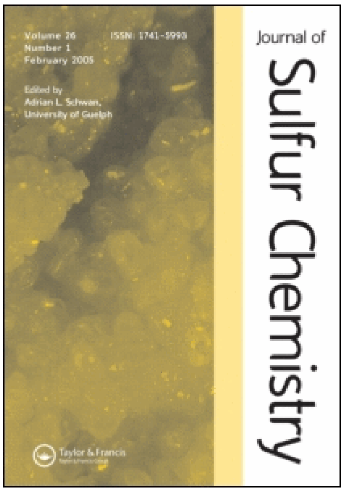

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Photolysis and photo-oxidation of 3,4-di-*tert*-butylthiophene 1-oxide

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Photolysis and photo-oxidation of 3,4-di-*tert*-butylthiophene 1-oxide

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The irradiation of a degassed solution of 3,4-di-*tert*-butylthiophene 1-oxide in benzene gave 3,4-di-*tert*-butylthiophene, bis(3,4-di-*tert*-butyl-2-furyl) disulfide, and 3,4-di-*tert*-butylfuran in 26%, 15%, and 9% yields, respectively, while the oxidation with singlet oxygen produced 3,4-di-*tert*-butyl-5-hydroxy-2-furanone, di-*tert*-butylmaleic anhydride, and 3,4-di-*tert*-butylthiophene in 59%, 5%, and 2% yields, respectively.

Keywords: thiophene 1-oxide; deoxygenation; photochemistry; X-ray diffraction analysis; singlet oxygen

1. Introduction

Thiophene 1-oxides, the initial oxidation product of thiophenes, are not aromatic any longer (for reviews on the chemistry of thiophene 1-oxides, see (*1–3*)). As a result, they behave as highly reactive cyclic dienes. Thus, they can be isolated in pure form only when [2 + 4] self-dimerization is hampered by at least two bulky substituents at 2,4- (*4*), 3,4- (*4*), or 2,5-positions (*5–7*). We have been investigating the reactions of 3,4-di-*tert*-butylthiophene 1-oxide (**1**). The thermally stable but highly reactive 1-oxide **1** undergoes a range of addition reactions including Diels–Alder reactions with a variety of dienophiles (*3*, *8–10*). It can be kept for a long period of time in crystalline form without any appreciable decomposition. However, it may loose the oxygen atom to give 3,4-di-*tert*-butylthiophene (**2**), though in a low conversion, when heated in refluxing toluene and other solvents of higher boiling point, particularly when the intended reaction did not occur in those solvents. In addition, this conversion is seemingly accelerated upon exposure to indoor light. Reportedly, the photolysis of dibenzothiophene 5-oxide and the related 1-oxide generates an active oxygen atom (*11–17*); thus the photolysis of dibenzothiophene 5-oxide gives dibenzothiophene and oxidation products of the solvent, for example, phenol from benzene, and cylohexanol and cyclohexene from cyclohexane (*11*, *12*). With these in mind, we have examined the photolysis of **1**. Recently, the photochemistry of a series of polysubstituted thiophene 1-oxides has also been reported (*18–20*).

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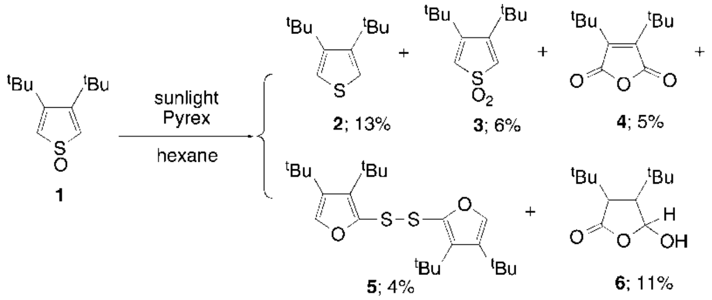
2. Results

The UV/vis spectrum of **1** shows the absorption maximum at 350 nm (ε988) in hexane and 333 nm (ε1293) in CH_3CN.

Initially, a hexane solution (0.014 *M*) of **1** in a Pyrex test tube was exposed to the sunlight for 5 h on a sunny winter day. The irradiation gave 3,4-di-*tert*-butylthiophene (**2**, 13%), 3,4-di-*tert*-butylthiophene 1,1-dioxide (**3**, 6%), di-*tert*-butylmaleic anhydride (**4**, 5%), bis(3,4-di-*tert*-butyl-2-furyl) disulfide (**5**, 4%), and 3,4-di-*tert*-butyl-5-hydroxy-2-furanone (**6**, 11%) with 17% recovery of **1** (Scheme 1). No oxidation products of hexane were observed in the reaction mixture.



