Additions of nucleophiles to 3-oxo-2,3-dihydrothiophene 1,1-dioxides. Formation of vinyl sulfides, thioacetals and enaminones

Nini Unn Hofsløkken and Lars Skattebøl

Department of Chemistry, University of Oslo, PO Box 1033 Blindern, N-0315 OSLO, Norway

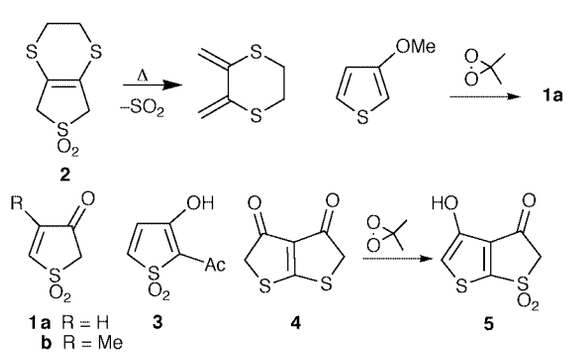
Received (in Lund, Sweden) 22nd March 1999, Accepted and transferred from Acta Chem. Scand., 2nd August, 1999

3-Oxo-2,3-dihydrothiophene 1,1-dioxide (**1a**) was prepared by oxidation of the commercially available 3-methoxythiophene with dimethyldioxirane. Some other substituted 3-methoxythiophene derivatives were oxidized as well. Although the yields of these reactions were low, the one-step method is preferred to the current literature procedures. 3-Oxo-2,3-dihydrothiophene 1,1-dioxide derivatives reacted with sulfur and nitrogen nucleophiles. Reactions took place with extrusion of sulfur dioxide even at room temperature. High yields of vinyl sulfides, thioacetals, bis-thioacetals, and enaminones were obtained from these reactions.

The 2-sulfolene derivative 3-oxo-2,3-dihydrothiophene 1,1-dioxide (**1a**) is ambivalent with regard to Michael additions of nucleophiles; it could behave either as an α,β-unsaturated ketone or as a vinyl sulfone by additions at carbons 2 and 3, respectively. We were actually interested in the selective addition of ethane-1,2-dithiol at carbon 3 with subsequent cyclisation to the 3-sulfolene derivative **2**. Previous work gave us reason to expect such a reaction path, provided compound **1a** would behave as a vinyl sulfone.[1] The thermally induced extrusion of sulfur dioxide from 3-sulfolenes is a well documented route to conjugated dienes,[2,3] and we anticipated that compound **2** would undergo such a thermal reaction with formation of 2,3-dimethylene-1,4-dithiane, the preparation and reactions of which were the original aims of our study. However, compound **1a** behaved exclusively as an α,β-unsaturated ketone by undergoing Michael additions at carbon 2 concomitant with sulfur dioxide extrusion. The present paper describes a novel way of preparing 3-oxo-2,3-dihydrothiophene 1,1-dioxide derivatives (**1**) and their reactions with thiols and amines. A preliminary account of part of the work has been reported.[4]

Results and discussion

At the time this project was initiated, there were two published, almost identical procedures for the preparation of ketone **1a**, of which we at first chose a four-step route starting from 3-sulfolene.[5] The overall yield of **1a** by this reaction sequence

