

Chlorinated Thiophenes. I. Reactions of Trichloro-2-thienylcarbinols

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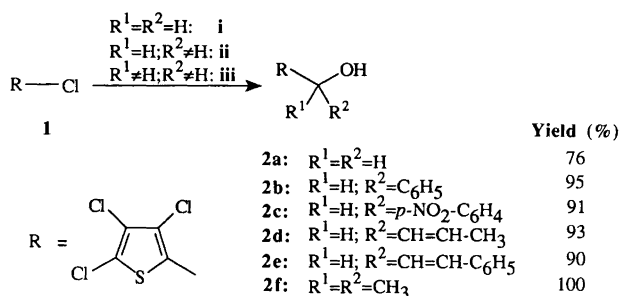
Skramstad, J. and Frøyen, P., 1993. Chlorinated Thiophenes. I. Reactions of Trichloro-2-thienylcarbinols. – Acta Chem. Scand. 47: 131–137.

In this paper we describe the synthesis of six trichloro-2-thienylcarbinols and their reactions with *p*-toluenesulfonic acid. When a phenyl or styryl group is present on the carbinol carbon, these compounds undergo a new type of elimination with rearrangement producing thiolactones in high yields. The structure of one of these new thiolactones was proved by single-crystal X-ray analysis. A surprising elimination reaction was observed when a dithienyl ether was treated with *p*-toluenesulfonic acid, affording the corresponding dithienylmethane in quantitative yield.

Dedicated to Professor Salo Gronowitz on the occasion of his 65th birthday.

In connection with work on environmental problems, we became interested in the chemistry of chlorinated thiophenes, some of which are found in the effluent from the pulp and paper industry.^{1,2} We found that surprisingly little is known of the chemistry of trichlorinated thiophenes in which there is a side chain in either the 2- or 3-position, and decided therefore to prepare some of these compounds and study their properties. In this paper we report the synthesis and some reactions of trichloro-2-thienylcarbinols with acids.

Synthesis. As starting material we used tetrachlorothiophene (1) prepared from hexachlorobutadiene and sulfur according to a known procedure.³ 1 was treated with butyllithium at -40°C and the resulting 3,4,5-trichloro-2-thienyllithium was reacted with five aldehydes and one ketone. Subsequent work-up gave the corresponding carbinols (2a–f) in good to excellent yields (Scheme 1).



Scheme 1. Synthesis of trichloro-2-thienylcarbinols from tetrachlorothiophene and carbonyl compounds. Reaction conditions, i: 1, BuLi, -78°C ; 2, Me_2NCHO ; 3, $\text{NaBH}_4\text{-EtOH}$. ii: 1, BuLi, -78°C ; 2, RCHO; 3, H_2O . iii: 1, BuLi, -78°C ; 2, Me_2CO ; 3, H_2O .

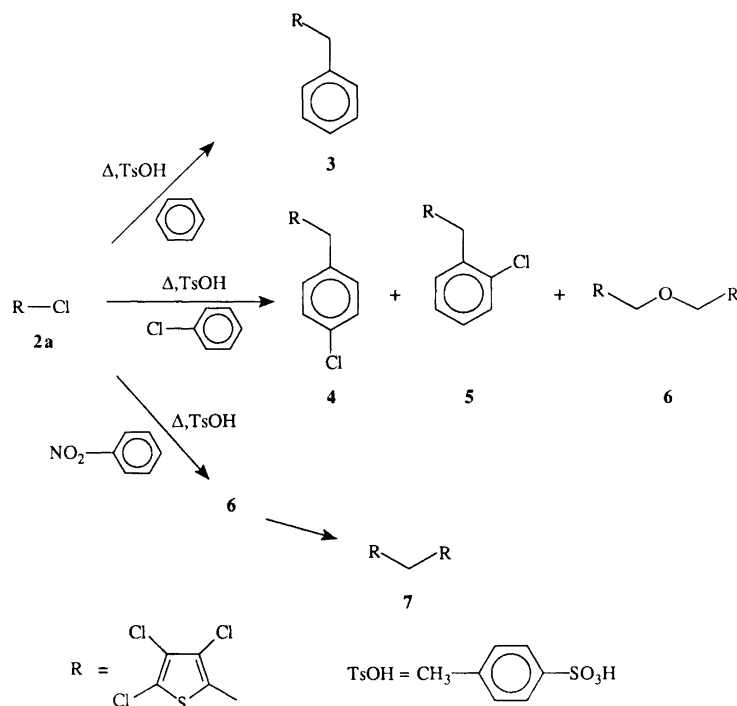
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Reactions. These six carbinols were thereafter treated with *p*-toluenesulfonic acid (TsOH) to generate the corresponding thenyl cations and observe their reactions. When the simplest member in the series, 2a, was treated with catalytic amounts of TsOH in refluxing benzene solution, a single product was formed. Spectroscopy (NMR, MS and IR, see the Experimental) revealed the substitution product 3, resulting from an electrophilic attack of the thenyl cation on the solvent (Scheme 2).

