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Synthesis and photooxygenation of 2-thiofuran derivatives: a mild and direct access to *O*,*S*-dimethyl and *O*-methyl-*S*-phenyl thiomaleates

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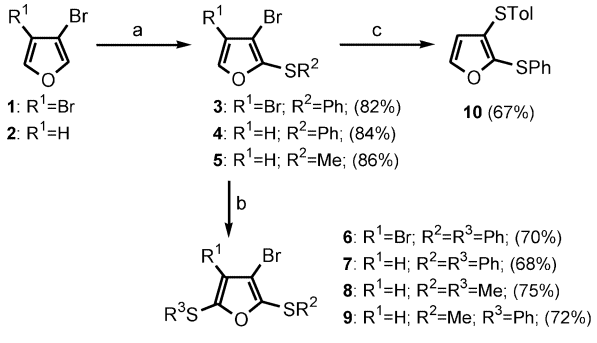
Abstract—New 3-bromo-2-thio and 3-bromo-2,5-bis-(thio) furan derivatives have been synthesized and their synthetic potential has been assessed by their conversion into *O*,*S*-dimethyl and *O*-methyl-*S*-phenyl thiomaleates via methylene blue sensitized photooxygenation.

Substituted furans are key structural units in a wide range of biologically active natural and synthetic products[1] and they have been frequently employed in organic synthesis as versatile building blocks.[2] One of the most interesting aspects of furan chemistry is the oxidative ring cleavage[3] to give 1,4-dioxo-2-alkenes which can be further transformed into complex molecules.[4] In the photooxygenation process, singlet oxygen, $^1O_2$, is transferred via [4+2] cycloaddition allowing a selective *cis*-1,4-dioxygenation.[5] In connection with our studies concerning the photooxygenation of substituted furans[6] we drew our attention toward 2,5-bis-(thio)furan derivatives which could be transformed into maleic acid thioesters by oxidative ring cleavage of the former compounds. Fumaric acid thioesters[7] and γ-oxo-α,β-unsaturated thioesters[8] have been used as useful dienophiles in the construction of natural products and polycyclic cage compounds and also as Michael acceptors in reactions with enamines.[9] Additionally, they are useful dienophiles in situations where the corresponding esters lacked the reactivity needed,[7a,c] and it is possible to carry out the chemioselective reduction of a thioester group without disturbing an ester or a lactone moieties.[7b,c]

In this paper we describe a regiocontrolled approach to 2-thiofuran and 2,5-bis-(thio)furan derivatives and the study of their sensitized photooxygenation as a direct and mild access to *O*,*S*-dimethyl and *O*-methyl-*S*-phenyl thiomaleates. To the best of our knowledge, the synthesis of these derivatives has not been described.

The synthesis of 2,5-bis-(thio)furan derivatives was planned starting from 3,4-dibromofuran[10] **1**, and 3-bromofuran **2**. We select these starting materials because they can undergo regiospecific metallation with LDA and subsequent electrophilic reaction at the carbon C2 as well as a second metal-proton exchange reaction at C5. Additionally, the metal-bromine exchange reaction at C3 by means of *n*-BuLi can be carried out.[11]

2-Thiofurans **3**, **4** and **5** were obtained in high yields by *ortho* metallation of **1** and **2** with LDA (1 equiv.) and subsequent treatment with the electrophile reagents (Me_2S_2 and Ph_2S_2; see Scheme 1). When compound **3** was subjected to a new set of metal–proton exchange reaction and then treatment with Ph_2S_2 the 2,5-bis-(phenylthio)furan **6** was obtained in 70% yield (Scheme



Scheme 1. *Reagents and conditions*: a. (i) LDA (1 equiv.); (ii) $R^2_2S_2$ (1.1 equiv.); b. (i) LDA (2.2 equiv.); (iii) $R^3_2S_2$ (2.2 equiv.); c. (i) *n*-BuLi (1 equiv.); (ii) *p*-Tol_2S_2 (1.1 equiv.).

