Chlorinated thiophenes. Part 2.[1] Trihalogenated hydroxythiophenes; preparation, reactions and tautomeric properties

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2-Hydroxy-3,4,5-trichlorothiophene (**4**), 3-hydroxy-4-bromo-2,5-dichlorothiophene (**5**) and 3-hydroxy-2,4,5-trichlorothiophene (**6**) have been synthesised. It was found that **4** exists in a carbonyl form, whereas in **5** and **6** the hydroxy forms were the major tautomers. Several derivatives of the trihalogenated hydroxythiophenes were prepared. *O*-Methylation was carried out with diazomethane and *O*-acetylation with acetyl chloride. Silylation of **4** was performed using *N*,*O*-bis(trimethylsilyl)acetamide. Compound **4** reacted with methylmagnesium iodide in an unexpected way by exchanging chlorine with magnesium iodide, giving 3,4-dichloro-2,5-dihydrothiophen-2-one (**16**) after hydrolysis. In an unsuccessful attempt to try to prepare thiophene isosteres of the infamous 2,3,7,8-tetrachlorodibenzo-*p*-dioxine, the new dimer 2,2′,3,3′,4,4′-hexachloro-2,2′,5,5′-tetrahydro-2,2′-bithiophen-5-one (**15**) was discovered, the crystal structure of which is reported.

Introduction

A large number of hydroxythiophenes have previously been studied with regard to their reactions and tautomeric properties.[2a] Much work has also been done concerning the kinetics of forming the equilibrium mixtures of these systems. It has been found that the 2-hydroxythiophene systems exist in one of two possible carbonyl forms. The 3-hydroxythiophene, on the other hand, exists both in a keto and an enol form.[2b]

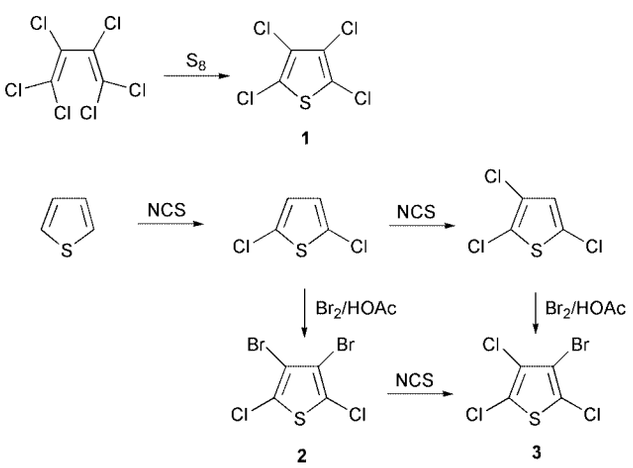
One of the aspects of this work has been the question of how halo, and especially chloro, substituents influence the thermodynamics and the kinetics of hydroxythiophenes. Particularly, we wanted to see whether thiophene isosteres of the infamous 2,3,7,8-tetrachlorodibenzo-*p*-dioxine could be prepared from chlorinated hydroxythiophenes.

In the present work trihalosubstituted 2- and 3-hydroxythiophenes have been investigated. Surprisingly, these systems are represented by very few reports in the literature.[2b] We have found that halo substituents do not influence the general tautomeric patterns of the hydroxythiophenes. On the other hand, some of the reactions of these compounds differ from what has previously been found.

Results and discussion

The tetrahalothiophenes, which served as starting material for the preparation of the hydroxythiophenes in this work, were synthesised as shown in Scheme 1. Tetrachlorothiophene (**1**) was made from hexachlorobutadiene and sulfur.[3] Chlorination of thiophene with *N*-chlorosuccinimide (NCS) in acetic acid gave 2,5-dichloro- and 2,3,5-trichlorothiophene which could be separated by distillation. Subsequent bromination with bromine in acetic acid afforded 3,4-dibromo-2,5-dichlorothiophene (**2**) and 3-bromo-2,4,5-trichlorothiophene (**3**), respectively. Temperature proved important in these reactions as bromine was replaced with chlorine above 60 °C.

The introduction of the hydroxy groups was accomplished by use of the method pioneered by Hörnfeldt,[4] the first step being the halogen–lithium exchange with *n*-butyllithium (Scheme 2).



Scheme 1

For the 2-chlorine–lithium exchange in **1** the reaction was carried out at −40 °C and for the 3-bromine–lithium exchange in **2** and **3** the reaction temperature was −78 °C. The trihalothienyllithium intermediates were treated with tributyl borate at −78 °C for 3 hours. Although the borate was added in excess, the reaction did not go to completion. After hydrolysis of the thienyl borate esters with hydrochloric acid the boric acids were oxidised with hydrogen peroxide, affording the three trihalogenated hydroxythiophenes **4**, **5** and **6**.

