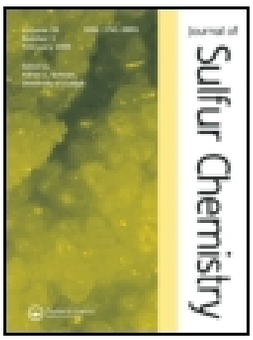

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Structure and thermal reactivity of some 2-substituted 1,3-oxathiolane *S*-oxides

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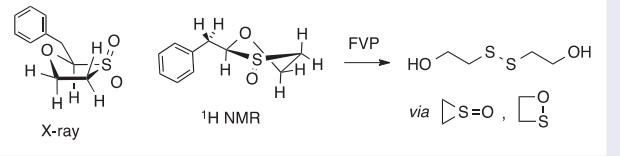
ABSTRACT

Isomerization of 2-benzylidene-1,3-dioxolane to 3-phenylbutyrolactone occurs readily under flash vacuum pyrolysis (FVP) conditions. 2-Diphenylmethyl-1,3-oxathiolane and 2-benzyl-1,3-oxathiolane have been prepared and the latter compound has been oxidized to the corresponding sulfoxide, whose structure and conformation are examined by ^{1}H NMR, and to the sulfone whose X-ray structure is determined. 2-Benzylidene-1,3-oxathiolane is also prepared and the behavior of the three *S*-oxidized oxathiolane derivatives upon FVP is examined. While extrusion of SO_n to give ethene and a carbonyl compound predominates in all three cases, the sulfoxide gives also bis(2-hydroxyethyl) disulfide, most likely formed via thiirane *S*-oxide and 1,2-oxathietane.



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1,3-Oxathiolane; pyrolysis; sulfoxide; sulphone; X-ray structure

1. Introduction

There has recently been increased interest in the use of gas-phase pyrolysis methods in the synthesis of heterocyclic compounds [1]. Sometime ago, Oda and coworkers described the thermal conversion of 2-benzylidene-1,3-dioxolanes such as **1** and **2** (Scheme 1) into the corresponding 3-phenylbutyrolactones **3** and **4** [2]. However, they used flow pyrolysis with the substrates introduced in benzene solution and carried through the furnace at atmospheric pressure by a stream of nitrogen gas. We were interested to re-examine this reaction under the more convenient and commonly used FVP conditions, and more importantly try to extend it to the 1,3-oxathiolane analogues (Scheme 2). We were aware of the possibility of SO or SO_2 extrusion intervening in these processes.

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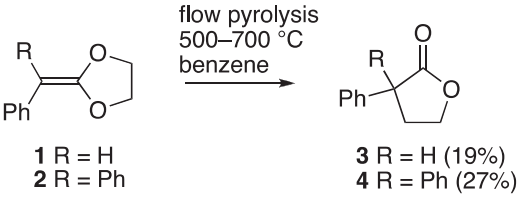
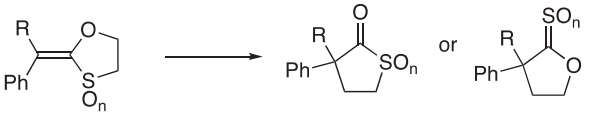


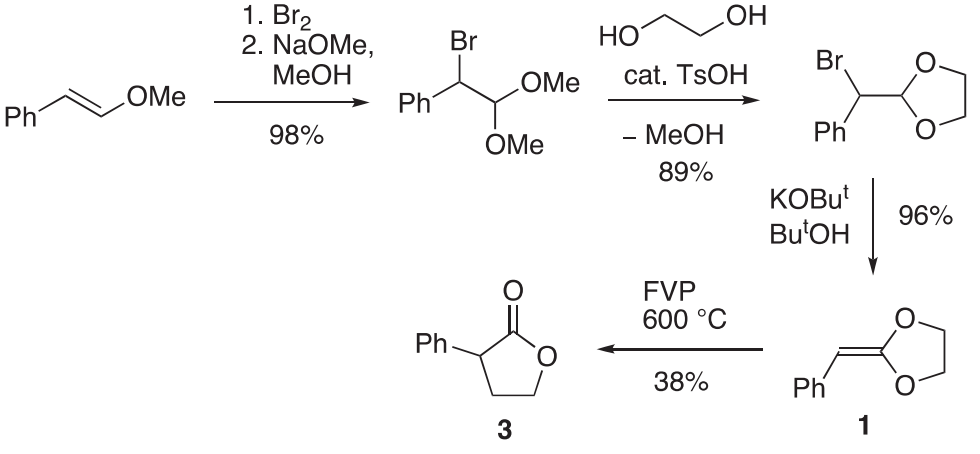
Scheme 1. Thermal conversion of 2-benzylidene-1,3-dioxolanes into 2-phenylbutyrolactones [2].