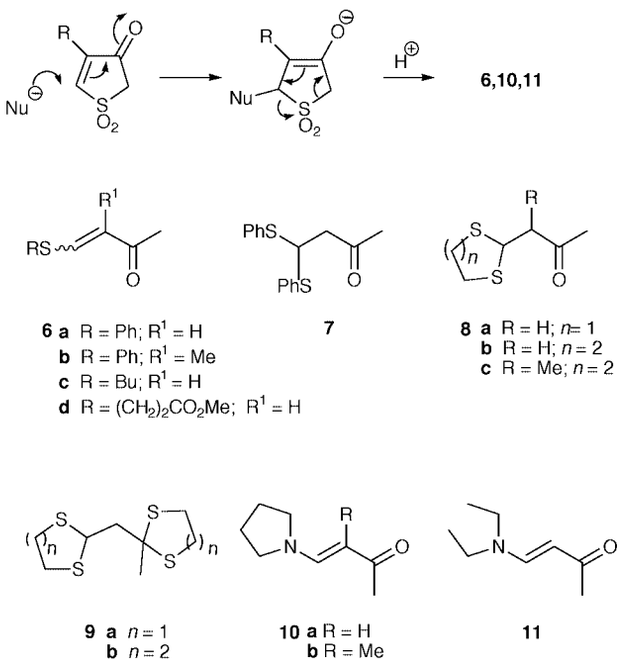


Scheme 1

was only 40%. This was not satisfactory and a simpler synthetic approach to this compound was sought. Oxidation of thiophenes may lead to the corresponding 1,1-dioxides and consequently the oxidation of 3-methoxythiophene can furnish the desired ketone in one step; 3-methoxythiophene is commercially available but is also easily prepared from the corresponding bromide. The problem was to find suitable oxidizing conditions.

Thiophene 1,1-dioxides are very reactive, being sensitive to acidic and basic conditions; moreover, with reactive properties as both diene and dienophile, the Diels–Alder type dimerization is a prevalent reaction. Peracids have previously been the most used reagents for oxidizing thiophenes to the 1,1-dioxides, but dimethyldioxirane seemed a better choice, particularly since it functions under neutral conditions. A few examples of the oxidation of thiophenes with this reagent have been reported.[6] The reaction of 3-methoxythiophene with dimethyldioxirane in aqueous acetone provided the ketosulfone **1a** albeit in only 27% yield, and we were unable to improve on this result. The oxidation of 2-acetyl-3-methoxythiophene[7] under the same conditions furnished the crystalline thiophene dioxide **3** in 33% yield; a strong intramolecular hydrogen bond explains the preference for the thiophene structure. Oxidations with the same reagent of 2-bromo-3-methoxythiophene,[8] 3,3-dimethoxy-2,2′-bithiophene[9] and 2-methoxythiophene[10] gave only resinous products. On the other hand, the oxidation of the thienothiophene derivative **4**[11] with four equivalents of dimethyldioxirane gave a quantitative yield of the dioxide **5**. Using a larger excess of the oxidizing reagent did not lead to any of the tetroxide but to the formation of polymeric products. These results were not particularly encouraging, but considering the time saved the oxidation of 3-methoxythiophene was still the method of choice for the preparation of **1a**; however, since 3-methoxy-3-methylthiophene is not readily available the ketone **1b** was prepared from 3,4-dimethyl-3-sulfolene in 40% yield according to a literature procedure.[12]

Heating a solution of **1a** and benzenethiol in toluene under reflux for 15 h, in the presence of a catalytic amount of pyridine, proceeded with extrusion of sulfur dioxide and formation of a 5:1 mixture of (*E*)- and (*Z*)-4-phenylthiobut-3-en-2-one (**6a**).[13] The ratio of stereoisomers was determined from the ^{1}H NMR spectra by the vicinal coupling constants of the olefinic protons. It was found that the rate of the reaction is strongly dependent on the presence of a base but also on the solvent used. In THF solution no reaction of **1a** took place without added base even after 20 h of reflux. Triethylamine can replace pyridine without any significant change in the reaction rate or product composition. With regard to solvents the results from reactions in THF were about the same as those in toluene, but