In the work-up of the trihalogenated hydroxythiophenes it was important to wash the ethereal solution with water only. Polymerisation started immediately if base had been added. In this context we also note that most of these compounds impart an enduring black stain on contact with the skin.

The trichlorinated hydroxythiophenes are stable when kept under nitrogen. The hydroxythiophenes with a bromine substituent, however, started to polymerise quite rapidly even when kept at temperatures below 0 °C under nitrogen.

Methoxy derivatives of the halogenated hydroxythiophenes were synthesised by reaction with diazomethane (Scheme 3).

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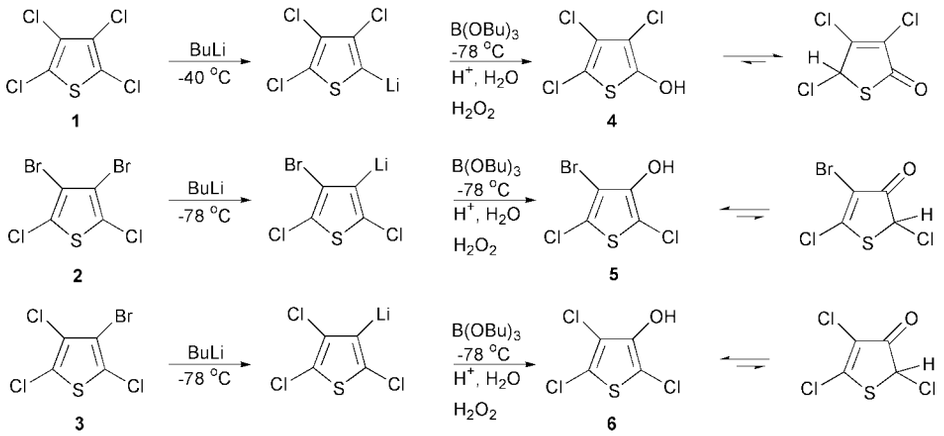
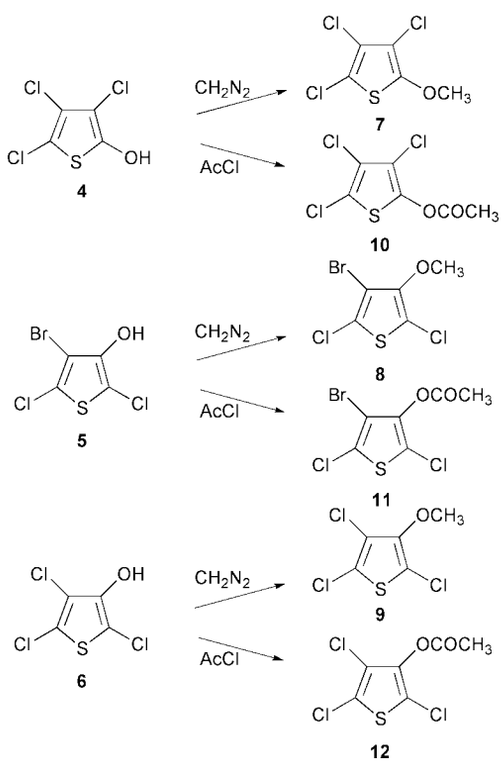


Scheme 2



Scheme 3

These reactions produced the methoxy compounds **7**, **8** and **9** in high yields. It was not possible to find a way to methylate the trihalogenated hydroxythiophenes by the use of methyl iodide or dimethyl sulfate, which are common reagents for methylating unchlorinated hydroxythiophenes. The hydroxythiophene systems studied also gave the acetates **10**, **11** and **12** by reaction with acetyl chloride, catalysed by triethylamine.

Dimer formation

N,*O*-Bis(trimethylsilyl)acetamide (BSA) was used as a silylating reagent for 2-hydroxy-3,4,5-trichlorothiophene. BSA is known as a very good reagent for silyl–proton exchange reactions and was used when the less sophisticated silylating reagents failed. 2-Trimethylsilyloxy-3,4,5-trichlorothiophene (**13**) is very hygroscopic, but otherwise relatively stable. It was found that **13**, after refluxing in acetonitrile for a couple of days, gave an interesting new compound. TLC (silica, pet. ether–diethyl ether, (2:1)) analysis revealed a single spot with a longer retention time than that of the starting material. After preparative TLC this unknown compound was found to be difficult to crystallise. High resolution MS analysis corresponded to the molecular formula $C_8Cl_4O_2S_2$. IR showed a major peak at 1720 cm^{-1}, which clearly indicates a carbonyl group. ^{1}H-NMR analysis gave no signals and ^{13}C-NMR was difficult to interpret. A reasonable suggestion was that a thiolactone dimer with structure **14** had formed, as hinted in Scheme 4. However, an X-ray diffraction analysis showed the compound to have the structure of **15**, with two chlorine atoms more than in **14**. A thermal-ellipsoid plot of the structure is shown in Fig. 1. Experimental detail and numeric results for the X-ray study are given in the Experimental section. The formation of **15** most probably occurred *via* the dimerisation of the corresponding monomeric radical, as depicted in Scheme 4. Another way of making the thiolactone dimer **15**, thus verifying the radical nature of the process, was found by treating 2-hydroxy-3,4,5-trichlorothiophene in a 45% aqueous alcohol solution with iron(III) chloride and potassium hexacyanoferrate(III). This reaction involves an oxidative step, inferred from the appearance of the characteristic colour of Prussian blue, which would accompany the production of iron(II) potassium hexacyanoferrate(III).

