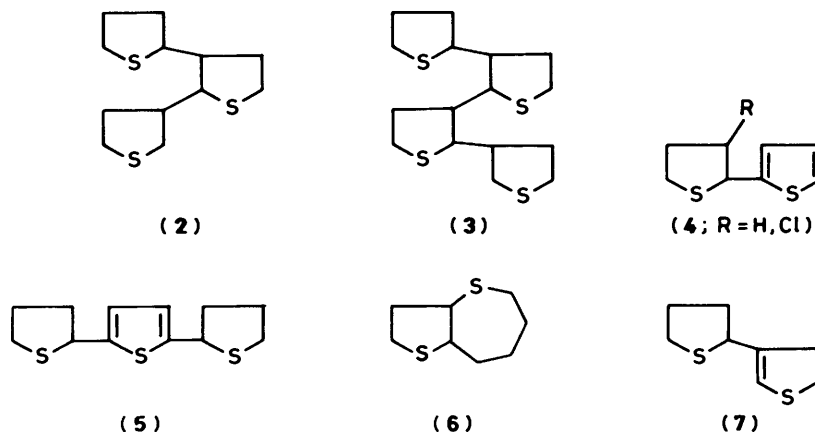
In marked contrast to the reaction of tetrahydrofuran with  $\text{TiCl}_4$ , tetrahydrothiophene did not afford ring-opened products. Instead, small quantities of ring-dimers were produced, possibly *via* initial chlorination and dehydrochlorination to produce 2,3-dihydrothiophene. An improved synthesis of 2,3-dihydrothiophene is reported.

Reaction of a wide variety of cyclic ethers with  $\text{TiCl}_4$  has been shown to produce mainly dimeric dichloro compounds or chloro alcohols, depending on the method of work-up.<sup>2</sup> For example, tetrahydrofuran readily yields either 1,9-dichloro-5-oxanonane or 9-chloro-5-oxanonan-1-ol, together with some simple ring-opened 1,4-dichlorobutane or 4-chlorobutan-1-ol. Titanium halides also form stable complexes with cyclic sulphides.<sup>3</sup> Attempted ring-opening and dimerization of tetrahydrothiophene with  $\text{TiCl}_4$  did not give ring-opened dimers but did afford a small quantity of a ring-dimer.

**Method.**—Tetrahydrothiophene was refluxed with  $\text{TiCl}_4$  for several hours after which water was added and the organic product was distilled to yield a small quantity of a dimeric compound,  $\text{C}_8\text{H}_{14}\text{S}_2$ . By  $^1\text{H}$  n.m.r. spectroscopy and synthesis this dimer of tetrahydrothiophene was shown to be 3-(tetrahydro-2-thienyl)tetrahydrothiophene (1) (Scheme); a possible route to this compound involves the intermediate, 2,3-dihydrothiophene. The latter was synthesized in good yield by pyrolysis of 2-benzoyloxytetrahydrothiophene. By introducing 2,3-dihydrothiophene into a reacting mixture of tetrahydrothiophene and  $\text{TiCl}_4$ , an increased yield of the dimer (1) was obtained, together with a number of other products (2)–(5), some of which were synthesized independently.

bicyclic structure (6). Structure (1) for the dimer was shown to be correct by independent synthesis. Refluxing a solution of 2-chlorotetrahydrothiophene<sup>4</sup> in benzene afforded the known dimer of 2,3-dihydrothiophene, *viz.* 4-(tetrahydro-2-thienyl)-2,3-dihydrothiophene (7).<sup>5</sup> Catalytic reduction of sulphur-containing compounds is hindered by poisoning effects and so the 2,3-dihydrothiophene dimer (7) was reduced to 3-(tetrahydro-2-thienyl)tetrahydrothiophene (1) by use of a mixture of triethylsilane and trifluoroacetic acid.<sup>6</sup> Analytical g.c. showed that the reduced product had been obtained as a mixture (*ca.* 1:1) of two diastereoisomers which could be separated by preparative scale g.c. Similarly, the dimer (1) obtained from the reaction of  $\text{TiCl}_4$  with tetrahydrothiophene was also obtained as a diastereoisomeric mixture (*ca.* 2:3). The  $^1\text{H}$  n.m.r. and mass spectra of both diastereoisomers were very similar.

