

## Unsaturated $\gamma$ -Thiolactones

### VI.\* The Structure of Some Oxidative Coupling Products of 5-Alkyl-substituted Thiolenes-2-ones

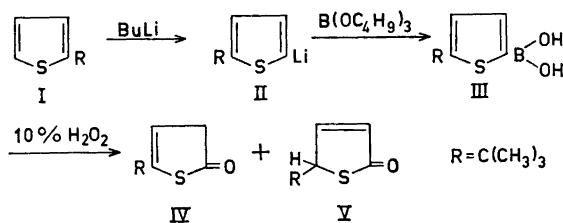
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The structures of some by-products obtained in the synthesis of the 5-tert.butyl- and 5-methylthiolenes-2-one systems have been elucidated.

5,5'-Ditert.butyl- and 5,5'-dimethyl-3,3'-di-3-thiolenes-2-ones have been synthesized and found to be identical with the by-products, indicating that the thiolenes-2-ones undergo phenolic oxidative coupling reactions.

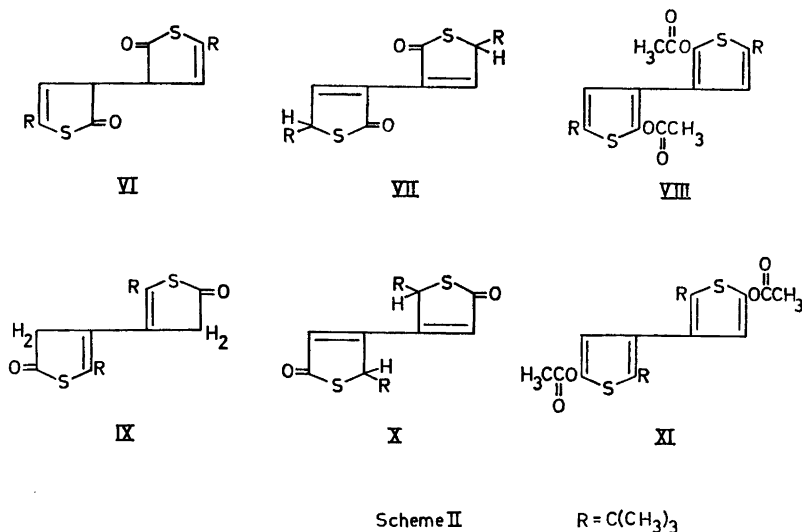
The 5-tert.butylthiolenes-2-one system is prepared from 2-tert.butylthiophene by metalation with butyllithium, followed by reaction of the resulting thienyllithium derivative with butyl borate. The boronic ester so obtained is hydrolyzed, the acid isolated and oxidized with 10 % hydrogen peroxide solution giving the tautomeric mixture of 5-tert.butyl-4- and 3-thiolenes-2-one (IV, V). The residue obtained upon distillation gives, when treated with chloroform, a crystalline compound of m.p. 218–220° which gives a correct analysis for  $C_{16}H_{22}O_2S_2$ . The IR-spectrum of this compound shows a  $C=O$  stretching frequency at  $1663\text{ cm}^{-1}$  and in its NMR-spectrum there are doublets



Scheme I

\* Part V. Ref. 3.

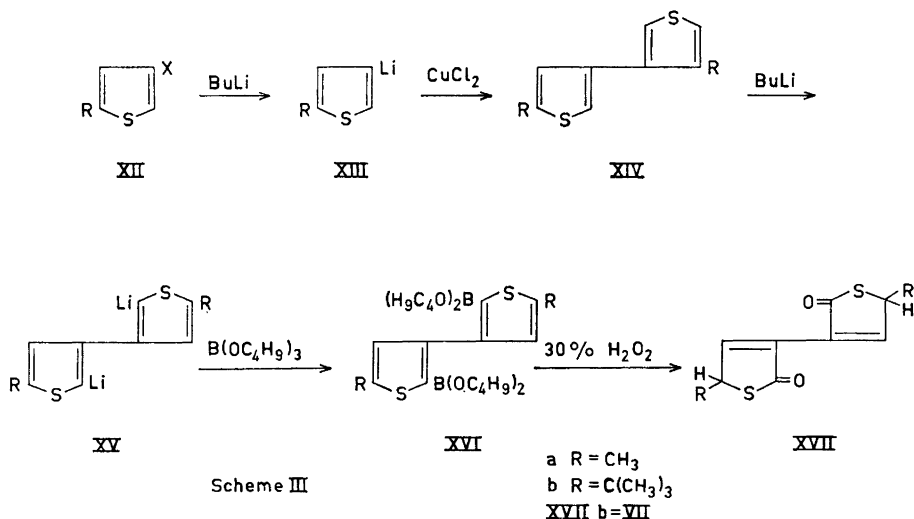
at 1.55  $\tau$  and 5.65  $\tau$  with splittings of 2.30 c/s, and a sharp singlet at 8.85  $\tau$ . The relative intensities of the three bands are 1:1:9 indicating that for each tert.butyl group there is present one aromatic hydrogen and one methine hydrogen. When this compound was treated with excess of acetyl chloride, another crystalline compound of m.p. 162–165° was obtained. Its IR-spectrum shows a C=O stretching frequency at 1760  $\text{cm}^{-1}$ , which is a shift towards higher frequency compared with the carbonyl stretching in the unacylated compound, and is in the same region as the C=O absorption of the acetoxythiophenes.<sup>1</sup> The NMR-spectrum of the acylated compound shows three sharp peaks at 3.45  $\tau$ , 7.75  $\tau$ , and 8.45  $\tau$  with relative intensities of 1:3:9, respectively. The simplicity of these two NMR-spectra indicates that the by-product is symmetric, its structure corresponding to one of the compounds VI, VII, IX, or X. The derived acetoxy compound would then have either structure VIII or XI.