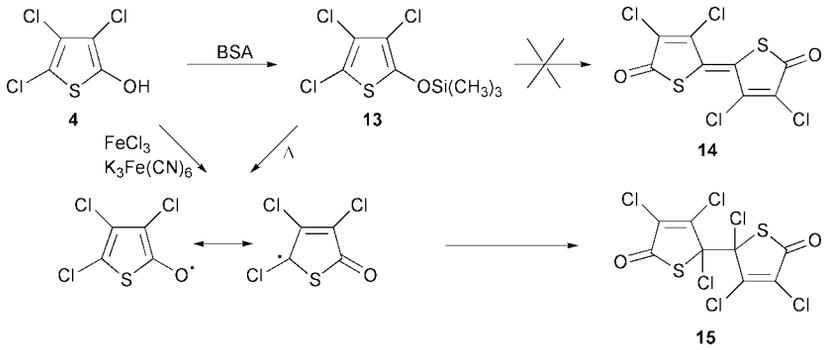
No dioxine formation

The production of chlorinated phenoxy acids, which have found widespread use as herbicides, is hampered by formation of highly toxic chlorinated dibenzo-*p*-dioxines as by-products. One of the main objectives of the present work was to find out whether thiophene isosteres of chlorinated dibenzo-*p*-dioxine could be formed from our halogenated hydroxythiophenes. Judging from the reactions of similar substituted benzenes the three hydroxythiophenes **4**, **5** and **6** should be excellent precursors for the formation of thiophene isosteres of chlorinated dibenzodioxines (*e.g.* **18** or **19**, Scheme 5). However, we did not succeed in detecting any such compounds upon treatment of the hydroxythiophenes with different bases under various reaction conditions, including high temperatures and prolonged reaction times. The only identifiable product was the dimer **15**.

This is an interesting result indicating that thiophene isosteres of phenoxy acids should be safer to produce and use than their benzene counterparts.

Grignard reaction

Little is known about the behaviour of chlorinated 2-hydroxythiophenes in reactions with Grignard reagents. We found it of interest to see whether this system reacts as an acid or as a carbonyl compound. Accordingly 2-hydroxy-3,4,5-trichlorothiophene (**4**) was added to a solution of methylmagnesium iodide in dry tetrahydrofuran. The mixture was stirred for one hour and then hydrolysed. Two products were formed in the reaction, one with shorter and one with longer retention time (TLC) than the reactant. The product with the longest retention time had spectroscopic data identical to **15**. The product with the shortest retention time was identified as 3,4-dichloro-2,5-dihydrothiophen-2-one (**16**, Scheme 6). This could be verified



Scheme 4

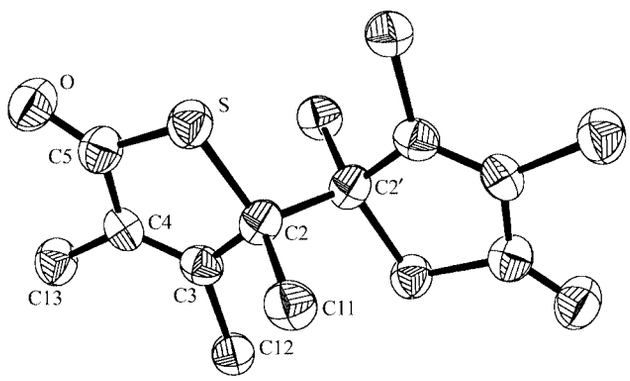


Fig. 1 Thermal-ellipsoid plot with atomic numbering for **15**. Ellipsoids are drawn at the 50% probability level.

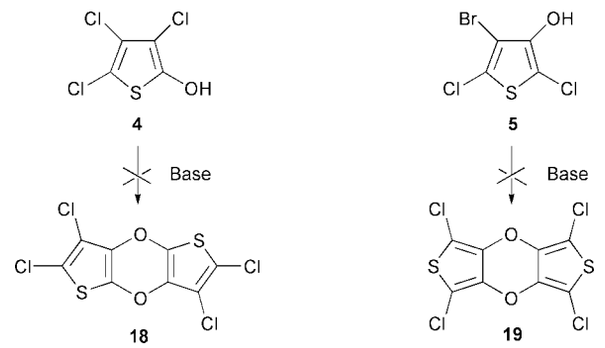
by adding benzaldehyde to the intermediate magnesium compound before hydrolysis. Then 2-benzylidene-3,4-dichloro-2,5-dihydrothiophen-5-one (**17**) could be isolated after hydrolysis. The identity of **17** has been established by independent synthesis and X-ray diffraction analysis.[1] Evidently an unprecedented chlorine–magnesium iodide exchange has taken place as shown in Scheme 6.