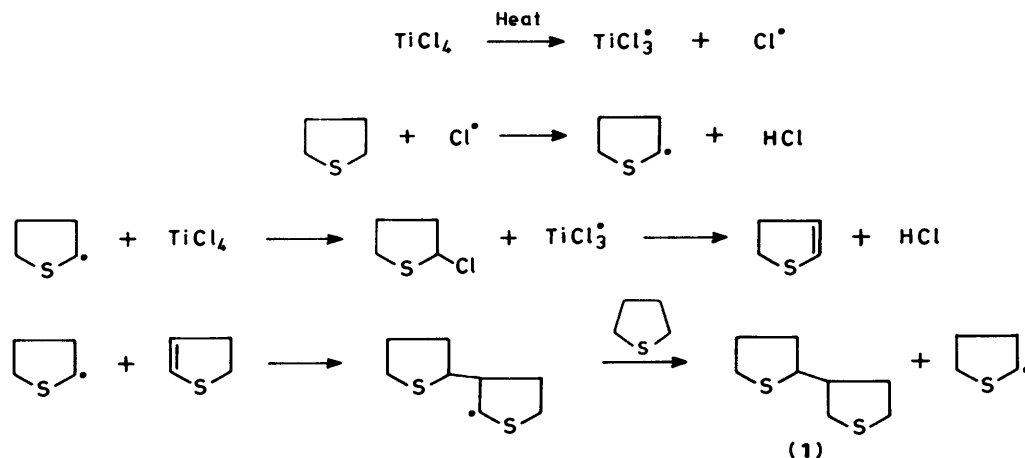
Formation of the dimer (1) probably resulted from a small amount of radical chlorination of tetrahydrothiophene by  $\text{TiCl}_4$  (Scheme) followed by elimination of  $\text{HCl}$  to give 2,3-dihydrothiophene; further radical reaction could give the product (1) as shown in the Scheme. A radical process is preferred as an explanation because an ionic process would require a hydride ion transfer in order to form the fully reduced species (1); ionic dimerization of 2,3-dihydrothiophene is known to give the unsaturated compound (7).<sup>5</sup> In the presence of a strong Lewis



### Results and Discussion

The molecular formula for compound (1) showed it to be a dimer of tetrahydrothiophene formed with loss of two atoms of hydrogen. This result, together with the mass and  $^1\text{H}$  n.m.r. spectra suggested that the dimer might have the bicyclic structure (1) or an analogous structure, or have the fused

acid such as  $\text{TiCl}_4$ , 2,3-dihydrothiophene is rapidly polymerized but, under radical conditions the polymerization is poor.<sup>7</sup> Gas chromatographic analysis showed that the tetrahydrothiophene did not contain either 2,3-dihydrothiophene or thiophene as impurities. That 2,3-dihydrothiophene was probably involved as an intermediate in the formation of the dimer (1) was



Scheme.

demonstrated by the increased yield of this dimer obtained when 2,3-dihydrothiophene was added to a reacting mixture of tetrahydrothiophene with  $\text{TiCl}_4$ . With this addition of extra 2,3-dihydrothiophene formation of a trimer (2) and a tetramer (3) was observed as well as enhanced production of the dimer (1).

Two other products of the reaction between tetrahydrothiophene and  $\text{TiCl}_4$  to which 2,3-dihydrothiophene had been added were the thiophene compounds (4) and (5). The presence of these compounds provided further evidence for the intermediacy of 2-chlorotetrahydrothiophene because the most likely route to their formation is a Friedel-Crafts reaction induced by  $\text{TiCl}_4$  between the 2-chloro compound and the small amount of thiophene occurring as an impurity from the synthesis of 2,3-dihydrothiophene. 2-(2-Thienyl)tetrahydrothiophene (4; R = H) has been reported<sup>8</sup> as a by-product in the synthesis of 5-(2-thienyl)tetrahydrothiophen-2-one but the disubstituted thiophene (5) has not been reported previously. The fully aromatic analogue of compound (5), *viz.* 2,2':5',2''-terthienyl, has been isolated from a variety of African marigold<sup>9</sup> and 2,4-bis-(2-thienyl)tetrahydrothiophene has been isolated from the reaction of thiophene with orthophosphoric acid.<sup>10</sup>

Compounds (4) and (5) were synthesized independently in good yields from the reaction between 2-chlorotetrahydrothiophene<sup>4</sup> and thiophene in the presence of  $\text{TiCl}_4$ . This synthesis was conducted in  $\text{CCl}_4$  at room temperature with an excess of thiophene, under which conditions none of the dimer (1), trimer (2), or tetramer (3) was produced; the result tends to confirm the radical mechanism suggested in the Scheme because, under these ionic conditions, formation of 2,3-dihydrothiophene, a necessary intermediate in the Scheme, is not favoured.