Scheme 1.

The structure of **4** was determined by comparison of the spectral data with those reported (*21*). The structure of **5** was determined by X-ray diffraction analysis as well as spectral data. All the spectral data of **6** indicated that it has the furanone structure given in Scheme 1. However, our ^1H NMR data did not agree with those reported; reportedly the two, chemically nonequivalent *tert*-butyl groups of **6** appeared as only one singlet (*21*), whereas our one showed two singlets at δ 1.41 and 1.43 in addition to two doublets of the OH and methine protons at ε 3.54 and 5.94, respectively. Therefore, the compound was subjected to X-ray diffraction analysis to unambiguously determine its structure. Molecular structures of **5** and **6** are shown Figures 1 and 2, respectively. Selected

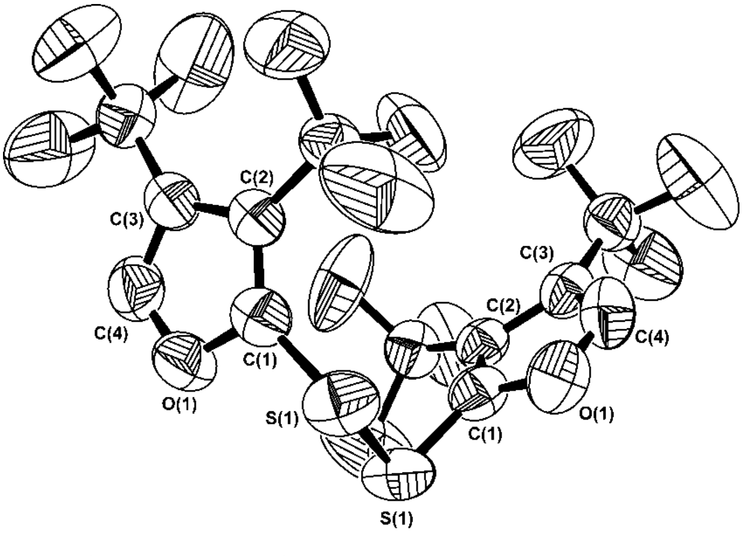


Figure 1. ORTEP plot of molecular structure of **5**.

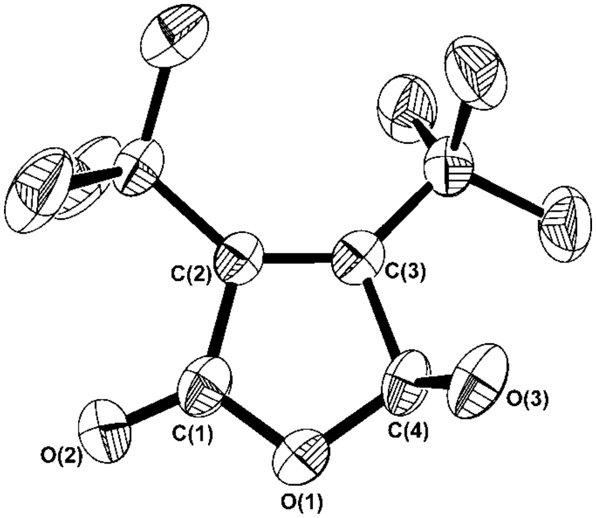


Figure 2. ORTEP plot of molecular structure of **6**.

data for **5** and **6** on bond lengths, bond angles, and dihedral angles are also summarized in Tables 1 and 2, respectively.

The paper (*21*) cited above reported that the oxidation of 3,4-di-*tert*-butylcyclopentadienone (**7**) with singlet oxygen ($^1O_2$) produced compounds **4** and **6** together with **8**, although it is questionable whether **6** actually formed (*vide supra*). In any event, because of the structural similarity of **1** and **7**, $^1O_2$ might be involved in the formation of **4** and **6** from **1**. Therefore, a degassed solution of **1** in benzene (0.0075 *M*) was irradiated with a small UV lamp (365 nm) for 3 h. The reaction produced **2** (26%), **5** (15%), and a new product, 3,4-di-*tert*-butylfuran (**9**, 9%) (*22*) (Scheme 2). The fact that **4** and **6** did not form reveals that these two compounds are formed by oxidation with $^1O_2$.

