Potentially Aromatic Thiophenium Ylides 4.* Formation and Cyclization of Methyl- and Methoxycarbonyl Substituted 2-(2′-Thienyl)benzoylcarbenes

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The catalytic decomposition of methyl- and methoxycarbonyl substituted 2-(2′-diazoacetylphenyl)thiophenes has been studied. The products are accounted for by assuming a primary formation of bicyclic thiophenium ylides. The ylides rearrange to thiopyrans, spirodihydrothiophenes, cyclopropathiophenes and naphthothiophenes depending on the substituents. The mechanisms for these reactions are briefly discussed.

Intra-molecular carbene attack on the sulfur atom in suitably substituted thiophenes are postulated to produce bicyclic thiophenium ylides.[2] Thus, catalytic decomposition of the diazo compound *1a* gives the unstable ylide *2a* which rearranges to the thiopyran *3a*, as recently reported in a short communication from this laboratory (Fig. 1).

As stable thiophenium ylides have been made by inter-molecular carbene attack on dimethylthiophenes,[3] we decided to try to stabilize *2a* by introducing two methyl groups in the thiophene part of the molecule. We report here the synthesis of the appropriate carbene precursors *1b* and *1c* together with the results of their catalytic decompositions. Also included are the experimental details for the synthesis and reactions of *1a* as these have not been reported earlier.

Results and discussion

The diazo keto esters *1a* and *1b* were made as outlined in Fig. 2. Dry Gomberg reactions provided the bromophenylthiophenes *4a* and *4b* in 67 % and 43 % yield, respectively. These were converted to the acid chlorides *5a* and *5b* via the acids in total yields of 66 % and 49 %, respec-

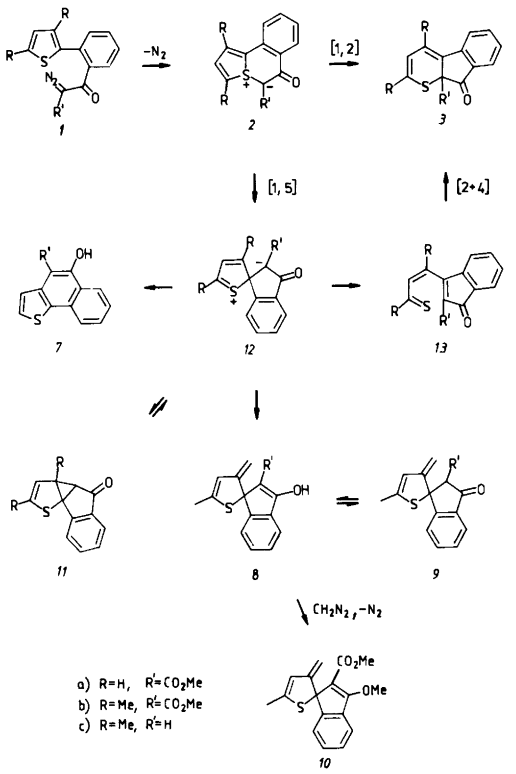

Fig. 1. Suggested reaction mechanisms for the catalytic reactions of *1a*, *1b* and *1c*.

*Part 3. See Ref. 1.

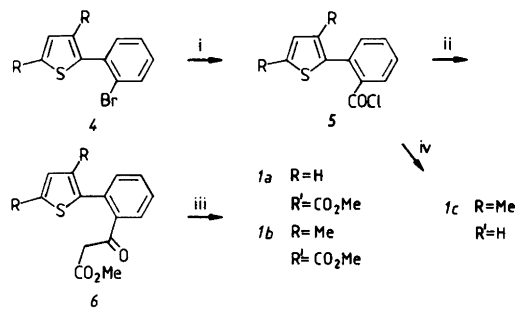

Fig. 2. Synthesis of the diazo keto esters *1a*, *1b* and *1c*. Reaction conditions: i) Mg, diethyl ether, CO_2, H^+, $SOCl_2$; ii) Dilithium methyl hydrogenmalonate, THF, H^+; iii) Tosylazide, triethylamin, benzene; iv) CH_2N_2.

tively. The acid chlorides were reacted with the dilithium salt of methyl hydrogenmalonate to give the keto esters *6a* and *6b*[4] in yields of 63 % and 68 %. A diazo transfer reaction with tosyl azide afforded the diazo keto esters *1a* and *1b*[5] in 92 % and 91 % yields. Treatment of *5b* with diazomethane eventually produced the diazo ketone *1c* in 95 % yield.