Several methods for the synthesis of 2,3-dihydrothiophene have been described.<sup>11-13,15</sup> In our hands, these methods either gave mixture of 2,3- and 2,5-dihydrothiophene, which were difficult to separate or gave poor yields. Thus, reduction of thiophene with sodium in liquid ammonia<sup>11</sup> gave a mixture of dihydrothiophenes from which 2,3-dihydrothiophene was obtained in only about 10% yield. Pyrolysis of the tosyl-hydrazone of 3-oxotetrahydrothiophene is reported to yield a mixture of dihydrothiophenes.<sup>12,13</sup> The Pummerer reaction on tetramethylene sulphoxide has been reported<sup>12</sup> to yield 2,3-dihydrothiophene, but we found no evidence for its formation in keeping with a similar earlier finding.<sup>14</sup> Thermal elimination of benzoic acid from 2-benzoyloxytetrahydrothiophene, an attractive synthetic route to 2,3-dihydrothiophene, gave only a 5–10% yield under the reported<sup>15</sup> conditions for its preparation; the product was contaminated with thiophene and tetrahydrothiophene, presumably formed by disproportionation.

We found that flash pyrolysis of the benzoyloxy compound, under nitrogen, at a closely controlled temperature gave consistently high yields of readily purified 2,3-dihydrothiophene, with little contamination from products of disproportionation.

### Conclusions

Reaction of tetrahydrothiophene (THT) with  $\text{TiCl}_4$  did not give ring-opened products and dimers, typically found in the reaction of cyclic ethers (such as tetrahydrofuran) with  $\text{TiCl}_4$ . Instead, a small yield of a diastereoisomeric mixture of the dimer (1) was formed, suggesting that  $\text{TiCl}_4$  could act as a weak radical-type  $\alpha$ -chlorinating agent to give a small amount of 2-chlorotetrahydrothiophene, some of which was dehydrohalogenated to 2,3-dihydrothiophene. Extended refluxing of THT with  $\text{TiCl}_4$  did not increase the yield of the dimer (1); this could imply the presence of a small quantity of an impurity responsible for the chlorination rather than  $\text{TiCl}_4$  itself. Several new thiophene compounds are reported, together with an improved synthesis of 2,3-dihydrothiophene.

### Experimental

**Reaction of Tetrahydrothiophene with  $\text{TiCl}_4$ .**—To a stirred excess of freshly distilled tetrahydrothiophene (40 ml), cooled to 0 °C, was added dropwise  $\text{TiCl}_4$  (10 g, 0.053 mol). A deep red solution, containing some red solid, was formed which was heated under reflux for 3 h. Water (100 ml) was added to the cooled reaction mixture and the organic reaction products were extracted with diethyl ether. Distillation of the ether and the excess of tetrahydrothiophene afforded a dark brown oil (40 mg) which was distilled to give 3-(tetrahydro-2-thienyl)tetrahydrothiophene (1), b.p. 102–105 °C/0.65 mmHg, as a mixture (*ca.* 2:3) of diastereoisomers (Found: C, 55.4; H, 7.9.  $\text{C}_8\text{H}_{14}\text{S}_2$  requires, C, 55.1; H, 8.1%) (see below for the separation of diastereoisomers). Repetition of the reaction with the reflux period extended to 72 h did not increase the yield of the dimer (1).