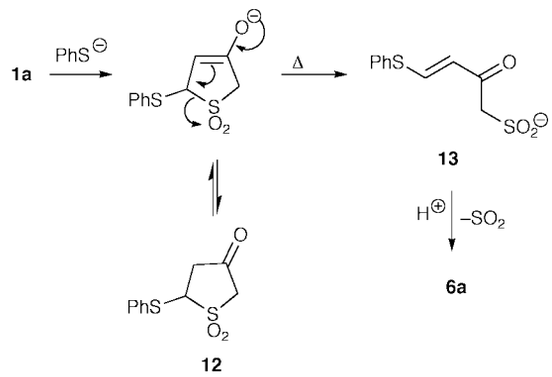


Scheme 2

ethanol proved to be by far the superior solvent giving rise to both increased reaction rates and higher selectivity; an ethanol solution of **1a** containing some pyridine was completely converted in less than one hour at room temperature to a 11 : 1 *E*/*Z*- mixture of **6a** in 87% isolated yield. Similarly, reactions of ethanol solutions of **1a** with butane-1-thiol and methyl 3-mercaptopropionate in the presence of pyridine furnished the ketones **6c**[14] and **6d** in 88 and 92% yields, respectively, as almost pure *E*-isomers. Depending on the reaction conditions, the product from the addition of benzenethiol to **1a** contained a small amount of the acetal **7**[15] formed by a Michael addition of thiophenol on **6a**; barely detectable amounts were generally present, except in the product from the reaction of **1a** with benzenethiol in ethanol–pyridine, which contained 13% of the acetal. A similar but intramolecular addition occurred in reactions with ethane-1,2-dithiol and propane-1,3-dithiol; the corresponding 1,3-dithiolane and 1,3-dithiane derivatives **8a**[16] and **8b**[16] were obtained in high yields. It is interesting to note that conducting the reactions of **1a** and **1b** with the same dithiols in the presence of toluene-*p*-sulfonic acid afforded high yields of the corresponding bis-thioacetals **9**.[17] Generally, the methyl-substituted ketone **1b** was significantly less reactive towards nucleophiles; with benzenethiol (*E*)-3-methyl-4-phenylthiobut-3-en-2-one (**6b**)[16] was obtained in 99% yield after 2.5 h of reflux in ethanol–triethylamine, and with propane-1,3-dithiol the thioacetal **8c**[16] was obtained in 85% yield after 56 h of reflux in ethanol–pyridine. Amines reacted readily with the ketones **1a** and **1b** as well, affording high yields of the corresponding enaminones **10**, exclusively as the *E*-isomers according to the ^{1}H NMR spectra; the use of two equivalents of the amine was necessary for complete conversion. Also in these additions **1b** reacted at a slower rate.

Separate reactions of **6a** with sodium methoxide, enamines, organozinc reagents and the monocarbanions of dimethyl malonate and nitroethane gave resinous products. In these experiments we assume that the above reagents have reacted as bases rather than nucleophiles and thus caused polymerization of **6a**. Houge-Frydrych *et al*. reported similar results from their attempts on the dimerization of **6a**.[12]

There are two distinctly different mechanisms that accommodate the results of the above reactions of compounds **1**. A Michael addition to the enone moiety generates an enolate anion which is a 3-sulfolene derivative, and it is well established that such compounds undergo thermal ring opening by a concerted chelotropic process in which sulfur dioxide leaves in a disrotatory mode. Usually, this reaction requires temperatures above 200 °C in order to proceed at a measurable rate, but certain substituents appear to have a pronounced rate enhancing effect, and examples where sulfur dioxide extrusion occurs at 60 °C in ethanol are known.[18] An alternative two-step mechanism in which the enolate anion of **12** undergoes ring-opening



Scheme 3

to the sulfinate anion **13** that subsequently extrudes sulfur dioxide to form **6a** is certainly a possibility; reaction of 3-sulfolene with sodium hydride in DMSO and in the presence of methyl iodide has been reported to occur with ring-opening and formation of the corresponding methyl sulfinate and methyl sulfone.[19] However, for several reasons we favour the former mechanism with concerted ring opening and sulfur dioxide extrusion. Following the reaction of **1a** with benzenethiol in refluxing THF–pyridine by TLC we noticed the formation of a transient intermediate, and quenching the reaction after 30 min furnished 5-phenylthio-3-oxo-2,3,4,5-tetrahydrothiophene 1,1-dioxide (**12**) in almost quantitative yield. Heating an ethanol solution of this compound under reflux for 40 min in the presence of triethylamine gave (*E*)-**6a** as the sole product in practically quantitative yield; a separate experiment showed no equilibration of a mixture of (*E*)- and (*Z*)-**6a** under the reaction conditions, indicating that the extrusion reaction takes place preferentially by an outward rotation of the phenylthio group. Furthermore, when 3-oxotetrahydrothiophene 1,1-dioxide[20] was heated with benzenethiol in a mixture of ethanol and triethylamine as solvent, sulfur dioxide extrusion occurred with formation of 4-phenylthiobutan-2-one,[21] albeit in only 4% yield after 91 h of reflux. On the other hand, the reaction of compound **12** under the same conditions as above but with the presence of a large excess of methyl iodide gave **6a** as the only product and failed to provide evidence for the involvement of intermediate **13** in the reaction. Additional studies are necessary in order to ascertain the mechanism of this reaction.