When rhodium(II) acetate was added to a solution of *1a* in benzene, the reaction was completed in 24 h at room temperature and the products were identified as the thiopyran *3a* (68 % yield) and naphthothiophene *7a* (25 % yield).[2] The structure of the thiopyran was proved by X-ray diffraction[6] and the naphthothiophene was identified by spectroscopic means (see Experimental).

Decomposition of the dimethyl substituted compound *1b* gave a different product mixture. The dimethylthiophyran *3b* was produced in only 22 % yield, whereas the major product (65 % yield, as calculated from NMR data) was identified by 2-D C–H heterocorrelated NMR as a 70:30 mixture of the spiro enol and spiro ketone *8b* and *9b*, respectively. The assignments of the methyl groups in *3b* were made by establishing a NOE effect between 4-Me and 5-H. The aromatic part was assigned by selective decoupling experiments. The acidity of the enol function made the isolation by flash chromatography difficult. The reaction mixture was therefore treated with diazomethane which selectively methylated the enol function,[7] giving the enol ether *10*. This made it possible to record an isolated yield of the enol ether of 70 %.

The reason for the prevalence of the enol *8b* in equilibrium with the ketone *9b* is evidently a result of an intra-molecular hydrogen bond between the enol and the ester functions in the former. This is also seen in the mass spectrum of *7b* where loss of MeOH ($m/z = 32$) is four times as abundant as the loss of MeO^+ ($m/z = 31$). *8b* is very susceptible to hydrolysis and decarboxylation. Even in benzene solution at room temperature it easily gives the decarboxylation product *9c* which as expected mainly exists in the keto form.

When a benzene solution of *1c* was treated as above with a catalytic amount of rhodium(II) acetate, unstable products were obtained. Therefore the reaction was carried out in an NMR tube. The reaction produced two products at about equal rates, and when the starting material was consumed the reaction mixture consisted of 47 % of the thiopyran *3c* and 47 % of the cyclopropathiophene *11c*. A small amount of the spiro ketone *9c* was also detected. Even after the disappearance of the starting material *1c*, the amount of thiopyran increased (although at half the rate). It turned out that the cyclopropathiophene was converted to thiopyran in the presence of the catalyst.

These results are summarized in Table 1.

As is evident from the table, there is a marked difference between these diazo compounds in their product distribution. Most likely the primary step is formation of a carbene or a carbenoid species which attacks the sulfur atom of the thiophene ring forming the ylides *2* (Fig. 1). Formation of thiopyrans *3* can then be envisioned as a [1,2] Stevens rearrangement. However, it is also possible that [1,5] sigmatropic rearrangements take place producing the zwitterionic intermediates *12*. Ring-opening of *12* to the thiocarbonyl compounds *13* followed by a [2+4] electrocyclization then give the thiopyrans *3*.

Support for the intermediates *12* comes from the work of Porter *et al.*[8,9] and also from the fact that all of our other products are easily explained as results of reactions of these intermetiates.

Interestingly, the most stable zwitterion *12b* (R=Me, R'=CO_2Me), gives the spiro dihydrothiophene *8b*⇄*9b* as the major product indicating that *12b* is more important than *2b* as a reaction intermediate. We conclude the formation of *8b*⇄*9b* is a result of the carbanionic center in *12b* acting as a base attacking one of the methyl protons in the adjacent methyl group. When the

Table 1. Isolated yields (%) from the rhodium(II) acetate catalysed decomposition of the diazo compounds.

Diazo compound	Thiopyran	Spiro dihydrothiophene	Cyclopropathiophene	Naphthothiophene
1	*3*	*10*	*11*	*7*
1a	68	–	–	25
1b	22	70	–	–
1c[a]	47 (92)	–	47 (0)	–
1d[b]	–	–	74	23

[a]These yields are calculated from NMR data.
[b]R = R′ = H from Ref. 1.

steric crowding in *12* is less pronounced, the zwitterion (*12c*, R=M2, R′=H) acts mainly as a nucleophile producing the cyclopropathiophene *11c*. This formation is, however, reversible, and eventually *11c* is converted to *3c* (together with a few percent of *9c*). The zwitterion *12* has the capacity of undergoing a [1,2] shift and for R=H, this will produce a more stable zwitterion. Aromatisation via proton abstraction and protonation at the oxygen atom will then give *7*.[1]

The cyclopropathiophene *11* is not observed for R′=CO_2Me. This could be due to steric reasons, but the ester group will stabilize the negative charge in the zwitterion and facilitate ring-opening of *11a* and *11b* to such an extent that the equilibrium could be totally driven to *12a* and *12b*.