**Reaction of Tetrahydrothiophene with  $\text{TiCl}_4$  in the Presence of 2,3-Dihydrothiophene.**—To a stirred excess of tetrahydrothiophene (130 ml) cooled to 0 °C was added dropwise  $\text{TiCl}_4$  (40 g, 0.21 mol). When the addition was complete, 2,3-dihydrothiophene (20 g, 0.23 mol; prepared as described below) was added slowly with stirring and then the mixture was warmed to 90–100 °C for 2 h. Water (200 ml) was added to the cooled reaction

mixture whereupon a solid (S) was precipitated and filtered off. The filtrate was extracted with diethyl ether. The dried ( $\text{MgSO}_4$ ), extracts were evaporated to give a brown gum (9 g) which was distilled to give two fractions: (i) b.p. 90–105 °C/0.7 mmHg (1.52 g) and (ii) b.p. 190–220 °C/0.7 mmHg (3.55 g). These fractions and the solid (S) were investigated further:

**The Solid (S).** The solid (12 g), thought to be a polymer,<sup>7</sup> was insoluble in the usual organic solvents [Found: C, 50.1; H, 6.9 (metallic residue, 5.8% by wt). A simple polymer of 2,3-dihydrothiophene would require C, 55.8; H, 7.0%].

**Fraction (i).** Column chromatography on silica gel, eluting with pentane–benzene (4:1), gave two components (A and B) with  $R_F$  values 0.74 and 0.32 respectively by t.l.c. on  $\text{SiO}_2$  with pentane–benzene (4:1). Component A was distilled to give 2-(2-thienyl)tetrahydrothiophene (**4**; R = H) (0.16 g), b.p. 62–65 °C/0.07 mmHg (lit.,<sup>8</sup> b.p. 72 °C/0.1 mmHg) (Found: C, 56.1; H, 5.9. Calc. for  $\text{C}_8\text{H}_{10}\text{S}_2$ : C, 56.4; H, 5.9%;  $m/z$  170 ( $M^+$ );  $\delta_{\text{H}}(\text{CDCl}_3)$  7.15 (1 H, dd,  $J$  5, 1 Hz), 6.96 (1 H, dd,  $J$  3, 1 Hz), 6.90 (1 H, dd,  $J$  5, 3 Hz), 4.78 (1 H, t,  $J$  6.6 Hz), 3.14 (1 H, m), 2.95 (1 H, m), 2.37 (1 H, m), 2.23 (1 H, m), and 2.04 (2 H, m). Component B was distilled to give 3-(tetrahydro-2-thienyl)-tetrahydrothiophene (**1**) (1.24 g), b.p. 80–82 °C/0.1 mmHg, as a mixture of diastereoisomers in a ratio of ca. 1:1. The latter was separated by preparative scale g.c. following independent synthesis (see below). Analytical data for the mixture of diastereoisomers were identical to those for the mixture obtained from the reaction of tetrahydrothiophene with  $\text{TiCl}_4$ ,  $m/z$  174 (80%;  $M^+$ ), 141 (12), 127 (25), 114 (13), 113 (42), 99 (14), 87 (100), 86 (11), 85 (19), and 45 (20);  $\delta_{\text{H}}(\text{CDCl}_3)$  3.30 (1 H, m), 2.85 (5 H, complex m), 2.58 (1 H, m), 2.15 (4 H, complex m) 1.86 (1 H, m), and 1.60 (2 H, m) (Found: C, 55.4; H, 7.9.  $\text{C}_8\text{H}_{14}\text{S}_2$  requires C, 55.1; H, 8.1%).