Compound IX is at once excluded as its NMR-spectrum would contain two bands with relative intensities 2:9. Compound X should give the relative intensities found but compared with the 5-alkyl-substituted 3-thiolen-2-ones the coupling constant obtained for the by-product is somewhat larger than  $J_{35}$ , which is 2.0–2.1 c/s.<sup>1</sup> If this by-product was obtained by a reaction analogous to the oxidative phenolic coupling, *ortho* coupling is much more probable than *meta* coupling,<sup>2</sup> making VI and VII more probable than X. From the relative intensities and coupling constants alone, it is not possible to distinguish between VI and VII, as in the 4-thiolen-2-ones  $J_{34}$  falls in the region 2.5–2.8 c/s, as does also  $J_{45}$  in the 3-thiolen-2-ones.<sup>1</sup> However, the high  $\tau$ -value of the tert.butyl group resonance indicates that this group is situated at an  $sp_3$ -hybridized carbon ( $\tau_{\text{C}(\text{CH}_3)_3}$  of V is at 8.90 and of IV at 8.72). Due to the more extensive conjugation in VII, this tautomer should also be

energetically more favoured than VI, which has two non-conjugated carbonyl groups and two isolated double bonds.

In the kinetic study of the 5-*tert*.butyl- and 5-methyl thiolene-2-one systems,<sup>3</sup> a side-reaction probably due to air oxidation was observed. When the solutions from the kinetic experiments were left standing for a fortnight, a crystalline material could be isolated in both cases. The compound derived from the 5-*tert*.butylthiolene-2-one system was identical with the by-product described above. To ascertain if the same type of reaction occurred also in the 5-methylthiolene-2-one system, an authentic sample of 5,5'-dimethyl-3,3'-di-3-thiolene-2-one (XVII a) was prepared. Also, in order to confirm the identity of the unknown by-product with compound VII, an authentic sample of 5,5'-di-*tert*.butyl-3,3'-di-3-thiolene-2-one (XVII b) was prepared. The syntheses of these compounds were performed as indicated in the following scheme.



The bithienyl XIV a has been prepared and described earlier.<sup>4</sup> The starting material was 2,4-dibromothiophene; the  $\alpha$ -bromine was exchanged for lithium and the corresponding thienyllithium was converted to 4-bromo-2-thiophene-aldehyde, which upon Wolf-Kishner reduction, gave XII a. Treatment with butyllithium followed by reacting the 3-thienyllithium derivative with cupric chloride gave XIV a. The same route was applied in the synthesis of XIV b; the synthesis of an appropriate 4-halo-2-*tert*.butylthiophene suitable for the halogen-metal exchange is discussed later. The bithienyls were then treated in the same way as 2-*tert*.butylthiophene (I) in order to obtain the di-thiolene-2-ones.

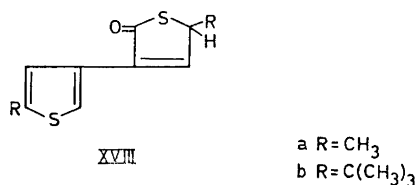
In the first synthesis of the methyl derivative, the boronic acid was isolated, but as it had a great tendency to deboronate, the yield of 5,5'-dimethyl-3,3'-di-3-thiolene-2-one upon oxidation was very low. An increase in yield was

obtained when the boronic ester was directly oxidized with 30 % hydrogen peroxide solution. This "one-pot" method was also utilized in the preparation of the thiolene-2-ones. Even if the yield in this case was not improved, and larger quantities of the more stable tautomeric form (V) was obtained, this direct method saves a lot of work if the preparation of the tautomeric mixture is the main interest.

The crude products from these syntheses were column chromatographed on silica gel. Three components could be separated, namely the recovered bithienyls (XIV), the dithiolene-2-ones (XVII), and smaller amounts of the 3(5'-alkyl-3'-thienyl)-5-alkyl-3-thiolene-2-ones (XVIII).

The NMR spectrum of 5,5'-dimethyl-3,3'-dithiolene-2-one consists of a doublet at 1.60  $\tau$  due to the 4-hydrogen and of a quartet of doublets at 5.50  $\tau$  due to the  $sp_3$ -hybridized hydrogen. The quartet structure is caused by coupling to the methyl group. The magnitude of the coupling, 7.40 c/s, indicates that the coupling is geminal. The methyl group has its absorption as a doublet at 8.35  $\tau$ . These data indicate that 5,5'-dimethyl-3,3'-dithiolene-2-one exists in its conjugated 3-thiolene form XVII a. When the substituent is changed to tert.butyl, the NMR-spectrum is identical with the NMR-spectrum of the by-product isolated in the synthesis of the 5-tert.butylthiolene-2-one system. As mentioned above, it is not possible from NMR data to distinguish between VI and VII, but since a tert.butyl group has smaller ability than a methyl group to stabilize a 4-thiolene-2-one form,<sup>1</sup> the conjugated form VII (= XVII b) must even in this case be the right structure. The by-product and an authentic sample of 5,5'-ditert.butyl-3,3'-di-3-thiolene-2-one had also identical IR-spectra and melting points. The amount of by-product obtained in the synthesis of the 5-methylthiolene-2-one system was not sufficient for running an NMR-spectrum. However, the IR-spectrum of it was similar to an authentic sample of 5,5'-di-methyl-3,3'-di-3-thiolene-2-one.