The formation of the zwitterionic intermediates can also be regarded as a one-step reaction from the carbenes, the carbene acting as an electrophile attacking the 2′-carbon in the thiophene ring. However, the importance of this reaction which, as far as we know, is unknown in the literature, has to be confirmed by further experiments.

Experimental

The NMR spectra were recorded on Varian A 60, XL 300 and Bruker VM 400 and CX P200 instruments. The IR spectra were recorded with a Perkin-Elmer 281 instrument. The MS spectra were obtained with VG Micromass 7070 F. GLC analyses were carried out with a Hewlett Packard 5700 A. HPLC analyses were performed with a Perkin-Elmer Series 2 liquid chromatograph with a LC 75 detector and with 5 μm LC-18 Supelcosil column. Column chromatography was carried out using Merck No. 9385 Silica 60. The melting points were obtained with a Reichert Thermopan melting point microscope and are uncorrected.

2-(2′-Bromophenyl)-3,5-dimethylthiophene (4b). Isoamyl nitrite (20.5 g, 0.175 mol) was added to a solution of 2-bromoaniline (20.5 g, 0.119 mol) in 2,4-dimethylthiophene[10] (172 g, 1.54 mol) at 70 °C under nitrogen. The reaction mixture was stirred for 4 h and the 2,4-dimethylthiophene was removed under reduced pressure. The fraction that distilled between 70 and 100 °C/1.3 Pa was collected and redistilled. Yield 13.8 g (43 %), b.p. 75–82 °C/1.3 Pa. MS [IP 70 eV; *m/z* (% rel.int.]: 269 (13), 268 (100), 267 (38), 266 (99), 265 (27), 253 (18), 251 (18), 187 (15), 185 (13), 172 (19), 171 (21), 153 (11), 152 (12), 115 (10), 111 (17). ^{1}H NMR (60 MHz, $CDCl_3$): δ 2.0 (3H, s), 2.5 (3H, s), 6.6 (1H, s), 7.2 (2H, m), 7.6 (1H, m).

2-(2′Carboxyphenyl)-3,5-dimethylthiophene. 2-(2′-Bromophenyl)-3,5-dimethylthiophene (11 g, 0.042 mol) in tetrahydrofuran (50 ml) was added to magnesium (1.3 g, 0.053 mol) covered with tetrahydrofuran (10 ml) at reflux under nitrogen. The reaction usually started after 4 h and after the violent reaction had ceased it was stirred for 30 min and then quenched on solid carbon dioxide covered with dry diethyl ether. The acid was worked up according to standard procedure. Yield 7.6 g (77 %), m.p. 150–155 °C. MS[IP 70 eV; *m/z* (% rel.int.)]: 233 (15), 232 (100), 231 (11), 215 (10), 214 (24), 213 (12), 204 (45), 203 (15), 189 (16), 188 (26), 187 (24), 186 (23), 184 (37), 173 (12), 172 (10), 171 (30), 153 (15), 128 (10), 115 (16), 111 (15). ^{1}H NMR (60 MHz, Acetone-d_6): δ 2.0 (3H, s), 2.4 (3H, s), 6.6 (1H, s), 7.5 (3H, m), 7.9 (1H m), 9.0 (1H, broad s).

2-(2'-Chloroformylphenyl)-3,5-dimethylthiophene (5b). To 2-(2'-carboxyphenyl)-3,5-dimethylthiophene (7.0 g, 0.030 mol) was added thionyl chloride (20 ml). The mixture was stirred for 4 h at room temperature and the excess thionyl chloride was evaporated and the residue distilled. Yield 4.8 g (64 %), b.p. 116–120 °C/1.3 Pa. MS[IP 70 eV; *m/z* (% rel.int.)]: 252 (20), 250 (52), 215 (100), 187 (20), 185 (10), 172 (11), 171 (12). ^{1}H NMR (60 MHz, $CDCl_3$): δ 2.0 (3H, s), 2.4 (3H, s), 6.6 (1H, s), 7.4 (4H, m).