**Fraction (ii).** Column chromatography on silica gel, eluting with a pentane–benzene (1:1) gave three components (C, D, and E) with  $R_F$  values 0.56, 0.31, and 0.17 respectively by t.l.c. on  $\text{SiO}_2$  with pentane–benzene (1:1). Component C was distilled to give 2,5-bis-(tetrahydro-2-thienyl)thiophene (**5**) as a viscous, yellow oil, b.p. 172–176 °C/0.3 mmHg (0.35 g),  $m/z$  256 ( $M^+$ );  $\delta_{\text{H}}(\text{CDCl}_3)$  6.72 (2 H, s), 4.69 (2 H, t,  $J$  6.7 Hz), 3.10 (2 H, m), 2.94 (2 H, m), 2.25 (4 H, m), and 2.01 (4 H, m) (Found: C, 55.7; H, 6.2.  $\text{C}_{12}\text{H}_{16}\text{S}_3$  requires C, 56.2; H, 6.3%). Component D was distilled to give a viscous yellow oil, b.p. 188–191 °C/0.2 mmHg (0.83 g), the analytical data for which suggested it was the trimer (**2**),  $m/z$  260 (12%;  $M^+$ ), 173 (10), 87 (100), 85 (13), 59 (11), 53 (14), and 45 (40);  $\delta_{\text{H}}(\text{CDCl}_3)$  3.42 (1 H, m), 3.23 (1 H, m), 2.98–2.60 (8 H, complex m), 2.40–1.98 (6 H, complex m), and 1.97–1.40 (4 H, complex m) (Found: C, 55.5; H, 7.7.  $\text{C}_{12}\text{H}_{20}\text{S}_3$  requires C, 55.4; H, 7.7%). Component E was isolated as a gummy red solid (10 mg) and may be the tetramer (**3**),  $m/z$  346 (2%;  $M^+$ ), 188 (75), 149 (78), and 87 (100). By analogy with component B in fraction (i), components D, E were probably mixtures of diastereoisomers.

**Synthesis of Diastereoisomers of 3-(Tetrahydro-2-thienyl)-tetrahydrothiophene (1).**—A solution of 2-chlorotetrahydrothiophene (**4**) (0.18 mol) in benzene (200 ml) was refluxed for 6 h, after which time no more HCl was evolved. The solution was cooled, washed with water, dried ( $\text{MgSO}_4$ ) and evaporated to give a residue which was distilled to afford 4-(tetrahydro-2-thienyl)-2,3-dihydrothiophene (**7**) (4.8 g), b.p. 85–100 °C/0.1 mmHg (lit.,<sup>10</sup> b.p. 89 °C/0.1 mmHg),  $m/z$  172 (100%;  $M^+$ ), 139 (23), 125 (77), 111 (36), 98 (23), 97 (63), and 91 (23);  $\delta_{\text{H}}(\text{CDCl}_3)$  5.98 (1 H, s), 4.17 (1 H, t,  $J$  6.7 Hz), 3.21 (2 H, m), 3.03–2.58 (4 H complex m), and 2.20–1.68 (4 H complex m). A mixture 4-(tetrahydro-2-thienyl)-2,3-dihydrothiophene (4.5 g, 0.026 mol), triethylsilane (15.0 g, 0.13 mol), and trifluoroacetate acid (26.9 g, 0.26 mol) was heated at 50 °C for 6 days. The reaction mixture was diluted with diethyl ether (50 ml), washed with aqueous

$\text{Na}_2\text{CO}_3$  and dried ( $\text{MgSO}_4$ ). After concentration of the ether solution, the residue was distilled to give 3-(tetrahydro-2-thienyl)tetrahydrothiophene (**1**) (3 g), b.p. 119–121 °C/1.5 mmHg as a mixture of diastereoisomers (Found: C, 55.2; H, 8.1.  $\text{C}_8\text{H}_{14}\text{S}_2$  requires C, 55.1; H, 8.1%). The isomers were separated by preparative scale g.c. on Celite coated with 10% Reoplex 100. Isomer 1:  $m/z$  174 (89%;  $M^+$ ), 141 (14), 127 (27), 114 (15), 113 (47), 99 (16), 87 (100), 85 (20), and 45 (20);  $\delta_{\text{H}}(\text{CDCl}_3)$ , 3.32 (1 H, q), 2.92 (1 H, m), 2.83 (4 H, m), 2.60 (1 H, t), 2.15 (4 H, complex m), 1.84 (1 H, m), and 1.58 (2 H, m). Isomer 2:  $m/z$  174 (73%;  $M^+$ ), 141 (11), 127 (21), 114 (12), 113 (37), 99 (14), 87 (100), 85 (19), and 45 (19);  $\delta_{\text{H}}(\text{CDCl}_3)$  3.25 (1 H, td), 2.84 (5 H, complex m), 2.53 (1 H, t), 2.14 (4 H, complex m), 1.86 (1 H, m), 1.62 (2 H, m). The  $^1\text{H}$  n.m.r. spectra of these isomers were so complex that even at 360 MHz with proton decoupling, we were unable to assign proton resonances fully.