Tautomeric properties

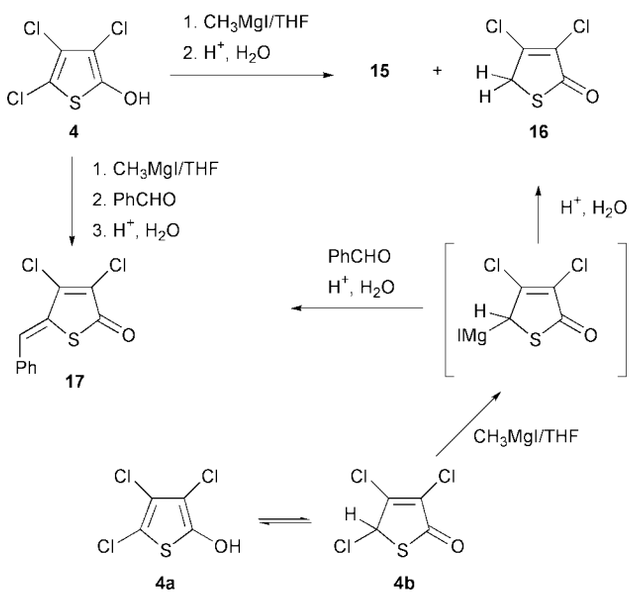
The 2-substituted hydroxythiophene systems give rise to three different tautomeric forms. In contrast to phenol, 2-hydroxythiophene exists almost exclusively in one of its carbonyl forms. These forms predominate because of the very stable thiolactone moiety. Several papers[2] have discussed how different substituents influence the tautomeric equilibrium of this system, particularly for monosubstituted compounds.

In the present work, 2-hydroxy-3,4,5-trichlorothiophene (**4**), 3-hydroxy-2,4,5-trichlorothiophene (**6**) and 3-hydroxy-4-bromo-2,5-dichlorothiophene (**5**) have been studied. The carbonyl structures of 2,5-dihydrothiophen-2-one were the only detectable tautomers of **4**. Hörnfeldt[5] found a 2:1 distribution between the 2,3-dihydrothiophen-2-one and the 2,5-dihydrothiophen-2-one studying a 5-chloro substituted system. In those cases the presence of 2,3-dihydrothiophen-2-one can be explained by the conjugation between chlorine and the 4,5-double bond. Other workers who have studied 3- and 4-monosubstituted 2-hydroxythiophene systems most commonly have found that the 2,5-dihydrothiophen-2-one form dominates the equilibrium.[2c]

For 3-substituted hydroxythiophene systems there are only two tautomeric structures possible, one hydroxy form and one carbonyl form. Many papers have shown that the hydroxy form dominates these equilibria.[2d] The two trihalogenated 3-hydroxythiophenes studied in this work had approximately the same ratio of hydroxy to carbonyl forms. 3-Hydroxy-4-bromo-2,5-dichlorothiophene (**5**) had a 1:2 ratio between the keto and hydroxy forms, and the analogous 2,4,5-trichloro substituted compound (**6**) had a ratio of 1:3.2. Manzara and Kovacic[6] found a 1:1 ratio between the hydroxy and carbonyl forms of 2,5-dichloro-3-hydroxythiophene.



Scheme 5



Scheme 6

Mass spectrometry has not been extensively used in the study of keto–enol equilibria. We found that MS analysis can be useful in obtaining information on the direction in which the equilibrium is displaced. In the MS-fragmentation of 2-hydroxy-3,4,5-trichlorothiophene (**4**) the intensity of the molecular ion was found to be one-third the intensity of the fragment corresponding to the loss of one chlorine atom. For 3-hydroxy-2,4,5-trichlorothiophene (**6**) the molecular ion had twice the intensity of the fragment due to loss of one chlorine. To explain this behaviour one has to look at the bond between carbon and chlorine in the different tautomeric forms. In general a bond between an sp^2-hybridised carbon and chlorine is stronger than between an sp^3-hybridised carbon and chlorine. In 2-hydroxy-3,4,5-trichlorothiophene, which exists in a carbonyl form, one chlorine is bonded to an sp^3-carbon. This is

not the case for 3-hydroxy-2,4,5-trichlorothiophene (**6**), in which the enol-form dominates; all the chlorines are bonded to sp^2-carbons.