Methyl 3-[2'-(2''-thienyl)phenyl]3-oxopropanoate (6a). To a solution of methyl hydrogenmalonate (6.8 g, 0.058 mol) in tetrahydrofuran (200 ml) under nitrogen was added 2,2'-bipyridyl (1 mg) as an indicator. After cooling to −70 °C, butyllithium (hexane) (75 ml, 1.6 M, 0.12 mol) was added slowly while allowing the temperature to rise to −5 °C near the end of the addition. After the pink indicator persisted at −5 °C the heterogenous solution was recooled to −70 °C and 2-(2'-chloroformylphenyl)thiophene (6.2 g, 0.028 mol) in tetrahydrofuran (20 ml) was added dropwise (15 min). The yellow solution was allowed to reach room temperature overnight and poured into a mixture of 1M hydrochloric acid (100 ml) and ether (400 ml). The organic phase was washed with saturated bicarbonate (60 ml), water (100 ml), dried and distilled. Yield 4.6 g (63 %), b.p. 145–148 °C/4.0 Pa. MS[IP 70 eV; *m/z* (% rel.int.)]: 260 (32), 200 (19), 188 (13), 187 (100), 172 (12), 171 (17), 159 (17), 115 (61). ^{1}H NMR (60 MHz, $CDCl_3$): δ 3.4 (2H, s), 3.6 (3H, s), 7.0 (2H, m), 7.4 (5H, m), in equilibrium with 10 % *methyl 3-[2'-(2''-thienyl)-phenyl]-3-ol-2-propenoate*. ^{1}H NMR (60 MHz, $CDCl_3$): δ 3.7 (3H, s), 5.2 (1H, s), 7.0 (2H, m), 7.4 (5H, m), 12.3 (1H, s).

Methyl 3-[2'-(3'',5''-dimethyl-2''-thienyl)phenyl]3-oxopropanoate (6b). The product was made as above. Yield (68 %), b.p. 164–168 °C/6.6 Pa. MS[IP 70 eV; *m/z* (% rel.int.)]: 228 (33), 228 (12), 227 (18), 216 (18), 215 (100), 214 (89), 213 (22), 200 (34), 199 (40), 187 (28), 186 (13), 185 (30), 184 (17), 172 (16), 171 (26), 153 (17), 152 (16), 128 (10), 115 (14). ^{1}H NMR (60 MHz, $CDCl_3$): δ 2.0 (3H, s), 2.4 (3H, s), 3.4 (2H, s), 3.6 (3H, s), 6.6 (1H, s), 7.5 (4H, m), in equilibrium with 10 % *methyl 3-[2'-(3'',5''-dimethyl-2''-thienyl)phenyl]3-ol-2-propenoate*. ^{1}H NMR (60 MHz, $CDCl_3$): δ 2.1 (3H, s), 2.4 (3H, s), 3.7 (3H, s), 5.1 (1H, s), 6.6 (1H, s), 7.5 (4H, m), 12.3 (1H, s).

Methyl 3-[2'-(2''-thienyl)phenyl]2-diazo-3-oxopropanoate (1a). To a solution of methyl 3-[2'-(2''-thienyl)phenyl]3-oxopropanoate (2.0 g, 0.0077 mol) and tosylazide (1.5 g, 0.0077 mol) in benzene (30 ml) was added triethylamine (0.78 g, 0.0077 mol) at room temperature. The solution was allowed to stand overnight. The white precipitate was filtered and hexane (150 ml) was added to precipitate more of the tosyl amide. The hexane was decanted and the residue was extracted with hexane (50 ml). The combined hexane solutions was evaporated to give a yellow oil which crystallized on standing. Yield 2.0 g (92 %), m.p. 71–73 °C (MeOH). MS[IP 70 eV; *m/z* (% rel.int.)]: 286 (6), 258 (52), 226 (32), 200 (22), 199 (60), 187 (42), 173 (16), 172 (100), 171 (93), 170 (31), 127 (17), 126 (12), 115 (53). ^{1}H NMR (60 MHz, $CDCl_3$): δ 3.6 (3H, s), 7.1 (2H, m), 7.4 (5H, m). IR (KBr): 2116 (s) cm^{-1}.

Methyl 3-[2'-(3'',5''-dimethyl-2''-thienyl)phenyl]2-diazo-3-oxo-propanoate (1b). The product was made as above. Yield (91 %), m.p. 65–68 °C. MS[CI, isobutane; *m/z* (% rel.int.)]: 315 (50), 288 (14), 287 (69), 286 (27), 256 (13), 255 (76), 229 (11), 228 (22), 227 (100), 215 (11), 199 (13). ^{1}H NMR (60 MHz, $CDCl_3$): δ 2.0 (3H, s), 2.3 (3H, s), 3.6 (3H, s), 6.5 (1H, s), 7.4 (4H, s). IR (KBr): 2118 (s) cm^{-1}.