Experimental

General

The NMR spectra were recorded on a Varian Gemini 200 instrument using $CDCl_3$ as solvent and internal standard. IR spectra were recorded on a Nicolet Magna IR Spectrometer 550. MS spectra were recorded on a Fison Instrument VG ProSpec Q.

Dimethyldioxirane

An acetone solution of this reagent was prepared according to a published procedure.[22] The concentration of dimethyldioxirane was determined by iodometric titration.

3-Oxo-2,3-dihydrothiophene 1,1-dioxide (1a)

Dimethyldioxirane (80 ml, 6.4 mmol) was added to a mixture of 3-methoxythiophene (287 mg, 2.51 mmol) in acetone (25 ml) at −40 °C. The reaction mixture was stirred at this temperature for 2 h. More dimethyldioxirane (10 ml) was added followed by water and a few drops of formic acid. After 30 min solvents were evaporated under reduced pressure leaving a crystalline residue, which was digested with cold propan-2-ol to give 90 mg (27%) of **1a** as slightly beige-coloured crystals, mp 127 °C (lit.,[5] 118–120 °C from AcOH).

2-Acetyl-3-hydroxythiophene 1,1-dioxide (3)

Dimethyldioxirane (50 ml, 4.00 mmol) was added to a solution of 2-acetyl-3-methoxythiophene (197 mg, 1.25 mmol) and water (45 mg, 2.50 mmol) in acetone (15 ml) at room temperature. After 2 h more dimethyldioxirane (25 ml) was added followed by a few drops of formic acid. 30 min later the solvents were evaporated under reduced pressure and the residue digested with cold propan-2-ol to give 73 mg (33%) of **3** as beige coloured crystals, mp 98–101 °C. ^{1}H NMR (200 MHz, acetone-d_6): δ 2.42 (s, 3 H), 6.97 (d, J 7.2, 1 H), 7.94 (d, J 7.2, 1 H), 11.56 (br s, 1 H). ^{13}C NMR (50 MHz, aceto-nitrile-d_3): δ 19.9, 110.4, 132.0, 145.8, 177.5, 185.2. IR (ATR):† 3550 (weak), 3136, 3072, 2928, 1664, 1590, 1430, 1383, 1353, 1276, 1210, 1140 cm^{-1}. MS (EI): m/z 174 (M^+,100), 159, 84, 69. HRMS(EI): found: 173.998212; calc. for $C_6H_6O_4S$: 173.998681.

4-Hydroxy-3-oxo-2,3-dihydrothieno[2,3-*b*]thiophene 1,1-dioxide (5)

A solution of dimethyldioxirane (32.3 ml, 2.33 mmol), 3,4-dioxo-2,3,4,5-tetrahydrothieno[2,3-*b*]thiophene (**4**, 100 mg, 0.581 mmol) in CH_2Cl_2 (25 ml) was stirred at −30 °C for 2 h. Then the solution was allowed to reach room temperature, and evaporation of solvents under reduced pressure gave 119 mg (100%) of **5** as orange coloured crystals, mp 78 °C (decomp.). ^{1}H NMR (200 MHz, acetone-d_6): δ 4.57 (s, 2 H), 7.00 (s, 1H). ^{13}C NMR (50 MHz, acetonitrile-d_3): δ 64.64, 115.7, 137.0, 148.4, 154.1, 179.2. IR (ATR): 3409, 1717, 1541, 1419, 1319, 1225, 1150 cm^{-1}. GC-MS (EI): m/z 204, 140, 114, 84, 73. HRMS(EI): found: 203.954258; calc. for $C_6H_4O_4S_2$: 203.955102.