Scheme 2. Possible thermal rearrangement of 1,3-oxathiolane systems.

2. Results and discussion

The synthesis of **1** was first carried out using the reported methods (Scheme 3) [3,4] and gave excellent yields of products which showed the expected NMR data although, due to the early date of the previous work, spectroscopic data were lacking for the intermediates in this pathway. Both α-bromophenylacetaldehyde dimethyl acetal [3] and 2-(α-bromobenzyl-1,3-dioxolane [5] gave ^{1}H NMR data in agreement with the previous reports, while their ^{13}C NMR data were recorded for the first time, and for the target product **1** neither ^{1}H nor ^{13}C NMR data appear to have been previously reported. When compound **1** was subjected to FVP in a conventional flow system at a pressure of 10^{-2} Torr with an estimated contact time of 10 ms, complete reaction was observed with a furnace temperature of 600°C to give as the main isolable product 2-phenylbutyrolactone **3**. Compound **3** showed the ^{1}H and ^{13}C NMR data in good agreement with previous reports [6] and the unexpectedly complex coupling pattern of the ^{1}H NMR spectrum was in excellent agreement with a previous detailed analysis of its spectrum [7] The product was obtained in 38%



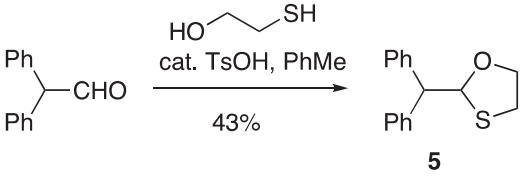
Scheme 3. Synthesis and thermal rearrangement of **1** to give **3**.

isolated yield which is double the yield obtained by Oda *et al.* [2] using benzene solution flow pyrolysis and encouraged us to examine the extension to sulfur analogues.

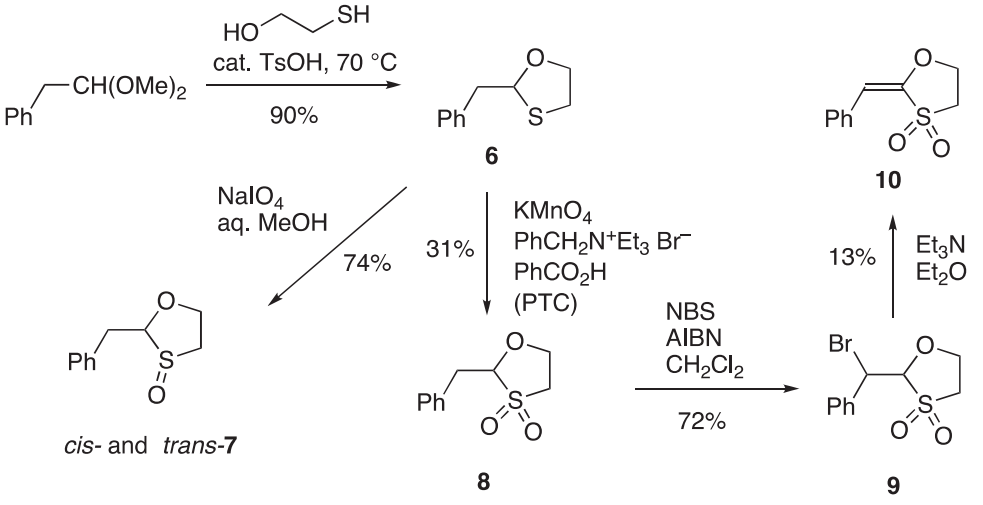
We first prepared the 2-diphenylmethyl-1,3-oxathiolane **5** from diphenylacetaldehyde (Scheme 4) and were able to fully characterize this previously unknown compound. The significant chemical shift differentiation of the two CH_2O protons (δ 4.39 vs. 3.87) pointed to a high degree of steric hindrance and we were unable to effect bromination of this compound under a range of conditions, so were unable to introduce the required exocyclic double bond.