2-(2'-Diazoacetylphenyl)-3,5-dimethylthiophene (1c). Diazomethane (Diazald) (0.60 g, 0.014 mol) in dry diethylether (20 ml) was added to 2-(2'-chloroformylphenyl)-3,5-dimethylthiophene (1.0 g, 0.004 mol) in dry diethyl ether (40 ml) in an ice bath. The reaction mixture was allowed to stand overnight and was then evaporated. The yellow oil resisted crystallization. Yield 0.97 g (95 %). MS[IP 70 eV; *m/z* (% rel.int.)]: 229 (14), 228 (60, M-N_2), 227 (16), 226 (23), 215 (20), 214 (11), 213 (36), 201 (12), 200 (57), 199 (100), 198 (11), 197 (15), 186 (16), 185 (93), 184 (68), 171 (13), 165 (24), 152 (27), 141 (12), 139 (12), 115 (23). ^{1}H NMR (300 MHz, C_6D_6): δ 1.09 (3-Me, s), 2.12 (5-Me, d, *J* 1.2 Hz), 4.73 (−CH=N_2, m), 6.25 (H3, q, *J* 1.2 Hz), 7.03 (2H, m), 7.22 (1H, m), 7.79 (1H, br.s). ^{13}C NMR (75 MHz, C_6D_6): δ 14.36 (3-Me), 14.97 (5-Me), 128.23, 128.56,

128.83 (−CH=N_2), 129.25, 130.71, 132.10, 132.76 (q), 132.99 (q), 136.18 (q), 138.21 (q), 140.00 (q), (C=O) not found. IR (film): 2094 cm^{-1} (s).

General procedure for catalytic decomposition of the diazocompounds. To a solution of the diazo compound (2 mmol) in benzene (50 ml) at room temperature was added rhodium(II) acetate (1 mg). After 1 to 70 h the solvent was evaporated and the product was separated with flash chromatography.

Catalytic decomposition of 1a. The diazo keto ester 1a was decomposed catalytically to give 68 % of 3a and 25 % of 7a.

Methyl 9-oxo-10H-benzo[3,4]cyclopenta[1,2-b] thiopyran-10-carboxylate (3a). MS[IP 70 eV; *m/z* (% rel.int.)]: 258 (16), 226 (25), 200 (14), 199 (100), 171 (18), 170 (18). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.67 (Me, s), 6.52 (H3, dd, *J* 9.1 and 5.7 MHz), 6.63 (H2, d, *J* 9.1 Hz), 6.74 (H4, d, *J* 5.7 Hz), 7.44 (H7, m, *J* 7.8, 7.0 and 1.1 Hz), 7.71 (H6, m, *J* 7.6, 7.4 and 1.1 Hz), 7.8 (H5 and H8, m). ^{13} C NMR (50 MHz, $CDCl_3$): δ 53.75 (Me), 57.96 (C10), 117.15 (C4), 122.18 (C5), 122.67 (C3), 123.62 (C2), 125.10 (C8), 125.73 (C4a), 129.21 (C7), 134.47 (C8a), 136.19 (C6), 148.66 (4b), 167.59 (ester C=O), 194.30 (C9; *J* (Me, H), 148.2 Hz, *J* (C4, H4) 161.8 Hz, *J* (C4, H3) 9.0 Hz, *J* (C5, H5) 163.5 Hz, *J* (C5, H7) 7.6 Hz, *J* (C3, H3) 166.8 Hz, *J* (C2, H2) 179.7 Hz, *J* (C2, H4) 6.7 Hz, *J* (C2, H3) 3.8 Hz, *J* (C8, H8) 167.3 Hz, *J* (C8, H6) 7.6 Hz, *J* (C7, H7) 165.5 Hz, *J* (C7, H5) 6.9 Hz, *J* (C6, H6) 161.8 Hz, *J* (C6, H8) 7.5 Hz.