When the solvent was changed to the less reactive chlorobenzene, while keeping the temperature at 80°C , substitution still occurred, this time giving both the *ortho*- 4 and the *para*-isomer 5 together with the ether 6, this last compound obviously being a result of attack of the thenyl cation on the starting material.

By use of nitrobenzene as the reaction medium, we expected no reaction with the solvent and none was observed. Two products, however, were formed. One was the ether 6, the other was identified (NMR, MS, IR, see the Experimental) as the dithienylmethane 7. This was an unexpected result for which we have found no precedence in the literature. Interestingly it turned out that, on prolonged reaction times, the amount of dithienylmethane increased at the expense of the ether. In fact by starting with pure ether 7 was obtained in almost quantitative yield. This suggests that 7 is formed by a rearrangement of the protonated ether, involving an *ipso*-attack on one of the thiophene rings producing the intermediate 8 from which formaldehyde and a proton is split off to give 7 (Scheme 3).

We then treated the phenyl-substituted thienylcarbinol 2b in the same way. In this case, however, the reaction took a totally different course, producing no substitution products at all. Instead a single product was isolated in high yield, the structure of which was supported by NMR, MS and IR and conclusively proved by single-crystal

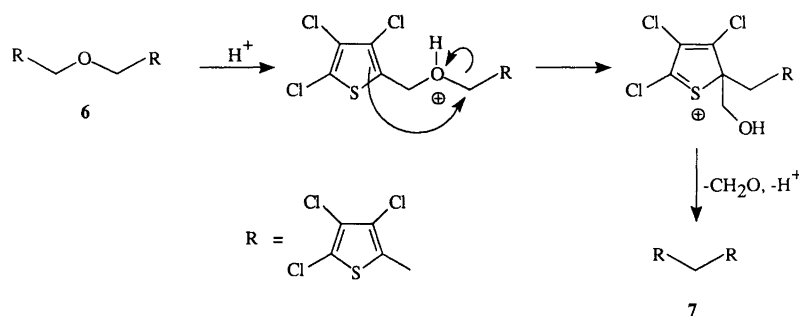


Scheme 2.

X-ray diffraction analysis to be the unsaturated thiolactone **9**, see Fig. 1. This change in reaction pathway probably occurs as a result of the enhanced stability of the thenyl cation due to the presence of a phenyl group (Scheme 4), presumably with **8b** as a major contributor to the resonance hybrid. At the same time the thenyl position is more sterically hindered impeding ether formation or electrophilic aromatic substitution. One possible reaction mechanism involving attack at the 5-position by the *p*-toluenesulfonate anion is outlined in Scheme 4. An alternative mechanism involving attack at the same position by water formed during the initial step, would also give the observed thiolactone **9**. In an attempt to differentiate between these mechanisms, we reacted **2b** with water and sulfuric acid in different concentrations. The only observed product was the ether **10**. This indicates that water is probably not the active nucleophile, hence the mechanism depicted in Scheme 4.

The geometry of the exocyclic double bond in **9** is worthy of comment. It is clearly shown in Fig. 1 that the configuration is *Z*. Obviously this is the thermodynamically most stable isomer, and models confirm that the *Z* isomer is sterically less hindered than the *E* isomer in the coplanar state. Actually the molecule adopts an almost perfect coplanar conformation with a torsion angle of only $1.5 (\pm 1)$ degrees as calculated from the crystallographic data.

Several reports in the literature deal with the synthesis of this type of thiolactone. The oldest report seems to be the one by Steinkopf who condensed hydroxythiophenes with benzaldehydes,⁴ a reaction type extensively studied by Hörnfeldt.⁵ These compounds have also been made by condensation of thioanhydrides with phenylacetic acid in fused sodium acetate at high temperatures⁶ or by reaction between thioanhydrides and Grignard reagents followed by elimination of water.⁷ Finally, Lawesson reacted



Scheme 3.