UV spectroscopy has been considered a powerful tool for the study of tautomeric properties of tautomeric systems. The UV spectra of the equilibrium mixtures studied in this work, however, were difficult to interpret with regard to the distribution between carbonyl and enol forms. Compared to the analogous alkylated hydroxythiophene systems the halogenated ones studied in this work showed a somewhat higher extinction coefficient.

Experimental

2,5-Dichlorothiophene and 2,3,5-trichlorothiophene

N-Chlorosuccinimide (210 g, 1.43 mol) was added to a stirred solution of thiophene (60.0 g, 0.714 mol) in acetic acid (500 ml) and refluxed for 2 hours. The reaction was interrupted when GC (3% SP-2100) showed 2,5-dichloro- and 2,3,5-trichlorothiophene in approximately the same concentrations. Water (250 ml) containing sodium chloride was added and the reaction mixture was extracted 5 times with diethyl ether. The ethereal phases were dried, filtered and evaporated. Distillation on a 40 cm Vigreux column gave 2,5-dichlorothiophene (27 g, 26%), bp 45 °C/11 mmHg (lit.[7] 162 °C/760 mmHg); *m*/*z* 152/154/156 (M^+, 100%/67%/10%) and 2,3,5-trichlorothiophene (35 g, 26%), bp 72 °C/11 mmHg (lit.[7] 198.6 °C/760 mmHg); *m*/*z* 186/188/190 (M^+, 94%/100%/30%).

2,3,4,5-Tetrachlorothiophene (1)

2,3,4,5-Tetrachlorothiophene (**1**) was prepared according to a method described in the literature.[7]

3-Bromo-2,4,5-trichlorothiophene (3)

To a solution of 2,3,5-trichlorothiophene (44 g, 0.23 mol) in acetic acid (150 ml) was added bromine (73.6 g, 0.46 mol) and the solution was then stirred for 2 days at 60 °C. More bromine (18.4 g, 0.12 mol) was added and the solution was stirred for another 2 days at the same temperature as before. After 4 days, GC (3% SP-2100) showed that the title product had formed in 80% yield. After cooling, water (100 ml) saturated with sodium chloride was added and the mixture was extracted 5 times with dichloromethane. The dichloromethane phases were washed vigorously with sodium thiosulfate until all the bromine had been reduced, then washed with sodium bicarbonate. After distillation the product was recrystallised from ethanol giving colourless needles of 3-bromo-2,4,5-trichlorothiophene (**3**) (33.2 g, 54%), bp 110 °C/11 mmHg, mp 42 °C; *m*/*z* 264/266/268/270 (M^+, 30%/61%/41%/11%), 185/187/189 (M − Br, 70/63/25).

2-Hydroxy-3,4,5-trichlorothiophene (4)

n-Butyllithium in hexane (70 ml of a 1.6 M solution, 0.11 mol) was added dropwise to 2,3,4,5-tetrachlorothiophene (22.0 g, 0.10 mol) in dry diethyl ether (100 ml) with stirring and cooling to −40 °C in a nitrogen atmosphere. After completion of the lithiation the mixture was cooled to −78 °C and tributyl borate (27.7 g, 0.12 mol) in dry ether (50 ml) was added. The reaction mixture was stirred for 3 hours at −78 °C and then shaken with hydrochloric acid (50 ml of a 2.0 M solution, 0.10 mol) after raising the temperature to 0 °C. The layers were separated and the aqueous phase extracted with diethyl ether. The combined ethereal phases were transferred to a flask and aqueous hydrogen peroxide (50 ml of a 10% solution, 0.15 mol) was added. The mixture was refluxed overnight, the reaction mixture cooled, the layers separated and the water phase extracted with ether. The combined ethereal phases were washed with water, dried over magnesium sulfate, evaporated and distilled to give the title compound (15.0 g, 74%), bp 72–76 °C/0.005 mmHg; *m*/*z* 202/204/206 (M^+, 33%/34%/10%), 167/169/171 (M − Cl, 100/73/12), 139/141/143 (M − COCl, 44/34/7); δ_H(300 MHz, $CDCl_3$) 6.08 (1 H, s, 5-H); δ_C(75 MHz, $CDCl_3$) 59.7 (5-C), 132.8 (4-C), 152.3 (3-C), 183.4 (2-C); ν_{max}/cm^{-1} 1690–1720br (CO); λ_{max}(MeOH)/nm: 207sh (log (ε/dm^3 mol^{-1} cm^{-1}) 3.42), 243 (4.00). The product could be kept almost unchanged for months in the refrigerator under nitrogen, only gradually it developed a yellow tinge.