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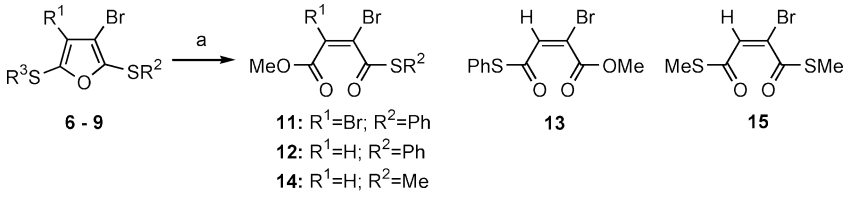
1). In the same way, the syntheses of **7** from **4**, and **8** from **5** were achieved in good yields using Ph_2S_2 and Me_2S_2 as electrophile reagents, respectively (Scheme 1). The unsymmetrical 2,5-bis(thio)furan **9** was similarly obtained by reaction of **5** with LDA and subsequent treatment with Ph_2S_2. On the other hand, when furan **4** was treated with *n*-BuLi (1 equiv.), it resulted in a 3-lithiofuran intermediate which was quenched with di-*p*-tolyldisulfide giving rise to 2,3-bis-(thio)furan **10** in 67% yield (Scheme 1). All thiosubstituted furans have been isolated as pure compounds and characterized by their spectroscopy data.[12]

With the precursors in hand the reactions of thiofuran derivatives **5-10** with singlet oxygen were then investigated.[13] In all experiments performed with 2,5-bis-(thio)furan derivatives, **6–9**, we found that the expected *S*,*S*-bis(thio) maleate derivatives were not formed except for furan **8**. However the corresponding *O*,*S*-dimethyl or *O*-methyl-*S*-phenyl thiomaleates were formed as a result of the loss of a phenylthio or a methylthio group from the starting furan derivatives. These results are collected in Table 1.

Thus, when photooxygenation of compound **6** was carried out the ^1H and ^{13}C NMR spectra of the reaction mixture just after irradiation showed the presence of 2,3-dibromo-*O*-methyl-*S*-phenyl thiomaleate **11**[14] (Table 1; entry 1). The characteristic peak of the methoxycarbonyl group appeared at δ_H 3.85 ppm and at δ_C 165.1 ppm while the phenylsulfanylcarbonyl group appeared at δ_C 186.2 ppm. The reaction was accompanied by the formation of a by-product resulting from the loss of a phenylthio group (only signals corresponding to aromatic protons were detected) but it could be removed, as insoluble material, by treatment with hexane.[13] In the same way, the reaction of **7** with $^1O_2$ afforded 3-bromo-*O*-methyl-*S*-phenyl thiomaleate **12** as the main product along with a small amount of its regioisomer **13** in a 94:6 ratio (entry 2). Again, spectroscopy data[14] of the reaction mixture show the peaks corresponding to a methoxycarbonyl group ($\delta_H = 3.89$ ppm; $\delta_C = 164.2$ ppm) and a phenylsulfanylcarbonyl group ($\delta_C = 193.1$ ppm) of the major **12**. An experiment carried out with **7** at −78°C showed that the temperature of the reaction had no influence on the products ratio but the starting furan was not consumed after 7 h of irradiation (entry 3). The use of Rose Bengal as photosensitizer requires higher temperatures (20°C) and the regioselectivity decreased slightly (entry 4). We also performed photooxidation of **7** in the presence of reduction agents such as Me_2S, thiourea and Ph_3P (entries 5–7). We found that the addition of these compounds had no influence on the nature of the final products but the regioselectivity decreased and both higher temperatures and longer irradiation times were necessary to consume the starting furan **7**. The photooxygenation of **8** afforded 3-bromo-*O*,*S*-dimethyl thiomaleate **14** and *S*,*S*-dimethyl bis(thio)maleate **15** in a 68:32 ratio (entry 8). Spectroscopic data[14] of the reaction mixture show the peaks corresponding to a methoxycarbonyl group ($\delta_H = 3.88$ ppm; $\delta_C = 164.1$ ppm) and a methylsulfanylcarbonyl group ($\delta_H = 2.48$ ppm; $\delta_C = 186.9$ ppm) for compound **14** while two methylsulfanylcarbonyl groups are present in the minor **15** ($\delta_H = 2.47$ and 2.39; $\delta_C = 186.9$ and 190.1).

In order to establish the right structure for **12**, **13** and **14**, the photooxidation of 2-(methylthio)-5-(phenylthio)-furan **9** was then performed. Thus, after

Table 1. Photooxygenation of 2,5-bis-(thio)furans **6–9**



Reagents and conditions: (a) O_2, MB, hν, CH_3OH, -40°C

Entry	Dithiofuran	Sensitizer/reduction agent	T (°C)	Irradiation time (h)	Product ratio[a] (%)		Yield (%)[b]
1	**6**	MB/none	−40	5.5	**11** (100)		96
2	**7**	MB/none	−40	3.5	**12** (94)	**13** (6)	93
3	**7**	MB/none	−78	7	**12** (94)	**13** (6)	28[c]
4	**7**	RB/none	20	6	**12** (86)	**13** (14)	93
5	**7**	MB/Me_2S	20	6	**12** (88)	**13** (12)	95
6	**7**	MB/thiourea	20	7	**12** (86)	**13** (14)	15[d]
7	**7**	MB/Ph_3P	−20	5	**12** (87)	**13** (13)	91
8	**8**	MB/none	−40	0.75	**14** (68)	**15** (32)	87
9	**9**	MB/none	−40	1	**14** (93)	**13** (7)	90