Probably due to deboronation, monosubstituted bithienyls XVIII were obtained. The NMR-spectra of these compounds proved their structures. The spectrum of 3(5'-methyl-3'-thienyl)-5-methyl-3-thiolene-2-one is given in Fig. 1. The quintet in the aromatic region is due to the 4'-hydrogen, which couples with comparable magnitude to the  $\text{CH}_3'$  group (1.10 c/s)<sup>5</sup> and to the 2'-hydrogen (1.25 c/s)<sup>6</sup> which have their absorptions at 7.55  $\tau$  and 2.25  $\tau$ , respectively. The 5-proton resonance at 5.60  $\tau$  has splittings of 7.15 c/s and 3.05 c/s, due to couplings to the geminal methyl group and to the 4-hydrogen, giving bands at 8.43  $\tau$  and 2.65  $\tau$ , respectively. These constants fall in the



Scheme IV

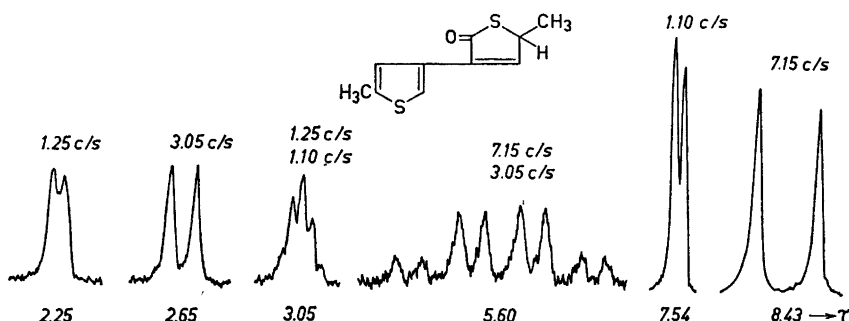
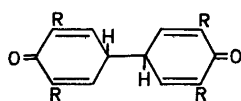


Fig. 1. NMR-spectrum of 3(5'-Methyl-3'-thienyl)-5-methyl-3-thiolen-2-one in deuteriochloroform.

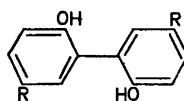
same intervals as the corresponding constants of the 5-alkyl-substituted 3-thiolen-2-ones.<sup>1,7</sup> The NMR-spectrum of the tert.butyl analogue is simpler, as the side chain couplings are missing. It consists of two doublets at 2.15  $\tau$  and 2.95  $\tau$  with splittings of 1.45 c/s, corresponding to the thiophene ring hydrogens,<sup>6</sup> and two doublets at 2.50  $\tau$  and 5.75  $\tau$ , with splittings of 3.00 c/s, belonging to the 3-thiolen-2-one ring absorptions. The tert.butyl groups in the two rings have their resonances at 8.55  $\tau$  and 8.85  $\tau$ , the tert.butyl group in the thiophene ring having absorption at lower field.

### Oxidative coupling reactions

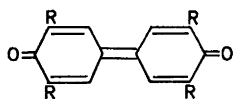
Several attempts were made to prepare the dithiolen-2-ones by oxidation of the monomers; positive results were obtained with potassium ferricyanide. When this reagent was applied to hindered phenols, products of the type



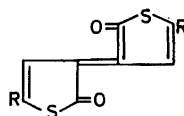
XIX



XX



XXI



XXII

Scheme V

R=C(CH<sub>3</sub>)<sub>3</sub>

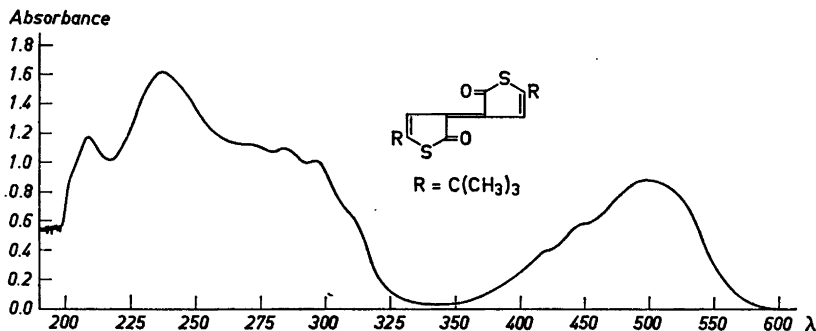


Fig. 2. UV-spectrum of 5,5'-ditert.butyl-3,3'-dehydro-di-4-thiolene-2-one in ethanol.