Methyl 5-hydroxy-naphtho[1,2-b]thiophene-4-carboxylate (7a). MS[IP 70 eV; *m/z* (% rel.int.)]: 258 (29), 227 (17), 226 (100), 171 (19), 170 (69), 169 (16), 126 (12), 85 (12). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.03 (Me, s), 7.36 (H2, d, *J* 5.5 Hz), 7.43 (H7, m, *J* 8.2, 7.0 and 1.2 Hz), 7.56 (H8, m, *J* 8.2, 7.0 and 1.4 Hz), 7.80 (H3, d, *J* 5.5 Hz), 7.87 (H9, dd, *J* 8.2 and 0.9 Hz), 8.36 (H6, m, *J* 8.4, 0.6 and 0.6 Hz), 12.74 (OH, s). ^{13}C NMR (75 MHz, $CDCl_3$)[x)]: δ 52.19 (Me), 101.44 (C4), 123.18 (C5a), 123.18 (C9), 125.13 (C2), 125.17 (C6), 125.46 (C7), 126.41 (C3), 130.18 (9b), 130.20 (C8), 131.56 (9a), 133.29 (C3a), 161.65 (C5), 172.18 (ester); *J* (Me, H) 147.9 Hz, *J* (C4, OH) 3.7 Hz, *J* (C5a, H7) 7.3 Hz, *J* (C5a, H9) 7.3 Hz, *J* (C9, H9) 158.1 Hz, *J* (C9, H7) 7.3 Hz, *J* (C2, H2) 185.0 Hz, *J* (C2, H3) 8.0 Hz, *J* (C6, H6) 164.2 Hz, *J* (C6, H8) 7.9 Hz, *J* (C7, H7) 161.7 Hz, *J* (C7, H9) 7.9 Hz, *J* (C3, H3) 172.7 Hz, *J* (C3, H2) 4.9 Hz, *J* (C9b, H2) 4.3 Hz, *J* (C8, H8) 159.7 Hz, *J* (C8, H6) 8.9 Hz, *J* (C9a, H6) 6.7 Hz, *J* (C9a, H8) 6.7 Hz, *J* (C3a, H2) 10.1 Hz, *J* (C3a, H3) 4.6 Hz, *J* (C5, OH) 3.6 Hz, *J* (C5, H6) 3.6 Hz, *J* (ester, Me) 3.8 hz.

[x)] For the details of the spectral assignments of *7a* see ref. 11.

Catalytic decomposition of 1b. Rhodium(II) acetate decomposition of 1b gave 22 % of 3b and 65 % (NMR) of a 7:3 mixture of the spiro enol 8b and the spiro ketone 9b. Selective methylation of 8b with diazomethane (Diazald) gave an isolated yield of the enol ether 10 of 70 %.

Methyl 2,4-dimethyl-9-oxo-10H-benzo[3,4]cyclopenta[1,2-b]thiopyran-10-carboxylate (3b). MS[IP 70 eV; *m/z* (% rel.int.)]: 286 (5), 229 (6), 228 (17), 227 (100), 187 (7), 165 (6). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.17 (2-Me, d, *J* 1.5 Hz), 2.30 (4-Me, s), 3.63 (ester, s), 6.12 (H3, 1, *J* 1.5 Hz), 7.37 (H7, m, *J* 7.6, 7.3 and 1.0 Hz), 7.70 (H6, m, *J* 8.3, 7.2 and 1.2 Hz), 7.86 (H8, m, *J* 7.6, 1.2 and 1.2 Hz), 7.88 (H5, d, *J* 8.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.81 (4-Me), 23.06 (2-Me), 53,65 (OMe), 62.71 (C10); 119.23 (C4a), 125.07 ($C8^x$), 125.30 ($C5^x$), 126.06 (C3), 127.61 (C7), 130.48 (C4), 135.04 (C8a), 136.16 (C6), 136.40 (C2), 149.40 (C4b), 168.22 (ester C=O), 195.10 (C9); *J* (4-Me, H), 127.6 Hz, *J* (4-Me, H3), 4.3 Hz, *J* (2-Me, H), 129.4 Hz, *J* (2-Me, H3), 5.5 Hz, *J* (OMe, H), 148.1 Hz, *J* (C8, H8) 163.9 Hz, *J* (C8, H6) 7.6 Hz, *J* (C5, H5) 164.2 Hz, *J* (C5, H7) 7.9 Hz, *J* (C3, H3) 160.5 Hz, *J* (C3, 2-Me) 5.5 Hz, *J* (C3, 4-Me) 5.5 Hz, *J* (C7, H7) 162.4 Hz, *J* (C7, H5) 6.8 Hz, *J* (C7, H6) 2.5 Hz, *J* (C4, 4-Me) 6.8 Hz, *J* (C8a, H7) 6.7 Hz, *J* (C8a, H5) 6.7 Hz, *J* (C6, H6) 166.0 Hz, *J* (C6, H8) 7.6 Hz, *J* (C6, H7) 2.7 Hz, *J* (C2, H3) 7.4 Hz, *J* (C2, 2-Me) 3.7 Hz, *J* (C4b, H8) 7.1 Hz, *J* (C4b, H6) 7.1 Hz, *J* (ester C=O, OMe) 3.6 Hz, *J* (C9, H8) 3.5 Hz.