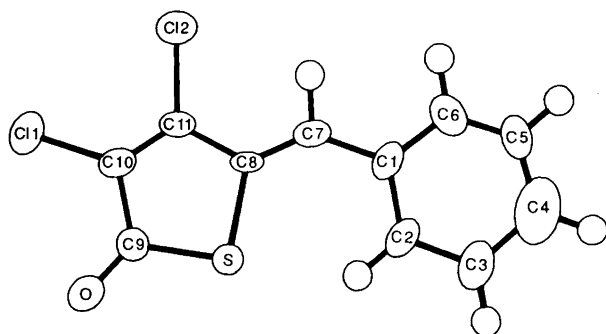
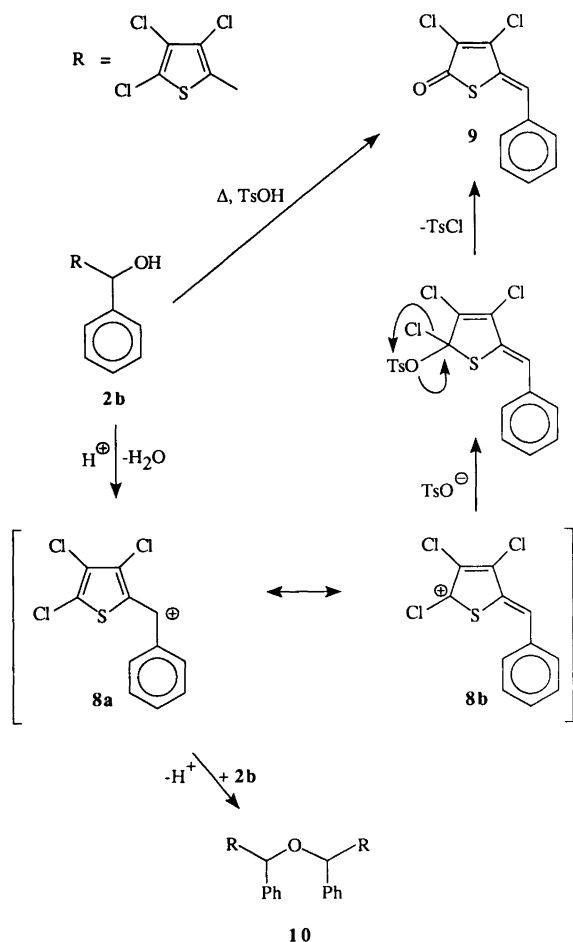


Fig. 1. Perspective drawing of the molecule **9** based on the single-crystal X-ray analysis, showing the numbering of atoms.

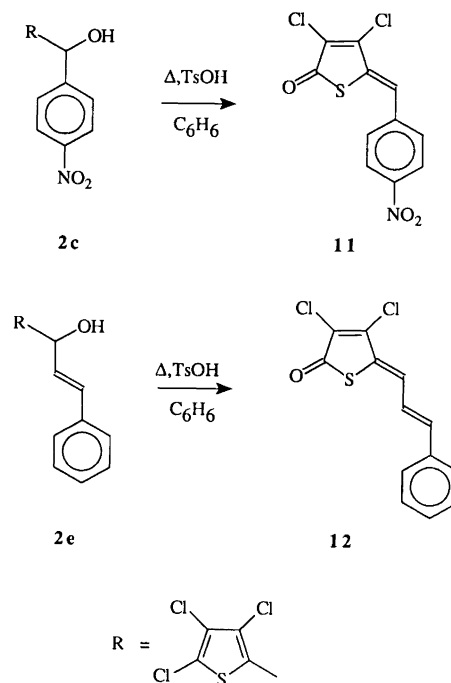
2-alkoxy-5-thienyllithium with aldehydes or ketones and treated the intermediate salt with acid under dealkylation to thiolactones.⁸

As our reaction constitutes a new way of preparing this type of thiolactone avoiding both high temperatures, organometallic reagents and unstable hydroxythiophenes, we proceeded to determine its scope and limitations. We therefore treated the carbinol **2c** with TsOH in benzene at 80°C and obtained a good yield of the corresponding *p*-nitrophenyl substituted thiolac-



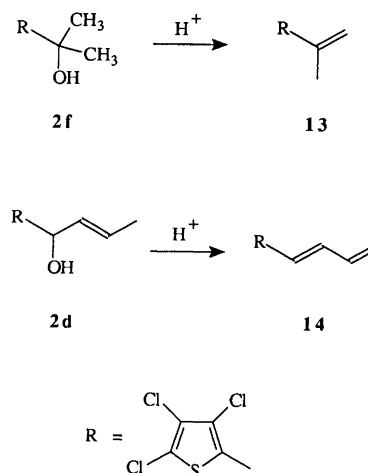
Scheme 4.

tone **11**. The applicability of the reaction was further demonstrated by the excellent yield of the polyunsaturated thiolactone **12** obtained from the allylic alcohol **2e** (Scheme 5).



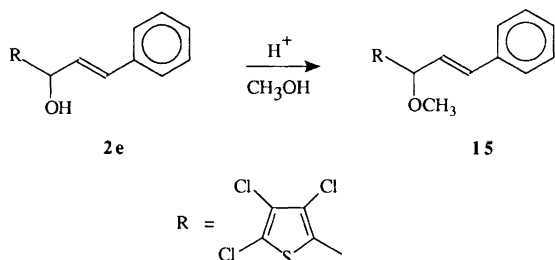
Scheme 5.

When TsOH was replaced with trichloroacetic acid, the same products were obtained in approximately the same yields, except that the *p*-nitrophenyl compound **2c** did not react with this weaker acid. It should also be noted that in the two cases where the thienyl carbinol contains a removable proton either at C-2 (**2f**) or C-4 (**2d**), deprotonation occurs, yielding the styrene analogue **13** or the diene **14**, both in quantitative yield (Scheme 6).