XIX and XX were isolated.<sup>8,9</sup> When the 5-tert.butyl-thiolene-2-one system was oxidized with potassium ferricyanide the indigoid compound XXII was obtained. It was characterized by its NMR-spectrum, which consisted of two sharp peaks at 2.45  $\tau$  and 8.65  $\tau$ , and by elementary analysis. The UV-spectrum of this red-brown substance with purple fluorescence is given in Fig. 2. Compound XXII was also obtained when chloranil was used as oxidizing agent. When VII was treated with potassium ferricyanide under identical conditions, the starting material was recovered in quantitative yield. This indicates that neither VII nor its tautomeric form VI, assuming that VII occurs in tautomeric equilibrium with VI, are intermediates in the oxidation. In the study of hindered phenols, potassium ferricyanide was the milder reagent giving compound XIX; the diphenoquinone XXI, corresponding to XXII, was obtained through base-catalyzed oxidation by oxygen.<sup>8</sup>

In the oxidation of the 5-methylthiolene-2-one system, the products were not well-defined. The 5-methylthiolene-2-one system is more reactive than the 5-tert.butylthiolene-2-one system due to the  $\alpha$ -hydrogens in the side chain and quinone methide-like intermediates can be formed as in the case of phenols.<sup>10</sup> These intermediates are probably even more reactive than the thiolene-2-ones and can be converted to a great number of dimeric species, which also is observed for phenols.<sup>11</sup>

#### Halogenation and dehalogenation of 2-tert.butylthiophene

When thiophene is alkylated with isobutylene using sulfuric acid as catalyst,<sup>12</sup> an isomeric mixture consisting of 2- and 3-tert.butylthiophene is obtained. This mixture is difficultly separated by distillation,<sup>13</sup> hence it was treated with butyllithium and carbon dioxide. The acids so obtained were separated by repeated crystallisation from ligroin.<sup>14</sup> 5-tert.butyl-2-thiophenecarboxylic acid is the less soluble isomer and is easily decarboxylated by using the copper and quinoline method<sup>19</sup> giving isomer-free 2-tert.butylthiophene.

In order to obtain a 4-halo-2-*tert.*butylthiophene for the halogen-metal exchange reaction in the synthesis of 5,5'-ditert.butyl-3,3'-bithienyl described above, 2-*tert.*butylthiophene was first dibrominated in acetic acid. The first bromine entered naturally the 5-position, but the second did not selectively go to the 4-position. The NMR-spectrum of this product showed two sharp peaks with relative intensities of 3:7 in the aromatic region. The dominating component at higher field ought to belong to the 4-substituted compound, in which the  $\beta$ -hydrogen is *ortho* to the *tert.*butyl group. The dehalogenated product, which was obtained by treatment with one equivalent of butyllithium at low temperature, verified this conclusion, as its NMR-spectrum showed that it consisted of 76 % 4-bromo-2-*tert.*butylthiophene and 24 % 3-bromo-2-*tert.*butylthiophene. These assignments are based on the coupling constants  $J_{35} = 1.40$  c/s and  $J_{45} = 5.15$  c/s, which fall in the intervals characteristic for 2,4- and 2,3-disubstituted thiophene compounds.<sup>6</sup> As the orientation of bromination in many cases is a function of the solvent,<sup>15</sup> carbon tetrachloride was used instead of acetic acid. Even if the 4-position was somewhat more favoured by the second bromine atom (76 % compared to 70 %), this improvement was not good enough. A more space-requiring reagent, however, had the desired effect. Thus iodination of 5-bromo-2-*tert.*butylthiophene with iodine-iodic acid<sup>16</sup> gave a more satisfying isomer distribution, 3-substitution being reduced to 15 %. In the dehalogenation reaction with butyllithium some rearrangement occurred, the product consisting of two different 2,4-disubstituted components. However, the best result was obtained when 2-*tert.*butylthiophene was diiodinated; the second iodine entered in 94 % the 4-position and in 6 % the 3-position. Upon dehalogenation, 97 % of the product consisted of 4-iodo-2-*tert.*butylthiophene. The isomer distribution was determined by integration of the *tert.*butyl peaks in the NMR-spectrum. The 3-iodo-2-*tert.*butylthiophene could not be separated by preparative gas-chromatography. However, it did not interfere in the bithienyl synthesis, as crystalline isomer-free 5,5'-ditert.butyl-3,3'-bithienyl was obtained after one recrystallization of the crude product from petroleum ether.

## EXPERIMENTAL

*2-tert.*Butylthiophene. A mixture consisting of 100 g (0.543 mole) of 5-*tert.*butyl-2-thiophene carboxylic acid,<sup>14</sup> 360 ml of quinoline, and 26.2 g of copper powder was carefully heated to reflux under stirring. After refluxing for one hour the mixture was distilled. The distillate was acidified with 6 N hydrochloric acid and extracted with ether. The ether phase was washed twice with dilute hydrochloric acid and once with water, dried over calcium chloride and distilled, giving 66 g (87 %) of 2-*tert.*butylthiophene, b.p. 167°,  $n_D^{20} = 1.4983$ . (Literature value<sup>13</sup> b.p. 163°/751 mm Hg,  $n_D^{20} = 1.4980$ ).