(*E*)- and (*Z*)-4-Phenylthiobut-3-en-2-one (6a)

A mixture of 3-oxo-2,3-dihydrothiophene 1,1-dioxide (100 mg, 0.757 mmol), benzenethiol (97 mg, 0.876 mmol) and pyridine (11 µl) in absolute ethanol (7 ml) was heated under reflux for 1 h. Saturated aq. $NaHCO_3$ solution was added at ambient temperature and the product was extracted with ether. The extract was dried ($MgSO_4$) and evaporated furnishing 118 mg (87%) of **6a** as a liquid, consisting of a 11 : 1 mixture of *E*/*Z*-isomers. The spectral data were in accordance with those of the literature.[23] ^{1}H NMR (200 MHz, CD_2Cl_2): δ *E*-isomer: 2.19 (s, 3H), 6.00 (d, J 15.3 Hz, 1H), 7.69 (d, J 15.3 Hz, 1H), 7.34–7.51 (m, 5H); *Z*-isomer: 2.27 (s, 3H), 6.37 (d, J 9.6 Hz, 1H), 7.25 (d, J 9.6 Hz, 1H), 7.34–7.51 (m, 5H).

In toluene as solvent the reaction gave after 15 h of reflux **6a** in 83% yield as a 5 : 1 mixture of *E*/*Z*-isomers.

(*E*)-3-Methyl-4-phenylthiobut-3-en-2-one (6b)

A solution of 4-methyl-3-oxo-2,3-dihydrothiophene 1,1-dioxide (50 mg, 0.342 mmol), benzenethiol (43 mg, 0.39 mmol) and tri-ethylamine (8 µl) in absolute ethanol (8 ml) was heated under reflux for 2.5 h. At ambient temperature sat. aq. $NaHCO_3$ was added and the product extracted with ether. The dried ($MgSO_4$) extract was purified by flash chromatography on silica gel (benzene–EtOAc 97 : 3) giving 65 mg (99%) of **6b** as a yellow liquid. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 1.89 (d, J 1.0 Hz, 3 H), 2.27 (s, 3 H), 7.38–7.55 (m, 6 H). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 13.6, 25.7, 128.8, 130.0, 131.5, 134.4, 143.8, 195.5. IR (CCl_4): 1650, 1540 cm^{-1}. GC-MS (EI): m/z 192 (M^+, 100), 178, 177, 149, 134, 116, 115, 110, 109, 105, 77, 65, 50, 45, 43.

(*E*)- and (*Z*)-4-(1-Butylthio)but-3-en-2-one (6c)

A solution of 3-oxo-2,3-dihydrothiophene 1,1-dioxide (100 mg, 0.934 mmol), butanethiol (84 mg, 0.934 mmol) and pyridine (11 µl) in absolute ethanol (7 ml) was heated under reflux for 1 h. At ambient temperature water was added and the product extracted with ether. The extract was dried ($MgSO_4$), filtered and evaporated giving 106 mg (88%) of **6c** as a dark yellow coloured liquid, consisting of an 21 : 1 mixture of *E*/*Z*- isomers. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 0.93 (t, J 7.7 Hz, 3 H), 1.37–1.69 (m, 4 H), 2.21 (s, 3 H), 2.80 (t, J 7.2 Hz, 2 H), 6.09 (d, J 15.3 Hz, 1 H, *E*-isomer), 6.29 (d, J 9.7 Hz, 1 H, *Z*- isomer), 7.06 (d, J 9.7 Hz, 1 H, *Z*-isomer), 7.61 (d, J 15.4 Hz, 1 H, *E*-isomer). ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.26, 22.6, 31.3, 32.4, 120.7 (CH, *Z*-isomer), 123.9 (CH, *E*-isomer), 147.6 (CH, *E*-isomer), 150.5 (CH, *Z*-isomer), 194.9. IR (CCl_4) 1665, 1525 cm^{-1}. GC-MS (EI): m/z 158 (M^+), 101 (100), 87, 43, 41, 29.