Scheme 6.

When methanol was used as the solvent with catalytic amounts of hydrogen chloride, compound **2e** gave the methyl ether **15** (Scheme 7). The corresponding compound was also obtained when the parent compound (without chlorine atoms) was treated the same way.⁹ Similarly, non-chlorinated **2b** is reported to give the corresponding ether when treated with hydrochloric acid in methanol.¹⁰



Scheme 7.

Experimental

The ¹H and ¹³C NMR spectral data were taken at operating frequencies of 60, 200, 300 and 50.3 and 75.4 MHz, respectively, on a Jeol JNM-PMX 60, a Varian Gemini-200 and a Varian XL-300 spectrometer. IR spectra were measured as films or in KBr discs with a Perkin Elmer 1310 infrared spectrometer. The mass spectra were obtained on a VG Micromass 7070 F and on a Hewlett Packard 5990a GC-MS instrument. Column chromatography was carried out using Merck No. 9385 silica gel 60. The melting points, determined with a Reichert Thermopan melting point microscope, are uncorrected.

General procedure for the preparation of the 3,4,5-trichloro-2-thienylcarbinols 2a-f. To a solution of tetrachlorothiophene (4.4 g, 0.02 mol) in dry diethyl ether (30 ml) was added over 0.5 h an equimolar amount of butyllithium (15% in hexane) under nitrogen at -78°C. When the addition was complete, the reaction mixture was stirred for 15 m, during which time the temperature was raised to -20°C. The solution was recooled to -78°C and the appropriate aldehyde (0.02 mol) in diethyl ether (20 ml) was added, whereafter the reaction mixture was warmed to room temperature and stirred for a further 15 min. An aqueous solution of ammonium chloride (20 ml) was added and the aqueous layer extracted with ether. The combined extracts were neutralized with aqueous sodium carbonate, washed with water, and dried over magnesium sulfate. The solvent was removed *in vacuo*, leaving the alcohol as a yellow oil, which was purified by column chromatography and/or crystallization.

3,4,5-Trichloro-2-thienylmethanol (2a). M.p. 100–102°C; MS [IP 70 eV; *m/z* (% rel. int.)]: 220 (19.5), 219 (12.7), 218 (73.8), 217 (50.8), 216 (100), 215 (98.4, *M*), 214

(51.8), 213 (80.7), 203 (16), 201 (41.6), 199 (44.2), 188 (13.3), 186 (13), 183 (49.6), 181 (64.7), 155 (33.8), 154 (23.4), 153 (52.3), 152 (35.2), 151 (19.5), 150 (17.1), 143 (20.5), 141 (20.9). ¹H NMR (200 MHz, CDCl₃): δ 2.49 (1 H, s, OH), 4.73 (2 H, s, CH₂). ¹³C NMR (50.3 MHz, CDCl₃): δ 58.75 (CH₂), 120.89, 123.51, 124.44, 134.86.

3,4,5-Trichloro-2-thienyl(phenyl)methanol (2b). M.p. 143°C; MS [IP 70 eV; *m/z* (% rel. int.)]: 295 (13.5), 293 (38.1), 291 (38.3, *M*), 280 (11.3), 279 (35.5), 278 (31), 277 (94.5), 276 (32.7), 275 (100), 243 (27.3), 242 (14), 241 (59.3), 240 (19.8), 239 (49.2), 230 (12), 228 (16.6), 215 (11), 207 (22.3), 206 (11.8), 205 (58.3). ¹H NMR (300 MHz, CDCl₃): δ 5.75 (1 H, d, *J* 7.7 Hz), 7.30–7.45 (5 H, m, H_{aromatic}).

3,4,5-Trichloro-2-thienyl(*p*-nitrophenyl)methanol (2c). M.p. 137°C; MS [IP 70 eV; *m/z* (% rel. int.)]: 339 (26.6), 337 (31.8, *M*), 335 (10.4), 304 (21.4), 302 (25.5), 219 (10.2), 217 (39.3), 215 (60.6), 213 (29.9), 186 (11.5), 154 (19.7), 152 (30.2), 151 (15.7), 150 (100), 143 (11.5), 141 (10.7), 120 (14.1), 115 (14.2), 107 (10.4), 105 (13.8), 104 (26.6), 92 (11.6), 79 (17.3). ¹H NMR (200 MHz, CDCl₃): δ 2.98 (1 H, br s, OH), 6.26 (1 H, s, H_{aliphatic}), 7.64 (2 H, d, *J* 9.0 Hz, *ortho*-H), 8.22 (2 H, d, *J* 8.9 Hz, *meta*-H). IR (film): 3400 (br s), 1595 (w), 1515 (s), 1415 (w), 1340 (s), 1320 (w), 1060 cm⁻¹ (m).