*5-tert.*Butyl-4-thiolen-2-one. 190 ml of ethereal 1.15 N butyllithium were added dropwise to 28 g (0.2 mole) of 2-*tert.*butylthiophene in 200 ml of anhydrous ether under nitrogen at room temperature at such a rate as to maintain gentle reflux. The resulting thienyllithium derivative was refluxed for a further half hour, cooled to  $-70^\circ$  and treated with 65 g (0.28 mole) of butyl borate in 150 ml of dry ether. After stirring at  $-70^\circ$  for 4 h, the reaction mixture was allowed to warm to  $0^\circ$  and then shaken with 100 ml of 2 N hydrochloric acid. The organic layer was separated and the aqueous phase extracted with ether. The combined ethereal phases were extracted with three portions of cold 2 N sodium hydroxide solution. After acidifying the alkaline solution with cold sulphuric acid, the oily boronic acid was immediately taken up in ether and the ethereal solution

treated dropwise with 100 ml of 10 % hydrogen peroxide solution under nitrogen. The stirred mixture was refluxed for 1.5 h, cooled, the layers separated, and the water phase extracted with ether. The combined ethereal phases were washed with cold water until the wash water did not oxidize ferrous ammonium sulphate, dried over magnesium sulphate and distilled, giving 19.3 g (62 %) of 5-*tert*.butyl-4-thiolene-2-one, b.p. 112–114°/11 mm Hg,  $n_D^{20} = 1.5044$ . (The spectroscopic data are given in Ref. 1).

When the residue after distillation was treated with chloroform, 0.5 g (1.6 %) of 5,5'-ditert.butyl-3,3'-di-3-thiolene-2-one, m.p. 218–220°, was obtained. The spectroscopic data were identical with those obtained for the authentic sample described below.

*5,5'-Ditert.butyl-2,2'-diacetoxy-3,3'-bithienyl*. 0.2 g (0.645 mmole) of 5,5'-ditert.butyl-3,3'-di-3-thiolene-2-one was refluxed for 4 h with excess of acetyl chloride. The unreacted acetyl chloride was removed at reduced pressure and the residue recrystallized from petroleum ether,\* giving a quantitative yield of 5,5'-ditert.butyl-2,2'-diacetoxy-3,3'-bithienyl, m.p. 162–165°. (Found: C 60.9; H 6.79; S 16.2. Calc. for  $C_{20}H_{26}O_4S_3$  (394.55): C 60.9; H 6.64; S 16.3). IR-spectrum (KBr): C=O 1760  $cm^{-1}$ . NMR-spectrum ( $DCCl_3$ ):  $\tau_{Bu} = 8.45$ ,  $\tau_{COCH_3} = 7.75$ ,  $\tau_{H_4} = 3.45$ .

*5-Iodo-2-tert.butylthiophene*. A mixture of 42 g (0.3 mole) of 2-*tert*.butylthiophene, 120 ml of acetic acid, 45 ml of water, 30 ml of carbon tetrachloride, 2.1 ml of conc. sulphuric acid, 30.6 g of iodine and 12.3 g of iodic acid was refluxed for 4 h. The reaction mixture was cooled to room temperature and 100 ml of water was added. The phases were separated and the water phase was extracted with carbon tetrachloride. The combined organic phases were washed with sodium hydrosulphite solution, dried over calcium chloride and distilled, giving 69 g (86.5 %) of 5-iodo-2-*tert*.butylthiophene, b.p. 114°/10 mm Hg,  $n_D^{20} = 1.5765$ . (Literature value<sup>17</sup> b.p. 123°/13 mm Hg,  $n_D^{22} = 1.5832$ ). NMR-spectrum ( $CCl_4$ ):  $\tau_{Bu} = 8.65$ ,  $\tau_{H_3} = 3.70$ ,  $\tau_{H_4} = 3.05$  and  $J_{34} = 3.70$  c/s.

*Iodination of 5-iodo-2-tert.butylthiophene*. 64 g (0.24 mole) of 5-iodo-2-*tert*.butylthiophene were iodinated as above with a mixture of 96 ml of acetic acid, 36 ml of water, 24 ml of carbon tetrachloride, 1.7 ml of sulphuric acid, 24.4 g of iodine and 9.8 g of iodic acid, giving 82 g (87 %) of an isomeric mixture, b.p. 174°/11 mm Hg,  $n_D^{20} = 1.6439$ . (Found: C 24.0; H 2.60. Calc. for  $C_8H_{10}I_2S$  (392.05): C 24.51; H 2.57). NMR-spectrum ( $CCl_4$ ): the product consisted of 94 % of 4,5-diiodo-2-*tert*.butylthiophene  $\tau_{Bu} = 8.65$ ,  $\tau_{H_3} = 3.40$ , and 6 % of 3,5-diiodo-2-*tert*.butylthiophene  $\tau_{Bu} = 8.50$ ,  $\tau_{H_4} = 2.90$ .

*Diiodination of 2-tert.butylthiophene*. 7 g (0.05 mole) of 2-*tert*.butylthiophene were treated in the same way as above with 40 ml of acetic acid, 15 ml of water, 10 ml of carbon tetrachloride, 0.7 ml of conc. sulphuric acid, 10.2 g of iodine, and 4.1 g of iodic acid, giving 14 g (72 %) of a mixture of 4,5-diiodo-2-*tert*.butylthiophene and 3,5-diiodo-2-*tert*.butylthiophene. The mixture was identical with the one described above.