Attention therefore turned to the 2-benzyl-1,3-oxathiolane series (Scheme 5). The oxathiolane **6** was readily prepared from phenylacetaldehyde dimethyl acetal and showed good agreement with the previously reported properties including ^{1}H and ^{13}C NMR spectra [8,9]. Oxidation using sodium periodate in aqueous methanol gave the previously unknown *S*-oxide **7** in good yield while potassium permanganate oxidation in the presence of benzoic acid [10] gave the known *S*,*S*-dioxide **8** in low yield. This also had properties in agreement with the reported values [8]. Since there have been relatively few structural studies of simple *S*-oxidized 1,3-oxathiolanes [11–13], we decided to examine the ^{1}H NMR spectrum of sulfoxide **7** in detail and to determine the X-ray structure of the sulfone **8**.

At first sight the ^{1}H NMR spectrum of **7** was unexpectedly complex (Figure 1, top) and this is attributed to the existence of *cis* and *trans*-isomers. Fortunately, a detailed study by Pihlaja *et al.* [14] succeeded in analyzing in detail the ^{1}H and ^{13}C NMR spectra of a range



Scheme 4. Synthesis of 2-diphenylmethyl-1,3-oxathiolane **5**.



Scheme 5. Synthesis of 2-benzyl-1,3-oxathiolane derivatives **6**–**10**.

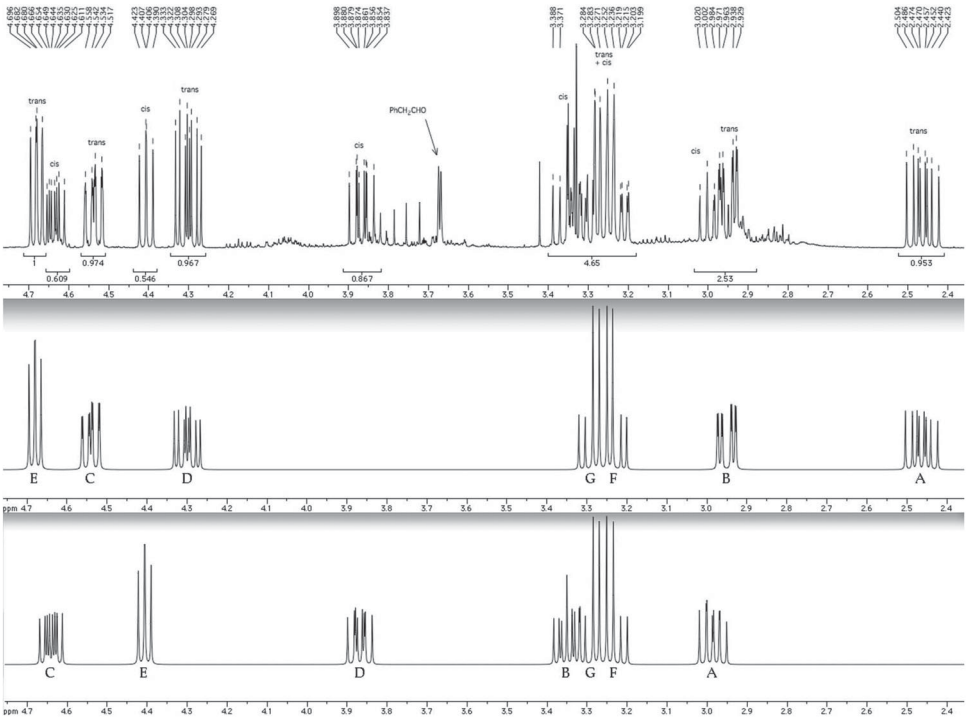
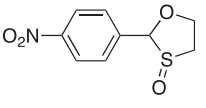


Figure 1. Aliphatic region of the ^{1}H NMR spectrum of **7** showing (top) experimental spectrum for mixture of *cis* and *trans*-isomers, (middle) simulation for *trans*-**7**, and (bottom) simulation for *cis*-**7**, both using values given in Table 1.



cis- and *trans*-**11**

Figure 2. Structure of previously investigated compound **11** [14].

of simple 1,3-oxathiolane *S*-oxides including the very similar example 2-(4-nitrophenyl)-1,3-oxathiolane *S*-oxide **11** (Figure 2). By comparing our spectra for **7** with the published values for **11** a remarkable degree of similarity was observed. In particular, the marked difference between δ_C for C-2 (100.1 vs. 110.8 for **11**, 100.2 vs. 110.4 for **7**) allowed us to unambiguously assign the isomer with the lower value as the *cis* and the higher as the *trans* by analogy. This then allowed assignment of each ^{1}H NMR signal for **7** to either *cis* or *trans* isomers using an HSQC correlation (Figure 1, Table 1). Starting from the chemical shift assignments and coupling constants reported for **11** [14], these parameters were optimized using simulation to match the observed spectra for **7**. The final values are shown in Table 1 and the resulting simulated spectra for *cis* and *trans* isomers (Figure 1, middle and bottom) are in almost perfect agreement with experiment. The very high degree of similarity in the pattern of coupling constants between **7** and **11**, and particularly the high degree of difference between the values of $J_{H4a-H5s}$ and $J_{H4s-H5a}$ for the *trans* isomer as