1-(3,4,5-Trichloro-2-thienyl)-2-buten-1-ol (2d). Oil; MS [IP 70 eV; *m/z* (% rel. int.)]: 260 (13), 258 (39), 256 (37.9, *M*), 245 (16.9), 243 (48.8), 241 (54), 217 (30.9), 215 (46.2), 213 (24.4), 206 (17.8), 205 (11.8), 203 (17.8), 201 (35.6), 199 (33.3), 190 (12.1), 168 (21.4). ¹H NMR (200 MHz, CDCl₃): δ 1.73 (3 H, d, *J* 6.5 Hz, CH₃), 2.31 (1 H, br s, OH), 5.45–5.64 (2 H, m, 1-H and 2-H), 5.84–5.95 (1 H, dq, *J* 14.9 and 6.5 Hz, 3-H).

After standing for some time this compound undergoes an allylic rearrangement to the conjugated isomer **4-(3,4,5-Trichloro-2-thienyl)-3-butene-2-ol (2d')**: M.p. 169–172°C; MS [IP 70 eV; *m/z* (% rel. int.)]: 258 (1), 256 (1.2, *M*), 241 (15), 240 (15.5), 239 (17.5), 258 (12), 219 (10), 205 (16.6), 204 (10.4), 203 (18.3), 201 (10.2), 199 (10.3), 170 (42.5), 169 (15.4), 168 (100). ¹H NMR (200 MHz, CDCl₃): δ 1.32 (3 H, d, *J* 6.3 Hz, CH₃), 4.10 (1 H, dq, *J* 7.2 and 6.3 Hz, 2-H), 5.93 (1 H, dd, *J* 7.2 and 15.9 Hz, 3-H), 6.70 (1 H, d, *J* 15.9 Hz, 4-H).

1-(3,4,5-Trichloro-2-thienyl)-3-phenyl-2-propen-1-ol (2e). Oil; MS [IP 70 eV; *m/z* (% rel. int.)]: 320 (6.8), 318 (7.6, *M*), 301 (5.7), 283 (16.7), 281 (11.1), 222 (19.2), 220 (15.5), 218 (10.4), 215 (10.2), 213 (10.7), 201 (16.2), 199 (16.1), 143 (13), 141 (14), 132 (15), 131 (28.1). ¹H NMR (200 MHz, acetone-*d*₆): δ 5.16–5.73 (1 H, m, H_{aliphatic}), 6.24–6.46 (1 H, m, H_{aliphatic}), 6.79–7.07 (1 H, m, H_{aliphatic}), 7.22–7.56 (5 H, m, H_{aromatic}).

2-(3,4,5-Trichloro-2-thienyl)propan-2-ol (2f). M.p. 81°C; MS [IP 70 eV; m/z (% rel. int.)]: 248 (1.5), 246 (4.5), 244 (4.7, *M*), 233 (8.9), 231 (25.4), 229 (25.7), 43 (100). ^1H NMR (200 MHz, CDCl_3): δ 1.71 (6 H, s, CH_3), 2.33 (1 H, br s, OH). IR (film): 3380 (br s), 2980 (m), 2960 (w), 1520 (w), 1445 (m), 1360 (m), 1315 (s), 1300 (m), 1225 (m), 1165 (m), 1135 (m), 950 (m), 910 (m), 800 cm^{-1} (s).

Reactions of 3,4,5-trichloro-2-thienylmethanol (2a) with p-toluenesulfonic acid in various solvents.

2-Benzyl-3,4,5-trichlorothiophene (3). To 3,4,5-trichloro-2-thienylmethanol **2a** (1.0 g, 4.6 mmol) in benzene (50 ml) at 81°C was added an equivalent amount of *p*-toluenesulfonic acid (0.95 g) and the mixture was heated to reflux for 1 h. The solution was thereafter cooled with ice, neutralized with aqueous sodium carbonate, washed with water, and dried over magnesium sulfate. The solvent (benzene) was removed *in vacuo* to give a yellow oil (1.20 g, 94%) identified as **3** by NMR and mass spectrometry. MS [IP 70 eV; m/z (% rel. int.)]: 280 (19.6), 278 (52.8), 276 (51, *M*), 245 (18.7), 243 (68.2), 241 (100), 207 (17), 206 (23.9), 205 (25.1), 200 (20.3), 199 (20.3), 171 (18.7). ^1H NMR (200 MHz, CDCl_3): δ 4.07 (2 H, s, CH_2), 7.23–7.33 (5 H, m, $\text{H}_{\text{aromatic}}$). ^{13}C NMR (50.3 MHz, CDCl_3): δ 34.84 (CH_2), 112.77, 127.75, 129.15, 129.19, 129.39, 129.43, 135.45, 138.05.