Methyl 3-(3-oxobut-1-enyl)thiopropanoate (6d)

A solution of 3-oxo-2,3-dihydrothiophene 1,1-dioxide (100 mg, 0.757 mmol), methyl mercaptopropionate (109 mg, 0.907 mmol) and pyridine (11 µl) in absolute ethanol (7 ml) was heated under reflux for 1 h. At ambient temperature brine was added and the product extracted with ether. The extract was dried ($MgSO_4$) and the solvents evaporated. The residue was purified by flash chromatography on silica gel (petroleum ether–EtOAc 6 : 4) furnishing 131 mg (92%) of **6d** as a slightly yellow-coloured crystals, mp 40 °C, consisting of a 22 : 1 mixture of *E*/*Z* isomers. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.23 (s, 3 H), 2.72 (m, 2 H), 3.01 (t, J 7.4 Hz, 2 H, *Z*-isomer), 3.10 (t, J 7.2 Hz, 2 H, *E*-isomer), 3.70 (s, 3 H, *Z*-isomer), 3.72 (s, 3 H, *E*-isomer), 6.13 (d, J 15.4 Hz, 1 H, *E*-isomer), 6.33 (d, J 9.8 Hz, 1 H, *Z*-isomer), 7.09 (d, J 9.8 Hz, 1 H, *Z*-isomer), 7.58 (d, J 15.4 Hz, 1 H, *E*-isomer). ^{13}C NMR (50 MHz, $CDCl_3$): δ 27.4, 28.1, 32.2, 33.9, 35.5, 52.3, 52.4, 120.1, 123.3, 144.9, 148.2, 170.4, 193.1. IR (CCl_4): 1730, 1660, 1525 cm^{-1}. GC-MS (EI): m/z 188 (M^+), 115, 101(100), 87, 59, 55, 45, 43. HRMS(EI): found: 188.050071; calc. for $C_8H_{12}O_3S$: 188.050716.

3-(1,3-Dithiolan-2-yl)propan-2-one (8a)

A solution of 3-oxo-2,3-dihydrothiophene 1,1-dioxide (100 mg, 0.757 mmol), ethane-1,2-dithiol (84 mg, 0.894 mmol) and pyridine (11 µl) in absolute ethanol (7 ml) was heated under reflux for 6 h. At ambient temperature water was added and the product extracted with ether. The dried ($MgSO_4$) extract was evaporated giving 129 mg (93%) of **8a** as a yellow-coloured liquid with spectral data in accordance with those of the literature.[17]

3-(1,3-Dithian-2-yl)propan-2-one (8b)

A solution of 3-oxo-2,3-dihydrothiophene 1,1-dioxide (75 mg, 0.568 mmol), propane-1,3-dithiol (75 mg, 0.697 mmol) and pyridine (8 µl) in absolute ethanol (7 ml) was heated under reflux for 6 h. At ambient temperature water was added and the product extracted with ether. The dried ($MgSO_4$) extract was evaporated and the residue purified by flash chromatography on silica gel (95 : 5, benzene–EtOAc) giving 88 mg (88%) of **8b** as colourless crystals, mp 64–68 °C (lit.,[17] 61–62 °C). The spectral data were in agreement with those published.[23]

3-(1,3-Dithian-2-yl)butan-2-one (8c)

A solution of 4-methyl-3-oxo-2,3-dihydrothiophene 1,1-dioxide

† ATR = Attenuated total reflectance.

(75 mg, 0.513 mmol), propane-1,3-dithiol (65 mg, 0.60 mmol) and pyridine (7 μl) in absolute ethanol (7 ml) was heated under reflux for 56 h. At ambient temperature sat. aq. $NaHCO_3$ was added and the product extracted with ether. The extract was dried ($MgSO_4$) and evaporated leaving 83 mg (85%) of **8c** as a liquid. The spectral data were in agreement with those published.[23]

(1,3-Dithiolan-2-yl)(2-methyl-1,3-dithiolan-2-yl)methane (9a)

A solution of 3-oxo-2,3-dihydrothiophene 1,1-dioxide (200 mg, 1.51 mol), ethane-1,2-dithiol (354 mg, 3.76 mmol), and toluene-*p*-sulfonic acid (25 mg, 0.131 mmol) in toluene (20 ml) was heated under reflux for 12 h. At ambient temperature sat. aq. $NaHCO_3$ was added and the product extracted with ether. The dried ($MgSO_4$) extract was concentrated and the residue purified by flash chromatography on silica gel (toluene as eluent) yielding 334 mg (93%) of **9a** as colourless crystals, mp 30–33 °C (lit.,[17] 30–32 °C).