**Preparation of 2,3-Dihydrothiophene.**—A simple pyrolysis apparatus was constructed, consisting of a vertically mounted Pyrex glass tube (14 mm id) packed loosely with glass wool and heated by a furnace for about 300 mm of its length.<sup>17</sup> The furnace was held at 300 °C. Crude 2-benzoyloxytetrahydrothiophene<sup>15</sup> (160 g), prepared from *t*-butyl perbenzoate and tetrahydrothiophene, was added dropwise down the centre of the heated vertical glass tube over a period of about 2 h. The products of pyrolysis were swept out of the reaction zone in a fast stream of  $\text{N}_2$  and were collected in a trap at –65 °C. The products were taken up in diethyl ether and the extracts were washed repeatedly with aqueous  $\text{Na}_2\text{CO}_3$  to remove benzoic acid. The ether layer was dried ( $\text{MgSO}_4$ ) and most of the ether was removed by distillation through a Vigreux column; the residual oil was fractionally distilled to give 2,3-dihydrothiophene (35 g, 53% yield), b.p. 110–115 °C/760 mmHg (lit.,<sup>11</sup> b.p. 112 °C/760 mmHg). This product contained very small amounts of thiophene and tetrahydrothiophene as impurities and was used without further purification.

**Synthesis of 2-(2-Thienyl)tetrahydrothiophene (4) and 2,5-Bis-(tetrahydro-2-thienyl)thiophene (5).**— $\text{TiCl}_4$  (8.0 g, 0.042 mol) was added dropwise with stirring to a solution of thiophene (10 g, 0.12 mol) in  $\text{CCl}_4$  (100 ml) at 0 °C. A solution of 2-chlorotetrahydrothiophene in  $\text{CCl}_4$  (ca. 0.09 mol) [prepared<sup>4</sup> from tetrahydrothiophene (8.0 g, 0.09 mol) and *N*-chlorosuccinimide (12.0 g, 0.09 mol) in  $\text{CCl}_4$  (100 ml) at 20–25 °C] was added slowly, with stirring, to the cooled mixture of  $\text{TiCl}_4$  and thiophene. The reaction mixture was stirred at room temperature for 96 h and then hydrolysed by the addition of water (100 ml). The organic layer was separated, dried ( $\text{MgSO}_4$ ), and evaporated to yield an oil which was chromatographed on silica gel (325 × 25 mm), using pentane–benzene (4:1) as the eluant, to give two fractions (1 and 2). Fraction 1, a yellow oil (2.96 g), was shown by analytical g.c.–m.s. to consist of 2-(2-thienyl)tetrahydrothiophene (**4**; R = H) (64% yield),  $m/z$  170 ( $M^+$ ), together with the *cis*- and *trans*-isomers of 3-chloro-2-(2-thienyl)tetrahydrothiophene (**4**; R = Cl); one isomer (29% yield) had  $m/z$  206 (32%), 204 (78,  $M^+$ ; Cl), 169 (50), 168 (36), 157 (32), 142 (57), 141 (42), 135 (41), 127 (44), 123 (23), 97 (100), 69 (25), and 45 (83) and the other (7% yield) had  $m/z$  206 (30%), 204 (79,  $M^+$ ; Cl), 169 (52), 168 (38), 157 (29), 142 (51), 141 (42), 135 (42), 127 (49), 123 (23), 97 (100), 69 (28), and 45 (84). The latter two isomers resulted from the presence of some 2,3-dichlorotetrahydrothiophene in the crude 2-chlorotetrahydrothiophene.<sup>4</sup> Fraction 2 was distilled to give, 2,5-bis-(tetrahydro-2-thienyl)thiophene (**5**) (1.35 g) as a viscous yellow oil, b.p. 170 °C/0.35 mmHg;  $\delta_{\text{H}}(\text{CDCl}_3)$  6.72 (2 H, s), 4.69 (2 H, t,  $J$  6.7 Hz), 3.10 (2 H, m), 2.94 (2 H, m), 2.25 (4 H, m), and 2.01 (4 H, m).

*Analytical Gas Chromatography.*—This was carried out on a column (3.1 m × 2 mm) of Celite (60–80 mesh) coated with 10% (w/w) of Reoplex 100 with a N<sub>2</sub> flow of 60 ml min<sup>-1</sup> at 200 °C. Under these conditions, the two diastereoisomers of compound (1) had retention times of 16.4 and 17.7 min. The three components of fraction 1 obtained (see above) in the synthesis of 2-(2-thienyl)tetrahydrothiophene had, respectively, retention times of 10.5, 23.0, and 33.3 min.