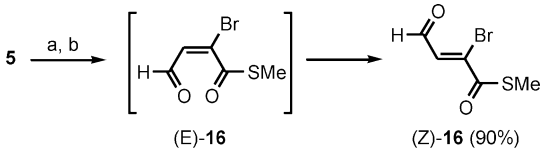
[a] Estimated by ^1H NMR.
[b] Crude yield of major compound.
[c] 67% of starting material was recovered.
[d] 78% of starting material was recovered.

irradiation 3-bromo-*O*,*S*-dimethyl thiomaleate **14** was formed as the main product together with 2-bromo-*O*-methyl-*S*-phenyl thiomaleate **13** in a 93:7 ratio (entry 9). Compound **14** comes from the loss of the phenylthio group at C5 and spectroscopy data are coincident with those of the major compound obtained from **8**. The minor **13** results from the loss of the methylthio group at C2 and spectroscopic data are coincident with the minor compound obtained from **7**. These results show that during the photooxygenation process of 2,5-bis(thio)furans the loss of the thiophenyl or thiomethyl group at C5 is preferred.

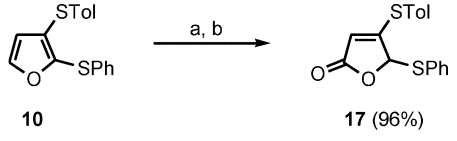
In the same way we studied the photooxygenation of furans unsubstituted at C5 **5** and **10**. Reaction of **5** with $^1O_2$ over 25 minutes, after treatment with Me_2S, lead to the expected methyl (*E*)-2-bromo-4-oxo-2-butenethioate **16** as the only product in 90% yield. This (*E*)-alkenal isomerized spontaneously to the corresponding *Z* isomer after seven days at room temperature (Scheme 2).

In contrast with the results obtained in the photooxygenation of 3-bromofurans (compounds **5**–**9**), which afforded open chain α,β-unsaturated thioesters (**11**–**16**), the reaction performed with 2,3-bis-(thio)furan **10** lead, after treatment with Me_2S, to the γ-butyrolactone **17**[15] as the sole product in nearly quantitatively yield (97% crude yield) (Scheme 3).

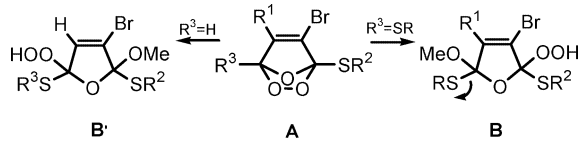
As it is well documented[5] photooxygenation of furan derivatives gives unstable endoperoxides **A** which, in alcoholic solutions, usually are regioselectively transformed into alkoxy-hydroperoxydihydrofurans (**B** or **B′**; Scheme 4) the regioselectivity being determined by the stabilization of the developing positive charge.[5a] The subsequent reduction of dihydrofurans, **B** and **B′**, produces *cis*-2-butene-1,4-diones.[5] For furans unsubstituted at C5, dihydrofurans such as **B′** are formed giving rise to alkenals, which is in accord with the result obtained for **5**. In photooxidations performed with 2,5-bis(thio)furans we found that a reduction agent is not necessary in order to obtain the final products and moreover the addition of such a reduction agent during the irradiation had no influence on the reaction course. These results suggest that a ready transformation of dihydrofurans **B** into compounds **11**–**14** takes place as a consequence of the higher ability of phenylthio and methylthio groups to act as leaving groups in comparison with the methoxy one. The fact that compound **15** was formed in photooxidation of **8** could be explained taking into account that a methylthio group is a poorer leaving group than a phenylthio group. It should be noted that in order to remove the by-products resulting from the reduction process, the reaction mixture was treated with hexane or water to give a clean reaction mixture where only the photooxygenation products were detected.[13]



Scheme 2. *Reagents and conditions*: (a) O_2, MB, hν, CH_3OH, –40°C, 25 min; (b) Me_2S.



Scheme 3. *Reagents and conditions*: (a) O_2, MB, hν, CH_3OH, –40°C, 30 min; (b) Me_2S.



Scheme 4.