3-Hydroxy-4-bromo-2,5-dichlorothiophene (5)

The preparation was done according to the procedure for synthesis of 3-hydroxy-2,4,5-trichlorothiophene (**6**). Yield 9.7 g (31%), bp 92–94 °C/0.005 mmHg; *m*/*z* 246/248/250/252 (M^+, 71%/100%/52%/10%), 211/213/215 (M − Cl, 46/56/15); δ_H(300 MHz, $CDCl_3$) 5.67 (1 H, s, 2-H), 5–6 (br s, OH). The OH-proton was exchanged by adding D_2O. ν_{max}/cm^{-1} 1700–1705br (CO). Even though the product was kept in the refrigerator under nitrogen, polymerisation took place rapidly and the colour changed from dark red to black. In one week almost all the product had polymerised.

3-Hydroxy-2,4,5-trichlorothiophene (6)

The preparation was done according to the procedure for synthesis of 2-hydroxy-3,4,5-trichlorothiophene (**4**), except that the diethyl ether amounts were doubled and that the solution was cooled to −78 °C before the addition of *n*-butyllithium. Yield 11.9 g (59%), bp 76–78 °C/0.005 mmHg; *m*/*z* 202/204/206 (M^+, 97%/100%/31%), 167/169/171 (M − Cl, 57/40/7), 139/141/143 (M − COCl, 44/34/8); δ_H(300 MHz, $CDCl_3$) 5.69 (1 H, s, 2-H), 5–6 (br s, OH). The OH-proton was exchanged by adding D_2O. ν_{max}/cm^{-1} 1695–1710br (CO); λ_{max}(MeOH)/nm: 205sh (log (ε/dm^3 mol^{-1} cm^{-1}) 3.43), 244 (3.82). The product could be kept in the refrigerator under nitrogen, however the colour gradually turned dark red. After a few weeks the product slowly began to polymerise.

2-Methoxy-3,4,5-trichlorothiophene (7)

Diazomethane was generated by adding *N*-methyl-*N*-nitrosotoluene-*p*-sulfonamide (16.4 g, 0.076 mol) in diethyl ether (96 ml) to a solution of potassium hydroxide (3.8 g) dissolved in water (6 ml) and ethanol (21 ml) at 65 °C. The generated diazomethane in ether was distilled into an Erlenmeyer flask cooled in ice. To this flask 2-hydroxy-3,4,5-trichlorothiophene (**4**) (1.5 g, 0.0075 mol) in diethyl ether (25 ml) was added with a Pasteur pipette. The instantaneous reaction was evidenced by the evolution of nitrogen bubbles. The solution was washed with water, dried and evaporated. Sublimation gave the title compound (1.51 g, 94%) as colourless needles, mp 45 °C; *m*/*z* 216/218/220 (M^+, 40%/38%/13%), 201/203/20 (M − Me, 75/65/24), 173/175/177 (M − COMe, 61/63/20); δ_H(300 MHz, $CDCl_3$) 3.94 (s, Me); δ_C(75 MHz, $CDCl_3$) 62.2 (Me), 106.2, 111.4, 121.6, 154.0 (C-2); λ_{max}(MeOH)/nm: 243 (log (ε/dm^3 mol^{-1} cm^{-1}) 4.00), 208 (3.57), 255 (3.66).

3-Methoxy-4-bromo-2,5-dichlorothiophene (8)

The preparation was analogous to the synthesis of 3-methoxy-2,4,5-trichlorothiophene (**9**). The product (0.60 g, 69%) was isolated as a colourless liquid. *m*/*z* 260/262/264 (M^+), 245/247/249 (M^+ − Me, 100%), 217/219/221 (M − COMe); δ_H(200 MHz, $CDCl_3$) 3.92 (s, Me); δ_C(50 MHz, $CDCl_3$) 61.6 (Me), 107.4, 111.5, 122.1, 149.9 (3-C); ν_{max}/cm^{-1} 1500s.

3-Methoxy-2,4,5-trichlorothiophene (9)

Diazomethane was generated by adding *N*-methyl-*N*-nitrosotoluene-*p*-sulfonamide (8.2 g, 0.038 mol) in diethyl ether (48 ml) to a solution of potassium hydroxide (1.9 g) dissolved in water (3 ml) and ethanol (11 ml) at 65 °C. The generated diazomethane in ether was distilled into an Erlenmeyer flask

cooled in ice. To this flask 3-hydroxy-2,4,5-trichlorothiophene (**6**) (0.75 g, 0.0038 mol) in diethyl ether (15 ml) was added with a Pasteur pipette. The instantaneous reaction was evidenced by the evolution of nitrogen bubbles. The solution was washed with water, dried and evaporated. The product (0.56 g, 64%) was isolated by preparative thin-layer chromatography (silica gel 60 PF254, Merck 7747), with pet. ether (bp 40–60 °C) as eluent. *m*/*z* 216/218/220 (M^+, 25%/27%/10%), 201/203/20 (M − Me, 50/42/14), 173/175/177 (M − COMe, 37/38/11); δ_H(300 MHz, $CDCl_3$) 3.94 (s, Me); δ_C(75 MHz, $CDCl_3$) 61.2 (Me), 110.7, 119.2, 120.0, 148.3 (2-C); ν_{max}/cm^{-1} 1500s; λ_{max}(MeOH)/nm: 205 (log (ε/dm^3 mol^{-1} cm^{-1}) 3.59), 247 (3.85).