3,4,5-Trichloro-2-thienyl(p-chlorophenyl)methane (4), *3,4,5-trichloro-2-thienyl(o-chlorophenyl)methane (5)* and *bis(3,4,5-trichloro-2-thienyl) ether (6)*. A mixture of **2a** (0.70 g, 3.2 mmol) and TsOH (0.70 g) in chlorobenzene (25 ml) was heated at 80°C for 2 h. The reaction mixture was cooled to ambient temperature, neutralized with aqueous sodium carbonate, washed with water, and dried over magnesium sulfate. Chromatography (silica gel; petroleum ether–ether 4:1) gave 0.50 g of a yellow oil shown by GC–MS and NMR spectroscopy to be a mixture of **4** (0.40 g, 40%) and **5** (0.10 g, 10%) and (0.05 g, 7.4%) of a white solid, m.p. 97°C, shown by GC–MS and ^1H and ^{13}C NMR spectroscopy to be the ether **6**.

4: MS [IP 70 eV; m/z (% rel. int.)]: 312 (26), 310 (26.7, *M*), 279 (29.3), 278 (15.4), 277 (95), 275 (100), 243 (10.5), 242 (29.9), 241 (36.5), 240 (45.1), 239 (51.8), 207 (42.5), 205 (82.5), 204 (19.6), 203 (20.5), 201 (33.9), 199 (29.9), 170 (20.7), 169 (35.9).

5: MS [IP 70 eV; m/z (% rel. int.)]: 312 (16.3), 310 (14.5, *M*), 277 (33.4), 275 (31.1), 241 (14), 240 (14), 239 (18.7), 207 (13.3), 205 (27.9), 201 (12.9), 199 (13.6), 169 (21.1).

6: M.p. 97°C; MS [IP 70 eV; m/z (% rel. int.)]: 418 (8.4), 416 (9.6, *M*), 297 (13.2), 279 (10.1), 278 (12.5), 276 (14.7), 243 (19.2), 241 (27.7), 204 (22.3), 203 (38.7), 202 (64.4), 201 (100), 200 (65.5), 199 (95.6), 167 (22), 165 (30.9), 149 (67.3), 129 (10), 91 (27.5). ^1H NMR (300 MHz, CDCl_3): δ 4.67 (4 H, s, CH_2). ^{13}C NMR

(75.43 MHz, CDCl_3): δ 65.07 (CH_2), 122.12, 123.15, 124.81, 130.95.

4 + 5 (synthetic mixture): ^1H NMR (200 MHz, CDCl_3): δ 4.02 and 4.19 (2 H, s, CH_2 , relative intensity: 4:1), 7.10–7.32 (4 H, m, $\text{H}_{\text{aromatic}}$).

Bis(3,4,5-trichloro-2-thienyl)methane (7). A mixture of **2a** (0.50 g, 2.3 mmol) and TsOH (0.50 g) in nitrobenzene (3 ml) was stirred for 3 h at 85–92°C. The reaction mixture was thereafter cooled, diluted with ether (30 ml), neutralized with aqueous sodium carbonate, washed with water, and dried over magnesium sulfate. Diethyl ether and nitrobenzene were removed *in vacuo*, leaving 0.45 g of a yellow oil. The crude product was purified by chromatography (silica gel; petroleum ether–ether 4:1) to give **6** 0.038 g (8%) and **7** 0.41 g (92%) m.p. 95–96°C; MS [IP 70 eV; m/z (% rel. int.)]: 390 (14), 388 (29.6), 386 (34.9), 384 (17.7, *M*), 355 (24.8), 353 (69.2), 352 (11.8), 351 (100), 349 (58.6), 316 (12.2), 281 (19.9), 279 (17.4), 201 (16.7), 199 (16.6). ^1H NMR (200 MHz, acetone- d_6): δ 4.55 (2 H, s, CH_2). ^{13}C NMR (50.3 MHz, acetone- d_6): δ 27.79 (CH_2), 122.53, 123.66, 123.88, 130.81.

α, α' -*Bis(3,4,5-trichloro-2-thienyl)dibenzyl ether (10)*. M.p. 126°C; MS [IP 70 eV; m/z (% rel. int.)]: 570 (0.1), 568 (0.1, *M*), 462 (1.2), 295 (10.8), 293 (31.4), 291 (31.2), 279 (37.4), 278 (26.7), 277 (97.6), 276 (26.7), 275 (91.6), 243 (26.6), 242 (18.2), 241 (70.6), 240 (24.8), 239 (73.5), 230 (17.8), 228 (23.6), 215 (13.6), 207 (31.8), 206 (14.8), 205 (80.5), 170 (22.4), 169 (30.1), 126 (18.5), 125 (11.3), 115 (10.7), 105 (37.9). ^1H NMR (60 MHz, CDCl_3): δ 5.75–5.80 (2 H, d, CH, two diastereomers), 7.39 (10 H, s, $\text{H}_{\text{aromatic}}$).

General procedure for the preparation of thiolactones 9, 11, 12. To a refluxing solution of TsOH (5.0 mmol) in benzene (50 ml) was added in one portion 5.0 mmol of **2b**, **2c** or **2e**. The reaction mixture was heated at gentle reflux overnight. The solution was thereafter cooled to room temperature, neutralized with aqueous sodium carbonate, washed with water and dried over magnesium sulfate. Evaporation of the solvent followed by recrystallization (acetone) gave the pure thiolactones **9**, **11** or **12** in yields varying from 70 to 75%.