*Dehalogenation of diiodated 2-tert.butylthiophene*. 178 ml of ethereal 1.15 N butyllithium were added dropwise to 72 g (0.185 mole) of diiodated-2-*tert*.butylthiophene under nitrogen at  $-70^\circ$ . 5 min after the addition was completed, the reaction mixture was poured into water. The phases were separated and the water phase was extracted twice with ether. The combined ethereal phases were washed with water, dried over magnesium sulphate and distilled, giving 39 g (79 %) of monoiodo-2-*tert*.butylthiophene, b.p. 114–115°C/11 mm Hg,  $n_D^{20} = 1.5790$ . (Found: C 36.0; H 4.22; S 12.05. Calc. for  $C_8H_{11}IS$  (266.15): C 36.1; H 4.17; S 12.05). NMR-spectrum ( $CCl_4$ ): the product consisted of 97 % of 4-iodo-2-*tert*.butylthiophene  $\tau_{(CH_2)_3} = 8.65$ ,  $\tau_{H_3} = 3.30$ ,  $\tau_{H_4} = 2.95$ ,  $J_{24} = 1.30$  c/s, and 3 % of 3-iodo-2-*tert*.butylthiophene  $\tau_{(CH_2)_3} = 8.50$ ,  $\tau_{H_4} = 3.20$ ,  $\tau_{H_3} = 3.05$ ,  $J_{45} = 5.20$  c/s.

*5,5'-Ditert.butyl-3,3'-bithienyl*. 39 g (0.147 mole) of 4-iodo-2-*tert*.butylthiophene (97 % pure) in 100 ml of anhydrous ether were added during 5 min under vigorous stirring to 141 ml of ethereal 1.15 N butyllithium cooled to  $-70^\circ$  in a nitrogen-swept four-necked flask. After 5 min, 30.4 g (0.185 mole) of anhydrous cupric chloride were added and the mixture was stirred for 3 h at  $-70^\circ$ . After stirring at room temperature for an additional 3 h, 150 ml of 5 N hydrochloric acid were added with cooling and stirring. The phases were separated and the ether phase was extracted with 5 N hydrochloric acid in order to remove the cuprous chloride formed in the reaction. After washing the ether phase with water, sodium carbonate solution and again with water, the organic

\* The petroleum ether used in all experiments had b.p. 30–65°.



phase was dried and the volatile matter removed *in vacuo*. The crystalline residue was recrystallized from petroleum ether, yielding 9.8 g (48 %) of 5,5'-ditert.butyl-3,3'-bithienyl, m.p. 116–117°, as white needles. (Found: C 68.0; H 7.87; S 23.0. Calc. for  $C_{16}H_{22}S_2$  (278.48): C 69.0; H 7.96; S 23.03). NMR-spectrum ( $DCCl_3$ ):  $\tau_{C(CH_3)_3} = 8.60$ ,  $\tau_{H_3} = 2.90$ ,  $\tau_{H_4} = 3.00$  and  $J_{34} = 1.45$  c/s.

*5,5'-Ditert.butyl-3,3'-di-3-thiolene-2-one*. 55 ml of ethereal 1.10 N butyllithium were added dropwise to 7.7 g (0.0277 mole) of 5,5'-ditert.butyl-3,3'-bithienyl in 350 ml of anhydrous ether under nitrogen at room temperature at such a rate as to maintain gentle reflux. The mixture was refluxed for a further hour and then cooled to  $-70^\circ$  and treated with 18 g (0.078 mole) of butyl borate in 50 ml of dry ether. After stirring at  $-70^\circ$  for 4 h the reaction mixture was allowed to warm to room temperature and treated dropwise with 10 ml of 30 % hydrogen peroxide solution. The reaction mixture was then refluxed for one hour with vigorous stirring, cooled, the layers separated, the ether phase washed three times with water and dried over magnesium sulphate. After evaporating volatile matter, 7.2 g of crude product was obtained. NMR-analysis showed that it contained 76 % of 5,5'-ditert.butyl-3,3'-bithienyl and 24 % of a mixture of 3-(5'-tert.butyl-3,3'-thienyl)-5-tert.butyl-3-thiolene-2-one and 5,5'-ditert.butyl-3,3'-di-3-thiolene-2-one. The three components were separated on a column filled with silica gel and eluted with a 1:1 petroleum ether:chloroform mixture. The first fractions contained the bithienyl, then followed the mono-substituted bithienyl (*cf.* below), and last the dithiolene-2-one. Recrystallization from the same solvent mixture gave 1.3 g (15 %) of 5,5'-tert.butyl-3,3'-di-3-thiolene-2-one, m.p. 219–220°, in small white needles. (Found: C 61.2; H 7.10; S 20.35. Calc. for  $C_{16}H_{22}O_2S_2$  (310.48): C 61.9; H 7.14; S 20.66). IR-spectrum (KBr):  $C=O$  1663  $cm^{-1}$ . UV-spectrum (ethanol):  $\lambda_{max} = 246.5$   $m\mu$  ( $\log \epsilon = 4.17$ ). NMR-spectrum ( $DCCl_3$ ):  $\tau_{C(CH_3)_3} = 8.85$ ,  $\tau_{H_3} = 5.65$ ,  $\tau_{H_4} = 1.55$  and  $J_{45} = 2.30$  c/s.