(1,3-Dithian-2-yl)(2-methyl-1,3-dithian-2-yl)methane (9b)

A similar reaction of **1a** with propane-1,3-dithiol gave 91% of **9b** as colourless crystals, mp 76–77 °C (lit.,[17] 76–77 °C).

(*E*)-4-Pyrrolidinobut-3-en-2-one (10a)

A solution of pyrrolidine (89 mg, 1.26 mmol), and 3-oxo-2,3-dihydrothiophene 1,1-dioxide (75 mg, 0.568 mmol) in THF (10 ml) was stirred at room temperature for 2 h. Brine was added and the product extracted with ether. The dried ($MgSO_4$) extract was evaporated giving 69 mg (87%) of **10a** as a liquid. Spectral data agreed with those in the literature.[24] ^{13}C NMR (50 MHz, CD_2Cl_2): δ 25.5, 46.9, 52.4, 128.5, 148.5, 194.4.

(*E*)-4-Pyrrolidino-3-methylbut-3-en-2-one (10b)

A solution of 4-methyl-3-oxo-2,3-dihydrothiophene 1,1-dioxide (100 mg, 0.684 mmol) and pyrrolidine (107 mg, 1.50 mmol) in toluene (10 ml) was heated under reflux for 24 h. At ambient temperature brine was added and the product extracted with ether. The extract was dried ($MgSO_4$), filtered and evaporated giving 76 mg (73%) of **10c** as a brown-coloured liquid. ^1H NMR (200 MHz, CD_2Cl_2): δ 1.83–1.90 (m, 4 H), 1.90 (s, 3 H), 2.12 (s, 3 H), 3.49–3.56 (m, 4 H), 7.34 (s, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 12.3, 26.5, 27.2, 53.1, 107.2, 148.5, 195.1. IR (CCl_4): 2940, 2840, 1655, 1580, 1470, 1445, 1405, 1370, 1345, 1290, 1280, 1250, 1140, 1080 cm^{-1}. GC-MS (EI): *m*/*z* 153 (M^+, 100), 152, 138, 136, 120, 110, 97, 84, 82, 70, 69, 68, 55, 43, 42, 41, 39.

(*E*)-4-Diethylaminobut-3-en-2-one (11)

A solution of diethylamine (92 mg, 1.26 mmol), and 3-oxo-2,3-dihydrothiophene 1,1-dioxide (75 mg, 0.568 mmol) in THF (10 ml) was stirred at room temperature for 2 h. Brine was added and the product extracted with ether. The dried ($MgSO_4$) extract was evaporated giving 75 mg (94%) of **11** as a liquid. Spectral data agreed with those of the literature.[25] ^{13}C NMR (50 MHz, $CDCl_3$): δ 11.3, 14.7, 49.9, 95.4, 150.2, 194.2.

5-Phenylthio-2,3,4,5-tetrahydro-3-oxothiophene 1,1-dioxide (12)

A solution of 3-oxo-2,3-dihydrothiophene 1,1-dioxide (225 mg, 1.70 mmol), benzenethiol (226 mg, 2.05 mmol), pyridine (24 μl) in THF (15 ml) was gently heated at 60 °C for 30 min. Evaporation gave 39 mg (95%) of **12** as yellow-coloured crystals, mp 94–98 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 2.86–2.98 (dd, *J* 6.7,18.6 Hz, 1 H), 3.32–3.46 (dd, *J* 18.6, 7.7 Hz, 1 H), 3.31 (d, *J* 17.8 Hz, 1 H), 3.63 (d, *J* 17.8 Hz, 1 H), 4.74 (dd, *J* 7.7, 6.7 Hz, 1 H), 7.35–7.45 (m, 3 H), 7.60–7.70 (m, 2 H). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 46.8, 57.8, 68.0, 130.8, 131.1, 135.6, 197.7. IR (ATR): 3058, 2994, 2926, 1754, 1440, 1324, 1197, 1179, 1128 cm^{-1}. MS (EI): *m*/*z* 242, 178, 163, 136, 109, 91. HRMS (EI): found: 242.007322; calc. for $C_{10}H_{10}O_3S_2$: 242.007138.