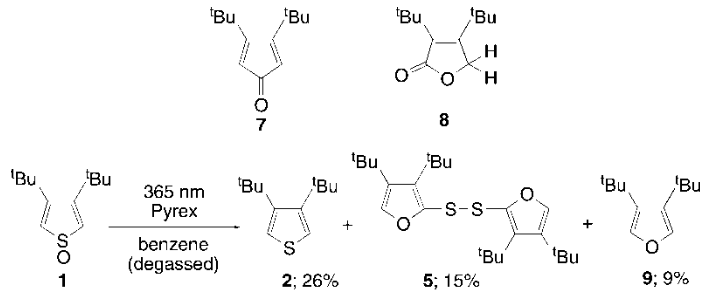
Indeed, a separate experiment showed that $^1O_2$ oxidation of **1** gives **4** and **6**. Thus, a dilute solution of **1** in CH_3CN was exposed to the sunlight for 3 h in the presence of oxygen, with

Table 1. Selected bond lengths, bond angles, and dihedral angles from the X-Ray structure of **5**.

Bond lengths [Å] and angles [°] for **5**	
C(1)-C(2) 1.356(4)	C(2)-C(1)-O(1) 111.1(3)
C(1)-O(1) 1.381(3)	C(2)-C(1)-S(1) 136.4(2)
C(1)-S(1) 1.744(3)	O(1)-C(1)-S(1) 112.5(2)
C(2)-C(3) 1.464(4)	C(1)-C(2)-C(3) 105.6(2)
C(3)-C(4) 1.340(4)	C(4)-C(3)-C(2) 104.3(3)
C(4)-O(1) 1.345(4)	C(3)-C(4)-O(1) 114.0(3)
S(1)-S(1) 2.0789(17)	C(4)-O(1)-C(1) 104.9(2)
	C(1)-S(1)-S(1) 104.2(10)
Dihedral angles [°] for **5**	
O(1)-C(1)-C(2)-C(3) −1.7(3)	C(2)-C(1)-O(1)-C(4) 1.9(3)
S(1)-C(1)-C(2)-C(3) 178.6(2)	S(1)-C(1)-O(1)-C(4) −178.3(2)
C(1)-C(2)-C(3)-C(4) 0.8(3)	C(2)-C(1)-S(1)-S(1) −113.6(3)
C(2)-C(3)-C(4)-O(1) 0.4(4)	O(1)-C(1)-S(1)-S(1) 66.7(2)
C(3)-C(4)-O(1)-C(1) −1.4(4)	

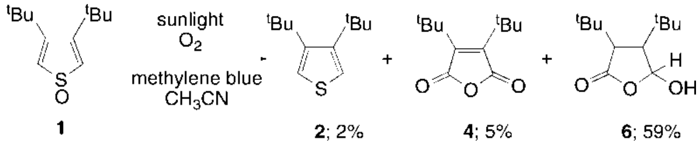
Table 2. Selected bond lengths, bond angles, and dihedral angles from the X-Ray structure of **6**.

Bond lengths [Å] and angles [°] for **6**	
C(1)-O(2) 1.216(2)	O(2)-C(1)-O(1) 119.6(2)
C(1)-O(1) 1.335(1)	O(2)-C(1)-C(2) 128.8(2)
C(1)-C(2) 1.484(3)	O(1)-C(1)-C(2) 111.53(19)
C(2)-C(3) 1.347(3)	C(3)-C(2)-C(1) 106.13(19)
C(3)-C(4) 1.522(4)	C(2)-C(3)-C(4) 108.4(2)
C(4)-O(3) 1.403(2)	O(3)-C(4)-O(1) 109.33(18)
C(4)-O(1) 1.440(2)	O(3)-C(4)-C(3) 108.36(17)
	O(1)-C(4)-C(3) 105.19(19)
	C(1)-O(1)-C(4) 108.16(17)
Dihedral angles [°] for **6**	
O(2)-C(1)-C(2)-C(3) −170.0(2)	O(2)-C(1)-O(1)-C(4) 174.2(2)
O(1)-C(1)-C(2)-C(3) 6.8(3)	C(2)-C(1)-O(1)-C(4) −2.9(2)
C(1)-C(2)-C(3)-C(4) −7.5(2)	O(3)-C(4)-O(1)-C(1) 114.5(2)
C(2)-C(3)-C(4)-O(3) −110.9(2)	C(3)-C(4)-O(1)-C(1) −1.6(2)
C(2)-C(3)-C(4)-O(1) 6.0(2)	



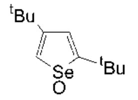
Scheme 2.

methylene blue as the photosensitizer, to give **6** as the major product (59%) in addition to **2** (2%) and **4** (5%) (Scheme 3).