In summary the results describe above demonstrate that 3-bromo-2-thiofurans **5**–**9** are pivotal compounds in the synthesis of *O*,*S*-dimethyl, and *O*-methyl-*S*-phenyl thiomaleates (compounds **11**, **12** and **14**) as well as the 4-oxo-2-butenethioate **16** by methylene blue sensitized photooxygenation using methanol as solvent. We also report that the 2,3-bis-(thio)furan **10** bearing a tolylthiogroup at C3 lead only to the γ-butyrolactone **17**. Studies devoted to the use of compounds **11–16** as dienophiles and as Michael acceptors are currently in progress.

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12. All new *2-thiofurans* were characterized on the basis of their ^{1}H NMR (δ in ppm, $CDCl_3$, 300 MHz), ^{13}C NMR (δ in ppm, $CDCl_3$, 75 MHz) and MS spectral data.
Compound **3**: mp 66–67°C (hexane); ^{1}H NMR: 7.24–7.28 (m, 5H, H-arom), 7.44 (s, 1H, H-5); ^{13}C-NMR: 104.0, 114.0 (C-3, C-4), 127.6, 129.3, 129.5 (CH-arom), 132.9 (C-arom), 141.6, 147.1 (C-5, C-2); MS: *m*/z (%) 336/334/332 (48/100/51, M^+). Compound **4**: mp 25°C (hexane); ^{1}H NMR: 6.55 (d, 1H, *J* 2.1 Hz, H-4), 7.18–7.29 (m, 5H, H-arom), 7.5 (d, 1H, H-5); ^{13}C NMR: 110.6 (C-3), 115.5 (C-4), 126.8, 128.2, 129.2 (CH-arom), 134.5 (C-arom) 142.9, 146.4 (C-5, C-2); MS: *m*/*z* (%) 256/254 (74/76, M^+). Compound **5**: ^{1}H NMR: 2.37 (s, 3H, SCH_3), 6.44 (d, 1H, *J* 2.2 Hz, H-4), 7.41 (d, 1H, H-5); ^{13}C NMR: 17.9 (SCH_3), 106.2 (C-3), 115.0 (C-4), 144.9, 145.6 (C-5, C-2); MS: m/z (%) 194/192 (48/51 M^+). Compound **6**: mp 77–78°C (hexane); ^{1}H NMR: 7.26–7.28 (m, 10H, H-arom); ^{13}C NMR: 113.0 (C-3, C-4), 127.6, 129.3, 129.5 (CH-arom), 132.9 (C-arom), 147.0 (C-2, C-5). MS: *m*/*z* (%) 444/442/440 (4/9/3 M^+). Compound **7**: mp 77–78°C (hexane); ^{1}H NMR: 6.73 (s, 1H, H-4), 7.19–7.25 (m, 10H, H-arom); ^{13}C NMR: 110.9 (C-3), 122.2 (C-4), 127.1, 127.3, 129.2 (CH-arom), 133.4 (C-arom), 146.4, 148.5 (C-2, C-5); MS: *m*/*z* (%) 364/362 (35/32, M^+). Compound **8**: ^{1}H NMR: 2.42, 2.44 (two s, each 3H, SCH_3), 6.44 (s, 1H, H-4); ^{13}C NMR: 18.1 (SCH_3), 106.8 (C-3), 117.6 (C-4), 147.5, 150.6 (C-2, C-5); MS: *m*/*z* (%) 240/238 (3/1, M^+). Compound **9**: ^{1}H NMR: 2.42 (s, 3H, SCH_3), 6.72 (s, 1H, H-4), 7.22–7.32 (m, 5H, H-arom); ^{13}C NMR: 17.6 (SCH_3), 105.8 (C-3), 122.7 (C-4), 127.5, 128.6, 129.2 (CH-arom), 133.8, 134.6 (C-arom, C-2), 146.3 (C-5); MS: m/z (%) 302/300 (44/46, M^+). Compound **10**: ^{1}H NMR: 2.30 (s, 3H, CH_3–C_6H_4–), 6.37 (d, 1H, *J* 2.1 Hz, H-4), 7.25–7.28 (m, 9H, H-arom); 7.52 (d, 1H, H-5); ^{13}C NMR: 21.0 (CH_3–C_6H_4–), 115.3 (C-4), 125.6 (C-3), 126.7, 128.5, 129.1, 129.8, 130.1 (CH-arom), 131.4, 135.1, 136.9 (C-arom), 144.6, 146.1 (C-2, C-5); MS: *m*/*z* (%) 298 (100, M^+).