2-Acetoxy-3,4,5-trichlorothiophene (10)

To 2-hydroxy-3,4,5-trichlorothiophene (**4**) (1.0 g, 0.005 mol) in acetyl chloride (2 ml) was carefully added triethylamine in excess while stirring. The title product was formed spontaneously. The solution was dissolved in diethyl ether and washed with water and diluted hydrochloric acid. After drying and evaporation, sublimation gave colourless needles of the desired product (0.80 g, 67%), mp 105–106 °C. High resolution MS: found 243.8916, calc. for $C_6H_3Cl_3O_2S$: 243.8919; *m*/*z* 244/246/248 (M^+, 7%/7%/2%), 202/204/206 (M − $COCH_2$, 5/5/2), 43 (COMe, 100); δ_H(300 MHz, $CDCl_3$) 2.37 (s, Me); δ_C(75 MHz, $CDCl_3$) 20.2 (Me), 109.8, 117.2, 120.4, 140.6 (C-2), 166.3 (C=O).

3-Acetoxy-4-bromo-2,5-dichlorothiophene (11)

The preparation was analogous to the synthesis of 3-acetoxy-2,4,5-trichlorothiophene (**12**). The initially colourless liquid (0.66 g, 61%) became reddish after standing for some days under nitrogen. *m*/*z* (CI, isobutane) 288/290/292 (M^+, 3%/8%/2%), 246/248/250 (M − $COCH_2$, 36/44/22), 43 (COMe, 100); δ_H(200 MHz, $CDCl_3$) 2.29 (s, Me); δ_C(50 MHz, $CDCl_3$) 20.2 (Me), 106.9, 115.8, 123.0, 140.9 (C-2), 167.4 (C=O).

3-Acetoxy-2,4,5-trichlorothiophene (12)

To 3-hydroxy-2,4,5-trichlorothiophene (**6**) (1.0 g, 0.005 mol) in acetyl chloride (2 ml) was carefully added triethylamine in excess while stirring. The product was formed spontaneously. Diethyl ether was added, the organic solution was washed with water and dilute hydrochloric acid, dried ($MgSO_4$), filtered and evaporated. The product was isolated by the use of preparative thin-layer chromatography (silica gel 60 PF 254, Merck 7747) with diethyl ether–pet. ether (bp 40–60 °C) (1 : 10) as eluent. This gave a colourless liquid (0.50 g, 47%) which became reddish after standing for some days in the refrigerator under nitrogen. *m*/*z* 244/246/248 (M^+, 3%/3%/1%), 202/204/206 (M − $COCH_2$, 22/22/7), 43 (COMe, 100); δ_H(200 MHz, $CDCl_3$) 2.33 (s, Me); δ_C(50 MHz, $CDCl_3$) 20.1 (Me), 115.4, 119.0, 121.0, 139.4 (C-3), 167.4 (C=O).

2-Trimethylsilyloxy-3,4,5-trichlorothiophene (13)

2-Hydroxy-3,4,5-trichlorothiophene (**4**) (9.0 g, 0.045 mol) was dissolved in dry acetonitrile (25 ml) and *N*,*O*-bis(trimethylsilyl)acetamide (9.0 g, 0.045 mol) was added at room temperature. The reaction was completed within 5 min. The solution was thereafter dried, the acetonitrile removed under vacuum and the product distilled to give the title compound (9.5 g, 77%), bp 73–74 °C/0.01 mmHg; *m*/*z* 274/276/278 (M^+, 10%/9%/4%), 73 ($SiMe_3$, 100); δ_H(60 MHz, $CDCl_3$) 0.33 (s, Me). The distilled product could be kept for months in the refrigerator under nitrogen although the colour became dark.

2,2′,3,3′,4,4′-Hexachloro-2,2′,5,5′-tetrahydro-2,2′-bithiophen-5-one (15)

2-Trimethylsilyloxy-3,4,5-trichlorothiophene (**13**) (10.0 g, 0.036 mol) in dry, purified acetonitrile (75 ml) was refluxed under stirring for 90 hours. The mixture was dissolved in diethyl ether and extracted with water, sodium bicarbonate solution and sodium hydroxide (1.0 M). The product (1.04 g, 17%) was isolated by the use of preparative thin-layer chromatography (silica gel 60 PF254, Merck 7747) with pet. ether (bp. 40–60 °C)–diethyl ether (2 : 1) as eluent. Mp 146 °C. High resolution MS: found 331.8112, calc. for $C_8Cl_4O_2S_2$: 331.8094; *m*/*z* 332/334/336/338 (M^+, 64%/89%/48%/13%), 304/306/308/310 (M − CO, 4/6/3/1), 297/299/301/303 (M − Cl, 18/19/8/1), 276/278/280/282 (M − 2CO, 47/59/31/8), 269/271/273/275 (M − COCl, 40/42/17/4), 241/243/245/247 (M − COCOCl, 27/26/10/2); δ_H(300 MHz, $CDCl_3$) no signals; ν_{max}/cm^{-1} 1720s (CO).