Scheme 3.

Previously, we reported the synthesis of 2,4-di-*tert*-butylselenophene 1-oxide (**10**), the first example of monocyclic selenophene 1-oxide isolated in pure form (*23*). 1-Oxide **10** reacted with triphenylphosphine (Ph_3P) and thioanisole, without irradiation, to produce Ph_3PO and methyl phenyl sulfoxide, respectively. Meanwhile **1** was inert to Ph_3P in the dark. The irradiation of a degassed solution of **1** and Ph_3P (1:1 molar ratio) in benzene gave thiophene **2** (10%), furan **9** (32%), Ph_3PO (27%), and Ph_3PS (56%) (Scheme 4). Incidentally, letting **10** stand in solution affords 2,4-di-*tert*-butylselenophene and furanone **11** (*23*). The latter corresponds to **6** formed from **1** by $^1O_2$ oxidation. Previously we reported the synthesis of furan **9** in a low yield (12%) by flash vacuum pyrolysis of 1,1-dioxide **3** (*22*). The present reaction is more practical than this pyrolysis as a method for the synthesis of **9**.



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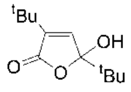

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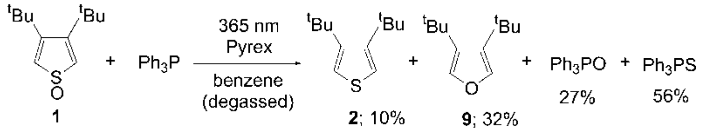
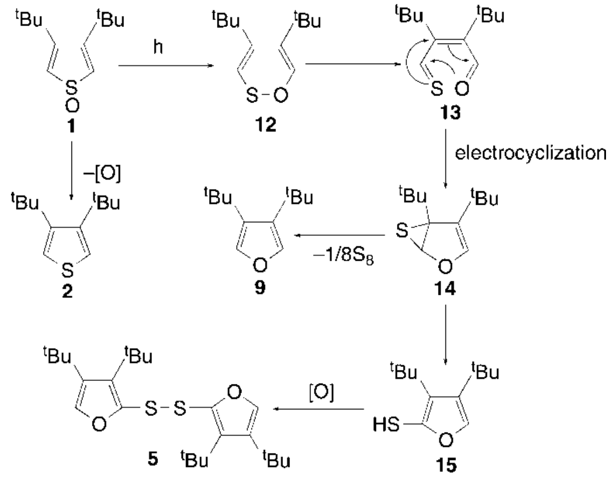


Scheme 4.

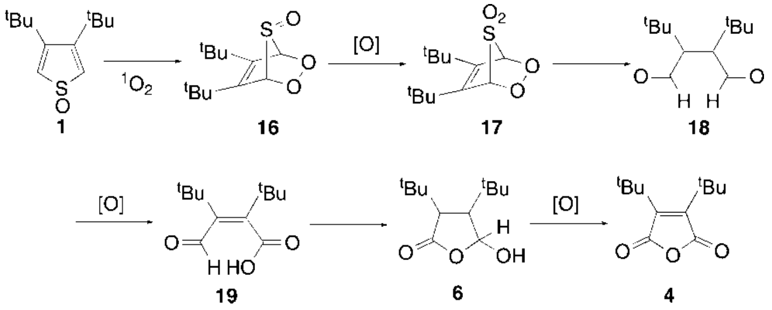
3. Discussion

The following mechanism would explain the results of the photolysis of **1** (Scheme 5). The first step is a photo-induced ring-expansion, initiated by homolytic cleavage of the C−S bond, to give 1,2-oxathiin **12** (*20*). Then **12** isomerizes to **13** that undergoes an electrocyclization to give **14** (*24*, *25*). The episulfide **14** either extrudes sulfur with a driving force of aromatization to give furan **9** or isomerizes to thiol **15**. Finally, **15** is oxidized to disulfide **5**. 1-Oxide **1** might be involved in this oxidation. However, we cannot rule out the possibility that it takes place during the purification process, although we could not find **15** in the reaction mixture by ^{1}H NMR analysis. The two facts that (1) the yield of thiophene **2** did not increase in the presence of Ph_3P, while that of furan **9** increased and that (2) no disulfide **5**, *i.e.*, its precursor **15**, was formed in the presence of Ph_3P suggest that (a) photochemical loss of the oxygen atom from **1** is a slower process than the ring-expansion to **12** and (b) the sulfur transfer from **14** to Ph_3P proceeds efficiently.