5-Benzylidene-3,4-dichlorothiophen-2(5H)-one (9). M.p. 141°C; MS [IP 70 eV; m/z (% rel. int.)]: 258 (40.1), 256 (57.4, *M*), 195 (26.8), 194 (13.8), 193 (100), 158 (40.5), 149 (26.8), 114 (10), 96 (10.8), 79 (12.6). ^1H NMR (300 MHz, acetone- d_6): δ 7.50–7.74 (5 H, m, $\text{H}_{\text{aromatic}}$), 7.80 (1 H, s, $\text{H}_{\text{aliphatic}}$). ^{13}C NMR (75.4 MHz, acetone- d_6): δ 127.33, 129.70, 130.20, 131.48, 131.54, 134.24, 134.73, 183.55, 206.08 (C=O).

An X-ray crystal structure investigation of the title compound **9** was performed in order to establish the configuration of the molecule. The crystals of **9** belong to the monoclinic system with space group $P2_1/n$, cell dimensions $a = 7.036(2)$, $b = 11.560(4)$, $c = 13.592(2)$ Å,

$\beta = 103.55(2)^\circ$ and $Z = 4$ ($D_x = 1.58 \text{ g cm}^{-3}$). Using $2\theta_{\text{max}} = 50^\circ$ and Mo K_α radiation, and choosing an observed–unobserved cut-off at $2.5\sigma(I)$, a total of 827 observed reflections were recorded on an automatic diffractometer at room temperature. The crystals were of poor quality and were mounted in a capillary tube. No correction for absorption or secondary extinction was applied (crystal size $0.5 \times 0.1 \times 0.1 \text{ mm}$). The structure was solved by direct methods¹¹ and refined by full-matrix least-squares techniques.¹² Weights in least-squares were calculated from the standard deviations in intensities, $\sigma(I)$, taken as shown in eqn. (1), $\sigma(I) = [C_1 + (0.02C_2)^2]^{1/2}$ where C_1 is the total number of counts and C_2 the net count. Anisotropic temperature factors were used for non-hydrogen atoms. The maximum RMS amplitudes of thermal vibration range from 0.24 to 0.40 Å. Hydrogen atom positions were calculated and included in the structure factor calculations but not refined. The R -value arrived at was as high as 11.7% (the weighed value $R_w = 11.7\%$) for 827 observed reflections. Final fractional coordinates with estimated standard deviations for the non-hydrogen atoms are listed in Table 1. Bond distances and bond angles, with estimated standard deviations, are given in Table 2. A perspective drawing of the molecule showing the numbering of atoms is given in Fig. 1. Lists of thermal parameters, hydrogen atom parameters, and observed and calculated structure factors are available on request from P. Groth at this institute.

3,4-Dichloro-5-(p-nitrobenzylidene)thiophen-2(5H)-one (11). M.p. 207–209°C. MS [IP 70 eV; m/z (% rel. int.)]: 305 (15.7), 304 (10.7), 303 (76), 302 (15), 301 (100, M), 284 (10), 273 (16.2), 271 (21.7), 257 (10.7), 255 (15.3), 240 (12.1), 238 (32.6), 220 (10), 208 (13.6), 194 (35.7), 193 (14), 192 (91.1), 157 (18.7), 113 (22.7), 96 (16.6), 89 (13.1). $^1\text{H NMR}$ (200 MHz, CDCl_3): δ 7.61 (1 H, s, $\text{H}_{\text{aliphatic}}$), 7.73 (2 H, d, J 8.8 Hz, *ortho-H*), 8.32 (2 H, d, J

Table 1. Final fractional coordinates and equivalent temperature factors with estimated standard deviations for non-hydrogen atoms.

Atom	x	y	z	U_{eq}^a
Cl1	0.6559(11)	0.3961(5)	0.3384(4)	0.076
Cl2	0.6218(11)	0.1278(5)	0.2614(4)	0.077
S	0.7822(11)	0.1558(4)	0.5824(4)	0.058
O	0.763(3)	0.382(1)	0.570(1)	0.080
C1	0.765(3)	−0.129(2)	0.519(1)	0.049
C2	0.812(4)	−0.116(2)	0.625(2)	0.066
C3	0.847(4)	−0.212(2)	0.689(2)	0.074
C4	0.832(4)	−0.328(3)	0.643(2)	0.096
C5	0.785(4)	−0.330(2)	0.540(2)	0.081
C6	0.753(4)	−0.239(2)	0.484(2)	0.071
C7	0.729(3)	−0.029(2)	0.454(1)	0.046
C8	0.726(3)	0.082(2)	0.465(1)	0.045
C9	0.746(3)	0.291(2)	0.525(1)	0.055
C10	0.695(3)	0.277(2)	0.413(1)	0.047
C11	0.684(4)	0.170(2)	0.387(1)	0.052

^a $U_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3$.