*3(5'-tert.butyl-3'-thienyl)-5-tert.butyl-3-thiolene-2-one*. The crude material obtained by chromatographic separation in the above preparation was recrystallized from petroleum ether, giving 0.25 g of white crystals, m.p. 93–94°. (Found: C 65.6; H 7.67; S 22.05. Calc. for  $C_{16}H_{22}OS_2$  (294.48): C 65.3; H 7.53; S 21.8). IR-spectrum (KBr):  $C=O$  1660 and 1671  $cm^{-1}$ . UV-spectrum (ethanol):  $\lambda_{max} = 208$ , 237, 262  $m\mu$  ( $\log \epsilon = 4.35$ , 4.00, 4.06). NMR-spectrum ( $DCCl_3$ ):  $\tau_{C(CH_3)_3} = 8.85$ ,  $\tau_{C(CH_3)_3}' = 8.55$ ,  $\tau_{H_3} = 5.75$ ,  $\tau_{H_4} = 2.50$ ,  $\tau_{H_3}' = 2.15$ ,  $\tau_{H_4}' = 2.95$ ,  $J_{45} = 3.00$  c/s and  $J_{24} = 1.45$  c/s.

*5,5'-Ditert.butyl-3,3'-dehydro-di-4-thiolene-2-one*. 1.65 g (0.01 mole) of 5-tert.butylthiolene-2-one \* in 25 ml of benzene were added dropwise under nitrogen to a well stirred mixture of 12 g of potassium ferricyanide, 50 ml of water, 100 ml of benzene and 2 g of potassium hydroxide. The red coloured solution was poured onto crushed ice, the benzene layer was separated, washed with water and dried over sodium sulphate. The solvent was removed at reduced pressure giving 1.2 g (78 %) of crude product. Crystallization from petroleum ether gave red-brown palettes with a purple fluorescence, m.p. 198–199°. (Found: C 61.9; H 6.48; S 20.4. Calc. for  $C_{16}H_{22}O_2S_2$  (308.46): C 62.3; H 6.54; S 27.14). IR-spectrum (KBr):  $C=O$  1670  $cm^{-1}$ . UV-spectrum Fig. 2. NMR-spectrum ( $DCCl_3$ ):  $\tau_{C(CH_3)_3} = 8.65$ ,  $\tau_{H_3} = 2.45$ .

*5,5'-Dimethyl-3,3'-bithienyl* was prepared as described in Ref. 4. NMR-spectrum ( $DCCl_3$ ):  $\tau_{CH_3} = 7.50$ ,  $\tau_{H_3} = 3.05$ ,  $\tau_{H_2} = 2.95$ ,  $J_{24} = 1.50$  c/s and  $J_{CH_3-H_4} = 1.05$  c/s.

*5,5'-Dimethyl-3,3'-di-3-thiolene-2-one* was prepared from 7.5 g (0.0387 mole) of 5,5'-dimethyl-3,3'-bithienyl, 75 ml of 1.15 N butyllithium, 25 g of butyl borate and 52 ml of 10 % hydrogen peroxide solution by a method analogous to the preparation of 5,5'-tert.butyl-3,3'-di-3-thiolene-2-one described above. NMR-analysis showed that the crude product, 7.4 g, contained 80 % unchanged bithienyl and 20 % of 3(5'-methyl-3'-thienyl)-5-methyl-3-thiolene-2-one and 5,5'-dimethyl-3,3'-di-3-thiolene-2-one. The three components were separated on a column filled with silica gel and eluted with a 1:1 mixture of chloroform:petroleum ether. Recrystallizing the third component from 3:1 petroleum ether:chloroform gave 1.5 g (17 %) of 5,5'-dimethyl-3,3'-di-3-thiolene-2-one, m.p. 165–168°, in yellow crystals. (Found: C 52.0; H 4.31; S 27.7. Calc. for  $C_{10}H_{10}O_2S_2$  (236.32): C 50.8; H 4.27; S 27.14). IR-spectrum (KBr):  $C=O$  1672  $cm^{-1}$ . UV-spectrum (ethanol):  $\lambda_{max} = 202$ , 241.5  $m\mu$  ( $\log \epsilon = 3.88$ , 4.15). NMR-spectrum ( $DCCl_3$ ):  $\tau_{C(CH_3)_3} = 8.35$ ,  $\tau_{H_3} = 5.50$ ,  $\tau_{H_4} = 1.60$ ,  $J_{H_3-CH_3} = 7.40$  c/s,  $J_{45} = 2.50$  c/s.

\* Either the 3- or the 4-thiolene-2-one form<sup>1</sup> or a mixture of both.

*3(5'-Methyl-3'-thienyl)-5-methyl-3-thiolene-2-one.* In the middle fraction of the synthesis described above, 0.2 g of this compound, m.p. 77–78°, was obtained in white crystals upon recrystallization from petroleum ether. (Found: C 56.5; H 4.70; S 30.50. Calc. for  $C_{10}H_{10}OS_2$  (210.3): C 57.1; H 4.79; S 30.50). IR-spectrum (KBr): C=O 1663  $cm^{-1}$ . UV-spectrum (ethanol):  $\lambda_{max} = 207, 247, 257 m\mu$  ( $\log \epsilon = 4.32, 4.00, 4.03$ ). NMR-spectrum ( $DCCl_3$ ): Fig. 1.