Scheme 5.

The following provides an explanation for the results of the oxidation of **1** with $^1O_2$ (Scheme 6). The initial step would be [2 + 4] cycloaddition of $^1O_2$ with **1** that gives **16**; the addition will occur at the *syn-π*-face with respect to the S=O bond (*8–10*). The oxidation of **16** by $^1O_2$ leads to the sulfone **17**, which spontaneously extrudes SO_2 to give **18** (*26*, *27* and the references cited therein). Oxidation of **18**, followed by cyclization of the resulting **19**, produces **6**, which would be oxidized further to finally lead to **4**.



Scheme 6.

We thus conclude that, unlike the case of dibenzothiophene 5-oxide, the photolysis of **1** does not generate an active oxygen atom by a unimolecular S—O bond cleavage (*11*, *12*); if it took place, it would be in very low efficiency.

4. Experimental

4.1. *Photolysis of 3,4-di-tert-butylthiophene 1-oxide (1) in hexane*

A solution of **1** (50 mg, 0.24 mmol) in 20 mL of hexane in a Pyrex test tube was exposed to the sunlight for 5 h in a sunny winter day. The irradiation of the above scale was done several times. The irradiation mixtures were combined and purified by silica gel column chromatography. After the products had been isolated in pure form and their structures determined by appropriate ways, the reaction mixture was analyzed by ^{1}H NMR with $Me_2C{=}NNHCO_2Me$ as the internal standard (MeO was used as the standard). It revealed that the irradiation gave 3,4-di-*tert*-butylthiophene (**2**, 13%), 3,4-di-*tert*-butylthiophene 1,1-dioxide (**3**, 6%), di-*tert*-butylmaleic anhydride (**4**, 5%), bis(3,4-di-*tert*-butyl-2-furyl) disulfide (**5**, 4%), and 3,4-di-*tert*-butyl-5-hydroxy-2-furanone (**6**, 11%) with 17% recovery of **1**. In one experiment, the residue of the irradiation mixture, not concentrated to dryness, was analyzed by ^{1}H NMR, but the formation of oxidation products of the solvent, such as hexanol, was not detected.

Di-*tert*-butylmaleic anhydride (**4**) (*21*). Colourless crystals (from pentane). Mp: 92.5–93.0°C. IR (KBr): 1758, 1825 cm^{-1} (C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.49 (s, 18H). MS (EI, 70 eV): m/z 210 ($M^+ + 1$).

Bis(3,4-di-*tert*-butyl-2-furyl) disulfide (**5**). Yellow needles (from EtOH). Mp: 103–104°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (s, 36H), 7.35 (s, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 31.9, 32.6, 32.7, 33.6, 135.5, 141.0, 142.5, 143.2. MS (EI, 70 eV) m/z 423 ($M^+ + 1$). Raman (neat): 466 cm^{-1}(S-S). UV (hexane) $\lambda_{max}(\varepsilon)$: 228 (7681), 277 (5768), 318 (5160) nm. Anal. Calcd. for $C_{24}H_{38}O_2S_2$: C, 68.20; H, 9.06. Found: C, 67.86; H, 9.18.

3,4-Di-*tert*-butyl-5-hydroxy-2-furanone (**6**). Colourless crystals (from hexane). Mp: 85–86°C. IR (KBr): 3345 (O—H), 1734 cm^{-1} (C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.41 (s, 9H), 1.43 (s, 9H), 3.54 (d, $J = 7.7$ Hz, 1H), 5.94 (d, $J = 7.7$ Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 30.9, 31.2, 33.2, 33.9, 95.9, 136.1, 165.4, 173.9. Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.91; H, 9.60. $^1O_2$ oxidation of cyclopentadienone **7** was reported to produce **4** and **6** (*21*). However, their melting points were not given. In addition, reportedly, the two *tert*-butyl groups of **6** appeared as only one singlet at δ 1.35 in $CDCl_3$.