## References

- 1 Part 17, I. D. Entwistle, R. A. W. Johnstone, and P. A. Delaney, preceding paper.
- 2 P. A. Delaney, Ph.D. Thesis, University of Liverpool, 1983.
- 3 I. G. Gol'dshtein, E. N. Kharlamova, and E. N. Gur'yanova, *Zh. Obshch. Khim.*, 1968, **38**, 1984 (*Chem. Abstr.*, 1968, **70**, 14904e); P. G. B. Perkins, *J. Chem. Soc. A*, 1970, 3229; G. W. A. Fowles, *Proc. Int. Conf. Co-ord. Chem.*, 8th Vienna 1964, 208; H. S. Ahuja and S. C. R. Jain, *J. Inorg. Nucl. Chem.*, 1968, **30**, 2459; K. Baker and G. W. A. Fowles, *Proc. Chem. Soc.*, 1964, 32; E. C. Alyea and E. G. Torrible, *Can. J. Chem.*, 1965, **43**, 3468; P. J. Hendra and D. B. Powell, *J. Chem. Soc.*, 1960, 5105.
- 4 P. A. Delaney and R. A. W. Johnstone, *Tetrahedron*, 1985, **41**, 3845.
- 5 T. Tsujikawa and M. Hayashi, *Chem. Pharm. Bull.*, 1977, **25**, 3147.
- 6 For some references to this 'ionic hydrogenation' see: D. N. Kursanov, Z. N. Parnes, G. I. Bolestova, and L. I. Belen'kii, *Tetrahedron*, 1975, **31**, 311; Yu. I. Lyakhovetskii, M. Kalinkin, Z. N. Parnes, F. Latypora, and D. N. Kursanov, *J. Chem. Soc., Chem. Commun.*, 1980, 766; Z. N. Parnes, Yu. I. Lyakhovetskii, M. Kalinkin, D. N. Kursanov, and L. I. Belen'kii, *Tetrahedron*, 1978, **34**, 1703.
- 7 A. L. Cardon and E. J. Goethals, *Makromol. Chem.*, 1974, **175**, 3147.
- 8 P. Rioult and J. Vialle, *Bull. Soc. Chim. France*, 1965, 3312.
- 9 L. Zechmeister and J. W. Sease, *J. Am. Chem. Soc.*, 1947, **69**, 273.
- 10 S. L. Meisel, G. C. Johnson, and H. D. Hartough, *J. Am. Chem. Soc.*, 1950, **72**, 1910; R. F. Curtis, D. M. Jones, and W. A. Thomas, *J. Chem. Soc. C*, 1971, 234.
- 11 S. F. Birch and D. T. McAllan, *J. Chem. Soc.*, 1951, 2556.
- 12 P. Y. Johnson, E. Koza, and R. E. Kohrman, *J. Org. Chem.*, 1973, **38**, 2967.
- 13 M. A. Gianturco, P. Friedel, and V. Flanagan, *Tetrahedron Lett.*, 1965, 1847.
- 14 E. N. Karaulova, G. D. Gal'pern, V. D. Nikitina, I. V. Cherepanova, and L. R. Barykina, *Neftakhimiya*, 1972, **12**, 104 (*Chem. Abstr.*, 1972, **76**, 153506p); E. N. Karaulova, G. D. Gal'pern, V. D. Nikitina, D. K. Zhestov, and I. V. Cherepanova, *Khim. Seraorg. Soedin., Soderzh. Neftakh. Neftprod.*, 1972, **9**, 190 (*Chem. Abstr.*, 1973, **79**, 125746k).
- 15 G. Sosnovsky, *Tetrahedron*, 1962, **18**, 903.
- 16 J. M. Cox and L. N. Owen, *J. Chem. Soc. C*, 1967, 1130.
- 17 For a description of a simple, but effective, pyrolysis apparatus see C. H. Depuy and R. W. King, *Chem. Rev.*, 1960, **60**, 431.

*Received 6th September 1985; Paper 5/1525*