Table 1 Crystallographic data for 2,2′,3,3′,4,4′-hexachloro-2,2′,5,5′-tetrahydro-2,2′-bithiophen-5-one (**15**)

Chemical formula	$C_8Cl_6O_2S_2$
Formula weight	404.90
Crystal system	Monoclinic
Space group	$P2_1/a$
Unit cell dimensions	a = 7.471(4) Å
	b = 13.560(7) Å
	c = 7.341(4) Å
	β = 118.440(10)°
Unit cell volume	V = 653.9(6) $Å^3$
Z	2
μ	14.90 mm^{-1}
R Values	$R1$ = 0.052 for 727 $F_o > 4\sigma(F_o)$
	0.058 for all data
	$wR2$ = 0.165 for all data
Temperature of data collection	120(2) K
Measured/independent reflections and R (int)	888/820, 0.047

Single-crystal X-ray data were measured with a Siemens P4/RA diffractometer. In addition to standard data reduction an empirical absorption correction[8] was applied. The structure was solved by direct methods (SHELXS-86[9]), and refined by full-matrix least-squares methods on all data with a β version of SHELXL-96.[10] Experimental details are given in Table 1. A view of the structure is given in Fig. 1. By crystallographic constraint the molecule is required to be centrosymmetric. The most conspicuous bond length is C2–C2′ at 1.60 Å. The C–S (1.84 and 1.77 Å) and C–Cl distances (1.77 and 1.70 Å (two)) are as expected for sp^3 and sp^2 hybridisation, respectively. The full data have been deposited with the Cambridge Crystallographic Data Centre.†

3,4-Dichloro-2,5-dihydrothiophen-2-one (16)

Methylmagnesium iodide was made by reacting magnesium (0.017 g, 0.040 mol) in dry tetrahydrofuran (THF) (20 ml) with methyl iodide (7.0 g, 0.050 mol) in dry THF (20 ml) under nitrogen with efficient magnetic stirring. 2-Hydroxy-3,4,5-trichlorothiophene (**4**) (3.0 g, 0.015 mol) in THF (10 ml) was then added to the Grignard reagent. The solution was stirred for one hour at ambient temperature and then hydrolysed with dilute hydrochloric acid. The mixture was extracted with diethyl ether, the ether extract washed with water, dried and evaporated. The product was isolated by preparative thin-layer chromatography (silica gel 60 PF 254, Merck 7747). Diethyl ether–pet. ether (1 : 2) applied as eluent gave the title compound (0.45 g, 18%), mp 78 °C (from pet. ether); *m*/*z* 168/170/172 (M^+, 3%/63%/10%), 133/135 (M − Cl, 59/20), 105/107 (M − COCl, 100/45); δ_H(300 MHz, $CDCl_3$) 4.14 (s, 2-H); δ_C(75 MHz, $CDCl_3$) 36.6 (5-C), 131.5 (4-C), 151.5 (3-C), 187.5 (2-C); ν_{max}/cm^{-1} 1690s (CO).

† CCDC reference number 188/247. See http://www.rsc.org/suppdata/p2/b0/b001570i/ for crystallographic files in .cif format.

2-Benzylidene-3,4-dichloro-2,5-dihydrothiophen-5-one (17)

Methylmagnesium iodide was made by reacting magnesium (0.002 g, 0.0021 mol) in dry THF (5 ml) with methyl iodide (0.35 g, 0.0025 mol) in dry THF (5 ml) under nitrogen with stirring. 2-Hydroxy-3,4,5-trichlorothiophene (**4**) (0.30 g, 0.0015 mol) in THF (5 ml) was then added to the Grignard reagent. The solution was stirred for one hour at ambient temperature, and benzaldehyde (0.45 g, 0.0045 mol) in THF (10 ml) was added. The mixture was hydrolysed with dilute hydrochloric acid, extracted with diethyl ether, washed with sodium hydroxide solution and water, dried and evaporated. The product was isolated by preparative thin-layer chromatography (Silica gel 60 PF 254, Merck 7747). Diethyl ether–pet. ether (1:2) served as eluting agent. Crystallisation gave the title compound (0.17 g, 43%) mp 140–141 °C (from ethanol) (lit.[1] 141 °C). MS and NMR data were in accordance with literature values.[1]

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