Acknowledgements

We want to thank the Research Council of Norway and Norsk Hydro for a stipend to N. U. H.

References

1 I. R. Fjeldskaar and L. Skattebøl, *Acta Chem. Scand.*, 1991, **45**, 410.
2 W. L. Mock, *J. Am. Chem. Soc.*, 1975, **97**, 3666, 3673.
3 N. S. Simpkins, *Sulphones in Organic Chemistry*, Pergamon Press, Oxford, 1993.
4 N. Hofsløkken, S. Flock and L. Skattebøl, *Tetrahedron Lett.*, 1996, **37**, 119.
5 G. A. Tolstikov, V. P. Kazakov, E. E. Shul'ts, R. G. Bulgakov and R. G. Kantyukova, *Zh. Org. Khim.*, 1984, **20**, 313.
6 Y. Miyahara and T. Inazu, *Tetrahedron Lett.*, 1990, **31**, 5955.
7 J. M. Barker, P. R. Huddleston, G. D. Khandelwal and M. L. Wood, *J. Chem. Res.* (*M*), 1991, 2333.
8 I. J. Turchi, J. B. Press, J. J. McNally, P. B. Bonner and K. L. Sorgi, *J. Org. Chem.*, 1993, **58**, 4629.
9 L. L. Miller and Y. Yu, *J. Org. Chem.*, 1995, **60**, 6813.
10 J. Sicé, *J. Am. Chem. Soc.*, 1953, **75**, 3697.
11 R. Gompper, E. Kutter and W. Typfl, *Liebigs Ann. Chem.*, 1962, **659**, 90; R. Gompper, R. Knieler and K. Z. Polhorn, *Z. Naturforsch.*, *Teil B*, 1993, **48**, 1621.
12 C. S. V. Houge-Frydrych, W. B. Motherwell and D. M. O'Shea, *J. Chem. Soc.*, *Chem. Commun.*, 1987, 1819.
13 R. K. Haynes, S. C. Vonwiller, J. P. Stokes and L. M. Merlino, *Aust. J. Chem.*, 1988, **41**, 881.
14 S. Akiyama, S. Nakatsuji, T. Hamamura, M. Kataoka and M. Nakagawa, *Tetrahedron Lett.*, 1979, 2809.
15 J. P. Cronin, B. M. Dilworth and A. M. McKervey, *Tetrahedron Lett.*, 1986, **27**, 759.
16 R. H. Shapiro and T. E. McEntree, Jr., *Tetrahedron*, 1969, **24**, 2809.
17 D. L. Coffen, K. C. Bank and P. E. Garrett, *J. Org. Chem.*, 1969, **34**, 605.
18 H. Takayama and T. Suzuki, *J. Chem. Soc.*, *Chem. Commun.*, 1988, 1044.
19 R. L. Crumbie and D. D. Ridley, *Aust. J. Chem.*, 1981, **34**, 1017; F. Näf, R. Decorzant and S. D. Escher, *Tetrahedron Lett.*, 1982, **23**, 5043.
20 H. Ahlbrecht and M. Ibe, *Synthesis*, 1988, 210.
21 P. Bakuzis and M. L. F. J. Bakuzis, *J. Org. Chem.*, 1981, **46**, 235.
22 W. Adam, J. Bialas and L. Hadjiarapoglou, *Chem. Ber.*, 1991, **124**, 2377.
23 D. Stossel and T. H. Chan, *J. Org. Chem.*, 1988, **53**, 4901.
24 A. Yu. Zaichenko, M. V. Kormer and A. I. Vil'davskaya, *Zh. Org. Khim.*, 1983, **19**, 923.
25 C. A. Maggiulli and Tang Ping-Wah, *Org. Prep. Proced. Int.*, 1984, **16**, 31.

Paper 9/07097D