*5-Bromo-2-tert.butylthiophene.* 11 ml (0.20 mole) of bromine in 50 ml of acetic acid were added dropwise to 28 g (0.20 mole) of 2-tert.butylthiophene in 100 ml of acetic acid at 0°. After addition, the ice-bath was removed, the reaction mixture was stirred at room temperature for 2 h, and then poured into ice-water. The product was extracted with five portions of ether, the combined ether phases were washed with sodium hydrosulphite and water and dried over magnesium sulphate. Distillation gave 32.4 g (74 %) of 5-bromo-2-tert.butylthiophene, b.p. 102°/12 mm Hg,  $n_D^{20} = 1.5360$ . (Literature value<sup>18</sup> b.p. 102–103°/16 mm Hg,  $n_D^{20} = 1.5291$ ). NMR-spectrum ( $CCl_4$ ):  $\tau_{C(CH_3)_3} = 8.66$ ,  $\tau_{H_3} = 3.50$ ,  $\tau_{H_4} = 3.25$  and  $J_{34} = 3.80$  c/s.

*Bromination of 5-bromo-2-tert.butylthiophene.* 10.9 g (0.05 mole) of 5-bromo-2-tert.butylthiophene in 50 ml of acetic acid were treated with 2.7 ml (0.05 mole) of bromine in 10 ml of acetic acid, and worked up as described above. Distillation gave a fore-run containing 2.1 g of 5-bromo-2-tert.butylthiophene and 5.5 g (38 %) of an isomeric mixture b.p. 132°/10 mm Hg,  $n_D^{20} = 1.5724$ . NMR-spectrum ( $CCl_4$ ): the product consisted of 70 % of 4,5-dibromo-2-tert.butylthiophene  $\tau_{C(CH_3)_3} = 8.67$ ,  $\tau_{H_3} = 3.40$ , and 30 % of 3,5-di-bromo-2-tert.butylthiophene  $\tau_{C(CH_3)_3} = 8.53$ ,  $\tau_{H_4} = 3.20$ .

*Dehalogenation of dibrominated 2-tert.butylthiophene.* To 4.5 g (0.0151 mole) of the dibrominated product obtained above were dropped 16 ml of 1.03 N butyllithium. After 5 min, the reaction mixture was poured into water. The phases were separated and the water phase extracted twice with ether. The combined ether phases were washed with water, dried over magnesium sulphate and distilled, giving 2.5 g (75 %) of an isomeric mixture, b.p. 103°/13 mm Hg.

NMR-spectrum ( $CCl_4$ ): product consisted of 76 % of 4-bromo-2-tert.butylthiophene  $\tau_{C(CH_3)_3} = 8.63$ ,  $\tau_{H_3} = 3.30$ ,  $\tau_{H_4} = 3.10$ ,  $J_{35} = 1.40$  c/s and 24 % of 3-bromo-2-tert.butylthiophene  $\tau_{C(CH_3)_3} = 8.49$ ,  $\tau_{H_4} = 3.20$ ,  $\tau_{H_3} = 3.10$ ,  $J_{45} = 5.15$ .

*Dibromination of 2-tert.butylthiophene.* 3.1 ml (0.057 mole) of bromine in 10 ml of carbon tetrachloride were added dropwise to 4 g (0.0286 mole) of 2-tert.butylthiophene in 25 ml of carbon tetrachloride. After stirring at room temperature for 2 h, 50 ml of conc. potassium hydroxide were added and the reaction mixture was refluxed for half an hour. When the reaction mixture had cooled to room temperature the phases were separated and the water phase extracted with carbon tetrachloride. The combined organic phases were washed with water, dried over calcium chloride and distilled, giving 6 g (70.5 %) of an isomeric mixture, b.p. 132°/10 mm Hg,  $n_D^{20} = 1.5720$ . NMR-spectrum ( $CCl_4$ ): the product consisted of 76 % 4,5-dibromo-2-tert.butylthiophene and 24 % of 3,5-dibromo-2-tert.butylthiophene with the same chemical shifts as given above.

*Iodination of 5-bromo-2-tert.butylthiophene.* A mixture of 16.4 g (0.075 mole) of 5-bromo-2-tert.butylthiophene, 30 ml of acetic acid, 12 ml of water, 7.5 ml of carbon tetrachloride, 0.6 ml of conc. sulphuric acid, 7.6 g of iodine and 3.0 g of iodic acid was refluxed for 3 h. When the reaction mixture had cooled to room temperature water was added, the phases were separated and the water phase extracted with carbon tetrachloride. The combined organic phases were washed with sodium hydrosulphite and water, dried over calcium chloride and distilled, giving 18.6 g (72 %) of an isomeric mixture, b.p. 152°/11 mm Hg,  $n_D^{20} = 1.6041$ . NMR-spectrum ( $CCl_4$ ): the product consisted of 85 % of 4-iodo-5-bromo-2-tert.butylthiophene  $\tau_{C(CH_3)_3} = 8.65$ ,  $\tau_{H_3} = 3.40$  and 15 % of 3-iodo-5-bromo-2-tert.butylthiophene  $\tau_{C(CH_3)_3} = 8.50$ ,  $\tau_{H_4} = 3.05$ .

The UV-spectra were recorded on an Unicam SP 800 B spectrometer using ethanol as solvent. The IR-spectra were recorded on a Perkin-Elmer Model 257 instrument. The NMR-spectra were obtained on a Varian Associates A-60 high resolution NMR-spectrometer. The chemical shifts are given as  $\tau$ -values. The elementary analyses were carried out at the Analytical Department of the Chemical Institute.

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