13. Sensitized photooxygenation reactions were carried out in anhydrous methanol as solvent, at –40°C, with bubbling oxygen and in the presence of methylene blue (MB) as photosensitizer (4×10^{-3} mmol), under irradiation with a 500 W tungsten lamp. When each reaction was complete, the solution was degassed at rt by bubbling with Argon. For furans **5** and **10**, Me_2S (2 equiv.) in CCl_4 was added to each solution just after irradiation. The solvent was removed on a rotatory evaporator and each residue was washed with hexane (for **6**, **7**, and **9**) or water (for **5**, **8** and **10**) and extracted with Cl_2CH_2.
14. Compounds **11**–**17** were characterized from the crude reaction mixture on the basis of their ^{1}H NMR (δ in ppm, $CDCl_3$, 300 MHz), ^{13}C NMR (δ in ppm, $CDCl_3$, 75 MHz), IR and MS spectral data.
Compound **11**: ^{1}H NMR: 3.85 (s, 3H, CH_3O), 7.13–7.32 (m, 5H, H-arom); ^{13}C NMR: 53.9 (CH_3O), 127.1, 127.4, 129.0 (CH-arom), 131.1, 133.0 (C-2, C-3), 137.0 (C-arom), 165.1 (COOMe), 186.2 (COSPh); IR (KBr) *v* (cm^{-1}): 1741, 1730; MS: *m*/*z* (%) 382/380/378 (1/5/1, M^+). Compound **12**: ^{1}H NMR: 3.89 (s, 3H, CH_3O), 6.53 (s, 1H, H-2), 7.17–7.47 (m, 5H, H-arom); ^{13}C NMR: 53.8 (CH_3O), 126.0, 129.8 (C-2, C-3), 127.2, 127.5, 129.1 (CH-arom), 137.0 (C-arom), 164.2 (COOMe), 193.1 (COSPh); IR (KBr) *v* (cm^{-1}): 1719, 1700; MS: *m*/*z* (%) 302/300 (3/1, M^+). Compound **13**: ^{1}H NMR: 3.81 (s, 3H, CH_3O), 6.66 (s, 1H, H-3), 7.17–7.47 (m, 5H, H-arom). Compound **14**: ^{1}H NMR: 2.48 (s, 3H, SCH_3), 3.88 (s, 3H, CH_3O), 6.51 (s, 1H, H-2); ^{13}C NMR: 12.6 (SCH_3), 53.6 (CH_3O), 125.1, 129.6 (C-2, C-3), 164.1 (COOMe), 186.9 (COSMe); IR (KBr) ν (cm^{-1}): 1727, 1668; MS: *m*/*z* (%) 209/207 (45/43, M^+–OMe). Compound **15**: ^{1}H NMR: 2.47, 2.39 (two s, 3H, SCH_3), 6.67 (s, 1H, H-3); ^{13}C NMR: 12.0, 12.4 (SCH_3), 125.8, 129.5 (C-2, C-3); 186.9, 190.1 (COSMe). Compound **16**: (*E*)-*isomer*: ^{1}H NMR: 2.43 (s, 3H, SCH_3), 6.65 (d, 1H, *J* 6.5, H-3), 9.94 (d, 1H, CHO); ^{13}C NMR: 13.8 (SCH_3), 137.2, 137.6 (C-2, C-3), 188.6, 189.3 (CHO, COSMe). (*Z*) *Isomer*: ^{1}H NMR: 2.42 (s, 3H, SCH_3), 7.19 (d, 1H, *J* 6.5, H-3), 10.00 (d, 1H, CHO); ^{13}C NMR: 13.8 (SCH_3), 130.8, 136.5 (C-2, C-3), 188.7 and 192.2 (CHO, COSMe); IR (KBr) ν (cm^{-1}): 1726, 1685; MS: m/z (%) 210/208 (17/17, M^+). Compound **17**: ^{1}H NMR: 2.31 (s, 3H, CH_3–C_6H_4–), 5.34 (d, 1H, *J* 3.5 Hz, H-4), 6.42 (d, 1H, H-5), 7.08–7.53 (m, 9H, H-arom); ^{13}C NMR: 21.2 (CH_3-C_6H_4–), 111.9 (C-5), 126.9 (C-4), 127.2, 128.9, 129.7, 136.5, 136.6 (CH-arom), 134.2 (C-3), 135.4, 140.6, 141.9 (C-arom), 164.9 (C-2); IR (KBr) *v* (cm^{-1}): 1790, 1767; MS: *m*/*z* (%) 314 (4%, M^+).
15. There are several reports in which endoperoxides rearranged to give butyrolactones. See Ref. 4a, 5a and (a) Waldemar, A.; Schuhmann, R. M. *Liebigs Ann.* **1996**, 635–640; (b) Freeman-Cook, K. D.; Halcomb, R. L. *Tetrahedron Lett.* **1998**, *39*, 8567–8570.