Spiro(methyl 3-hydroxy-2-indene-2-carboxylate)-1,2'-(5'-methyl-3'-methylen-2',3'-dihydrothiophene) (8b). MS[IP 70 eV; *m/z* (% rel.int.)]: 287

(16), 286 (75), 271 (24), 254 (30), 239 (46), 228 (20), 227 (71), 226 (100), 213 (11), 199 (12), 198 (21), 197 (20), 184 (18), 165 (26), 152 (12), 139 (14), 115 (11). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.34 (5′-Me, s), 3.84 (H2″, s), 4.95 (CH_2, s), 5.11 (CH_2, s), 6.24 (H4′, s), 7.6 (4H, m), 10.97 (OH, broad s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.49 (5′-Me), 51.68 (O_2Me), 71.40 (C1), 99.87 (CH_2), 105.76 (C2), 120.93, 123.96, 128.38, 130.46 (C4′), 131.40, 134.12 (q), 146.97 (q), 149.32 (q), 149.68 (q), 171.18 (ester), (C3) not found, in equilibrium with 30 % *spiro(methyl 3-oxo-2-indene-2-carboxylate)-1,2′-(5′-methyl-3′-methylen-2′,3′-dihydrothiophene)* (9b). ^{1}H NMR 300 MHz, $CDCl_3$): δ 1.50 (5′-Me, s), 3.72 (O_2Me, s), 3.96 (H2, s), 4.97 (CH_2, s), 5.11 (CH_2, s), 6.11 (H4′, s), 7.6 (4H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.17 (5′-Me), 52.49 (O_2Me), 62.10 (C2), 101.43 (CH_2), 123.69, 126.10, 129.37 (C4′), 129.48, 136.46. Quaternary carbon not found.

Spiro(methyl 3-methoxy-2-indene-2-carboxylate)-1,2′-(5′-methyl-3′-methylen-2′,3′-dihydrothiophene) (10). MS[IP 70 eV; *m/z* (% rel.int.)]: 301 (14), 300 (67), 285 (28), 269 (15), 267 (13), 255 (21), 253 (12), 243 (17), 242 (18), 241 (100), 240 (13), 239 (11), 228 (15), 227 (25), 226 (94), 215 (22), 213 (18), 212 (10), 211 (13), 198 (11), 197 (21), 165 (15), 152 (13), 139 (21), 115 (11). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.38 (5′-Me, d, *J* 0.7 Hz), 3.77 (ester, s), 4.21 (ester, s), 4.94 (CH_2, d, *J* 0.6 Hz), 5.10 (CH_2, d, *J* 0.6 Hz), 6.23 (H4′, q, *J* 0.7 Hz), 7.38 (H5 and H6, m), 7.49 (H7, m, *J* 7.1, 1.2 and 1.0 Hz), 7.84 (H4, d, *J* 8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.47 (5′-Me), 51.44 (O_2Me), 61.32 (OMe), 74.73 (C1), 99.74 (CH_2), 111.15 (C2), 120.78 (C4), 123.63 (C6), 127.53 (C5), 130.04 (C7), 130.10 (C4′), 136.66 (C5′), 147.45 (C7a), 148.07 (C3a), 149.83 (C3′), 164.32 (ester), 164.72 (C3); *J* (5′-Me, H), 127.8 Hz, *J* (5′-Me, H4′) 3.3 Hz, *J* (O_2Me, H) 146.5 Hz, *J* (OMe, H) 146.7 Hz), *J* (CH_2, H) 161.8 Hz, *J* (C4, H4) 163.9 Hz, *J* (C4, H6) 6.7 Hz, *J* (C6, H6) 161.8 Hz, *J* (C6, H4) 8.0 Hz, *J* (C5, H5) 166.1 Hz, *J* (C5, H7) 7.9 Hz, *J* (C7, H7) 160 Hz, *J* (C4′, H4′), 160.9 Hz, *J* (C4′, Me) 7.1 Hz, *J* (C5′, Me) 4.3 Hz, *J* (C7a, H6) 6.4 Hz, *J* (C7a, H4) 6.4 Hz, *J* (C3a, H7) 7.1 Hz, *J* (C3a, OMe) 2.4 Hz, *J* (C3′, H4′) 8.6 Hz, *J* (ester C=O, O_2Me) 3.9 Hz, *J* (C3, H4) 3.4 Hz, *J* (C3, OMe) 3.4 Hz.