Table 2. Bond distances (Å) and bond angles ($^\circ$) with standard deviations.

Distance		Distance	
Cl1–C10	1.70(3)	Cl2–C11	1.734(19)
S–C8	1.776(19)	S–C9	1.74(3)
O–C9	1.21(3)	C1–C2	1.41(3)
C1–C6	1.36(4)	C1–C7	1.45(3)
C2–C3	1.41(4)	C3–C4	1.47(4)
C4–C5	1.37(5)	C5–C6	1.28(4)
C7–C8	1.30(3)	C8–C11	1.45(3)
C9–C10	1.49(3)	C10–C11	1.28(3)
Angle		Angle	
C8–S–C9	92.9(10)	C2–C1–C6	116.1(20)
C2–C1–C7	120.2(19)	C6–C1–C7	123.7(18)
C1–C2–C3	120.9(21)	C2–C3–C4	118.6(22)
C3–C4–C5	115.0(24)	C4–C5–C6	124.2(24)
C1–C6–C5	125.3(22)	C1–C7–C8	137.2(17)
S–C8–C7	125.0(15)	S–C8–C11	106.3(14)
C7–C8–C11	128.7(17)	S–C9–O	125.3(16)
S–C9–C10	109.6(15)	O–C9–C10	125.2(19)
Cl1–C10–C9	119.3(16)	Cl1–C10–C11	128.9(16)
C9–C10–C11	111.8(18)	Cl2–C11–C8	118.5(15)
Cl2–C11–C10	122.1(16)	C8–C11–C10	119.4(17)

8.8 Hz, *meta-H*), IR (film): 1700 (s), 1505 (m), 1335 (s), 1095 (w), 1035 (w), 840 (m), 810 cm^{-1} (m).

3,4-Dichloro-5-(3-phenylpropenylidene)thiophen-2(5H)-one (12). M.p. 192–195°C. MS [IP 70 eV; m/z (% rel. int.)]: 284 (41.1), 283 (10.8), 282 (61.1, M), 249 (10.8), 247 (11.8), 221 (39), 220 (17), 219 (100), 218 (10.8), 186 (13.4), 185 (11.8), 184 (82.5), 183 (12), 152 (11.8), 139 (19.8), 115 (30.9). $^1\text{H NMR}$ (200 MHz, CDCl_3): δ 6.89–7.12 (2 H, m, 2'-H and 3'-H), 7.26–7.53 (6 H, m, 4'-H and $\text{H}_{\text{aromatic}}$). $^{13}\text{C NMR}$ (75.4 MHz, $\text{DMSO}-d_6$): δ 123.37, 126.63, 127.43, 128.04, 128.92, 130.10, 134.00, 135.41, 144.90, 145.64, 181.83, (C=O). IR (film): 1680 cm^{-1} (s) (C=O).

2-(1-Methylethenyl)-3,4,5-trichlorothiophene (13). A mixture of **2f** (0.65 g, 2.5 mmol) and trichloroacetic acid (TsOH gave the same results) in benzene (50 ml) was refluxed for 3 h. The solution was thereafter cooled to ambient temperature, diluted with diethyl ether (20 ml), neutralized with aqueous sodium carbonate, washed with water and dried over magnesium sulfate. Analysis of the solution by TLC showed, in addition to a minor amount of unchanged **2f**, only one product. Evaporation of the solvent followed by flash chromatography (silica gel; petroleum ether–ether 4:1), gave **13** (0.58 g, 98% based on **2f**) as a colorless oil. $^1\text{H NMR}$ (60 MHz, CDCl_3): δ 2.14 (3 H, s, CH_3), 5.41 (2 H, d, J 16 Hz, CH_2). IR (film): 1605 (w), 1510 (m), 1440 (s), 1370 (w), 1360 (s), 910 (w), 895 (s), 820 (m), 810 cm^{-1} (m).

2-(1,3-butadienyl)-3,4,5-trichlorothiophene (14). To a solution of TsOH (10 mmol) in boiling benzene was

added **2d** (10 mmol). The solution was heated at 81°C for 10 min, when the reaction was judged complete by TLC (silica gel; petroleum ether–ether 4:1). The reaction mixture was cooled, neutralized with aqueous sodium carbonate, washed with water and dried over magnesium sulfate. Gas chromatographic analysis showed the presence of one compound only. The solvent was removed by rotary evaporation, to yield a yellow oil (2.3 g, 95%), identified by GC–MS as the title compound **14**. MS [IP 70 eV; m/z (% rel. int.)]: 242 (5.2), 240 (15.1), 239 (6.3), 238 (15, *M*), 205 (12.6), 203 (18.2), 170 (44.1), 169 (19.3), 168 (100). IR (film): 2870–3000 (s), 1505 (s), 1445 (s), 1320 (s), 975 (s), 950 (m), 910 (s), 803 cm^{-1} (m).

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