4.2. *Photolysis of 3,4-di-tert-butylthiophene 1-oxide (1) in degassed benzene*

A solution of **1** (32.5 mg, 0.15 mmol) in 20 mL of benzene in a Pyrex test tube was carefully degassed and then irradiated with a small UV lamp (365 nm) for 3 h under argon. The irradiation was done several times. These were combined and purified by silica gel column chromatography. After the products had been isolated in pure form and their structures determined by appropriate ways, the reaction mixture was analyzed. It revealed that the irradiation gave **2** (26%), **5** (15%), and (**9**, 9%). In one experiment, the residue of the irradiation mixture, not concentrated to dryness, was analyzed by ^{1}H NMR, but the formation of oxidation products of the solvent, such as phenol, was not detected. 3,4-Di-*tert*-butylfuran (**9**) (22). Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (s, 18H), 7.20 (s, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 31.1, 32.5, 133.9, 140.3.

4.3. *Photooxidation of 3,4-di-tert-butylthiophene 1-oxide (1) with $^1O_2$*

A Pyrex test tube containing a solution of **1** (25 mg, 0.11 mmol) and methylene blue (2.2 mg) in 10 mL of CH_3CN was connected to a balloon filled with oxygen and the solution was exposed to the sunlight for 3 h on a sunny day. The irradiation was done several times. These were combined and purified by silica gel column chromatography. After the products had been identified, the reaction mixture was analyzed by ^{1}H NMR. It revealed that the irradiation gave **6** as the major product (59%) in addition to **2** (2%) and **4** (5%).

4.4. *Photolysis of 3,4-di-tert-butylthiophene 1-oxide (1) in the presence of triphenylphosphine (Ph_3P)*

A carefully degassed solution of **1** (33.3 mg, 0.16 mmol) and Ph_3P (40.3 mg, 0.15 mmol) in 20 mL of benzene was irradiated with a small UV lamp (365 nm) for 3 h under argon. The mixture was evaporated and the residue was analyzed by ^{1}H NMR, which revealed that thiophene **2** and furan **9** were formed in 10% and 32% yields, respectively. Then the reaction mixture was purified by silica gel column chromatography, which gave 11.4 mg (27%) of Ph_3PO and 25.0 mg (56%) of Ph_3PS in addition to a mixture of **2** and **9**.

A separate experiment revealed that **1** was inert to Ph_3P in the dark.

4.5. *X-Ray crystallographic analysis of 5 and 6*

Crystal data for **5** and **6** were recorded on a Bruker SMART APEX CCD area detector by using 0.30°-wide ω scans and graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å). Frame data (20 s, 0.30°-wide ω scans) were collected using the Bruker SMART software package. Peak integration was performed by the Bruker SAINT-Plus software package. Absorption correction was made by the software SADABS. Space group determination was done by the software XPREP. All calculations were performed by the Bruker SHELXTL 5.1 software package. The structure was solved by direct methods and refined with full-matrix least-squares by all independent reflections. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed at calculated positions.

5: $C_{24}H_{38}O_2S_2$, Mw = 442.66, monoclinic, space group $C2/c$; $a = 13.4762(9)$, $b = 17.7456(13)$, $c = 10.4824(8)$ Å; $Z = 4$; $V = 2478.3(3)$ Å^3; Dc = 1.133 g/cm^3, $\mu = 0.231$ mm^{-1}; measured reflections 8934, independent reflections 2954 [R(int) = 0.0291], $R = 0.0793$, Rw = 0.1974, GOF = 1.023.

6: $C_{12}H_{20}O_3$, $Mw = 212.28$, monoclinic, space group $P2(1)/c$; $a = 14.7163(8)$, $b = 14.7385(9)$, $c = 12.5534(7)$ Å; $Z = 8$; $V = 2473.1(2)$ Å^3; $Dc = 1.140$ g/cm^3, $\mu = 0.080$ mm^{-1}; measured reflections 12857, independent reflections 5603 [$R(\text{int}) = 0.0636$], $R = 0.0556$, $Rw = 0.0793$, GOF $= 0.965$.

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center, CCDC Nos. 670374 and 670375 for **5** for **6**, respectively. Copies of this information can be obtained from The Director, DDCD, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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