Catalytic decomposition of 1c. To the methyl diazo ketone 1c in a NMR tube was added the catalyst and the tube placed in the cavity of a NMR spectrometer. When the starting material was consumed the yields were 47 % of 11c and 47 % of 3c.

2,4-Dimethyl-10H-benzo[3,4]cyclopenta[1,2-b]thiopyran-9-one (3c). ^{1}H NMR (300 MHz, C_6D_6): δ 1.79 (2-Me, t, *J* 1.4 and 1.2 Hz) 1.79 (4-Me, s), 4.38 (H10, q, *J* 1.2 Hz), 5.75 (H3, q, *J* 1.4 Hz), 6.83 (H7, m, *J* 7.3 and 1.0 Hz), 7.10 (H6, m, *J* 8.3, 7.5 and 1.5 Hz), 7.38 (H8, m, *J* 8.3 Hz, 1.0 and 1.0 Hz), 7.75 (H5, m, *J* 7.6, 1.1 and 1.1 Hz). ^{13}C NMR (75 MHz, C_6D_6): δ 19.33 (4-Me), 23.13 (2-Me), 49.67 (C10), 117.45 (4a), 124.59 (C5*), 125.11 (C8*), 126.81 (C3), 127.44 (C7), 130.01 (C4), 135.10 (C6), 136.66 (C8a), 137.05 (C2), 148.24 (C4b), 198.46 (C9).

2,4-Dimethyl-4,10b-dihydro-inda[1′,2′-1,2]cyclopropa[1,3-b]thiophen-6-one (11c). ^{1}H NMR (300 MHz, C_6D_6): δ 0.86 (4-Me, d, *J* 1.5 Hz), 1.68 (2-Me, d, *J* 1.0 Hz), 2.00 (H5, m), 5.01 (H3, q, *J* 1.5 Hz), 6.86 (H8, m, *J* 8.7, 7.6 and 1.2 Hz), 7.01 (H9, m, *J* 8.6, 7.6 and 1.2 Hz), 7.32 (H10, d, *J* 7.3 Hz), 7.62 (H7, m, *J* 7.3, 1.0 and 1.0 Hz). ^{13}C NMR (75 MHz, C_6D_6): δ 13.30 (4-Me), 16.25 (2-Me), 39.37 (C5), 52.79 (C10b), 66.46 (C4), 123.69 (C10), 125.34 (C7*), 127.27 (C3*), 128.32 (C8), 134.05 (C9), 137.16 (C6a), 140.13 (C2), 148.58 (C10a), 198.74 (C6).

Spiro(3-indanone)-1,2′-(5′-methyl-3′-methylen-2′,3′-dihydrothiophene) (9c). ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.50 (5′-Me, s), 3.16 (H2, s), 4.94 (CH_2, s), 5.10 (CH_2, s), 6.07 (H4′, s), 7.62 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.84 (5′-Me), 51.17 (C2), 100.64 (=CH_2), 122.89 (C4), 126.05 (C7), 127.58 (C5), 128.96 (C4′), 135.93 (C6). Quaternary carbon not found.

References

1. Storflor, H. and Skramstad, J. *Acta Chem. Scand. B.* Submitted.
2. Storflor, H., Skramstad, J. and Nordenson, S. *J. Chem. Soc. Chem. Commun.* (1984) 208.

*Assignments uncertain.

3. Gillespie, R. J., Murray-Rust, J., Murray-Rust, P. and Porter, A. E. A. *J. Chem. Soc. Chem. Commun.* (1978) 83.
4. Wierenga, W. and Skulnick, H. I. *J. Org. Chem. 44* (1979) 310.
5. Wulfman, D. S., McGibboney, B. G., Steffen, E. K., Thinh, N. V., Daniel, R. S. and Peace, B. W. *Tetrahedron 32* (1976) 1257.
6. Nordenson, S., Storflor, H. and Skramstad, J. *To be published.*
7. Neeman, M. and Hashimoto, Y. *J. Am. Chem. Soc. 84* (1962) 2972.
8. Gillespie, R. J. and Porter, A. E. A. *J. Chem. Soc. Perkin Trans.* (1979) 2624.
9. Porter, A. E. A. *Personal communication* 1984.
10. Gronowitz, S., Cederlund, B. and Hörnfeldt, A.-B. *Chemica Scripta 5* (1974) 217.
11. Grace, D. and Storflor, H. *To be published.*

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