Table 1. Observed ^{1}H NMR chemical shifts (ppm) and coupling constants (Hz) for the *cis* and *trans* isomers of sulfoxide **7**.

	trans-7		Coupling	to	*cis*-7		Coupling	to
	δ_H	H-4s	H-5a	H-5s	δ_H	H-4s	H-5a	H-5s
H-4a	2.464	13.6	7.0	11.7	2.986	13.0	7.5	6.8
H-4s	2.95		1.0	4.3	3.35		5.3	7.9
H-5a	4.54			10.0	4.64			9.8
H-5s	4.30				3.868			
			CH_2Ph-1	CH_2Ph-2			CH_2Ph-1	CH_2Ph-2
H-2	4.68		5.6	6.4	4.406		6.8	6.0
CH_2Ph-1	3.23			14.0	3.23			14.0
CH_2Ph-2	3.29				3.29			

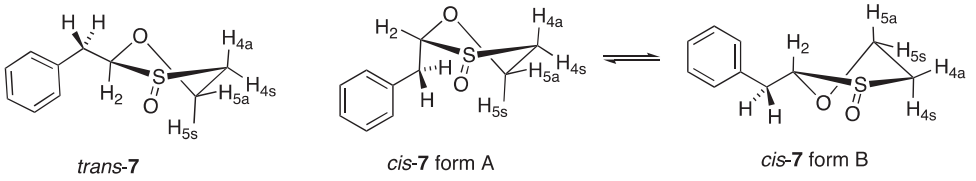


Figure 3. Solution conformations of *trans* and *cis*-**7** with protons labelled as *syn* (s) or *anti* (a) to the sulfoxide oxygen.

compared to the almost equal magnitude of these values for the *cis* isomer, leads us to the same conclusion as was reached for **11** [14]: that *trans*-**7** exists overwhelmingly as a single half-chair conformation while *cis*-**7** is an almost equal mixture of two alternative half-chair conformations labeled A and B (Figure 3).

A single-crystal X-ray diffraction study on the sulfone **8** gave a structure (Figure 4) showing an obvious 'envelope' conformation with the ring oxygen out of the plane of the remaining four essentially coplanar ring atoms and a ring angle of only 94.2° at sulfur. As far as we are aware, there are only two previous X-ray structures of 1,3-oxathiolane *S*,*S*-dioxides: the carbohydrate-derived compounds **12** [15,16] and **13** [17]. These both show

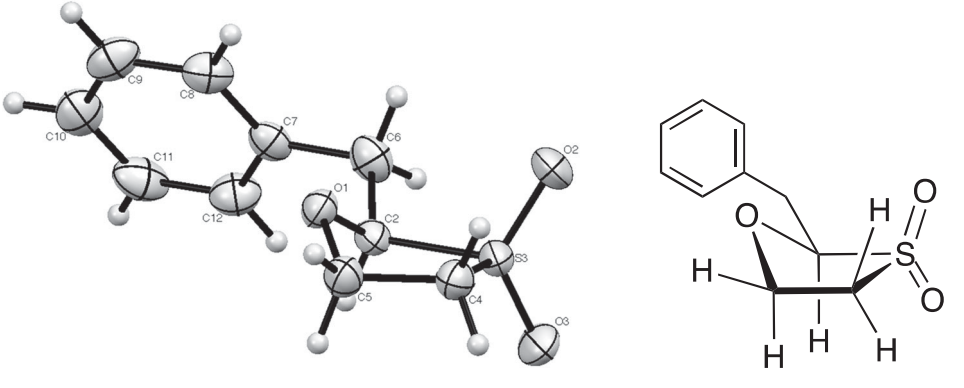


Figure 4. X-ray structure of **8** (ORTEP diagram, 50% probability level). Selected bond lengths and angles: O1-C2 1.403(2), C2-S3 1.824(2), S3-C4 1.773(2), C4-C5 1.522(3), C5-O1 1.444(2) Å; C2-O1-C5 107.60(14), O1-C2-S3 102.97(13), C2-S3-C4 94.17(9), S3-C4-C5 103.78(14), C4-C5-O1 107.32(16)°.

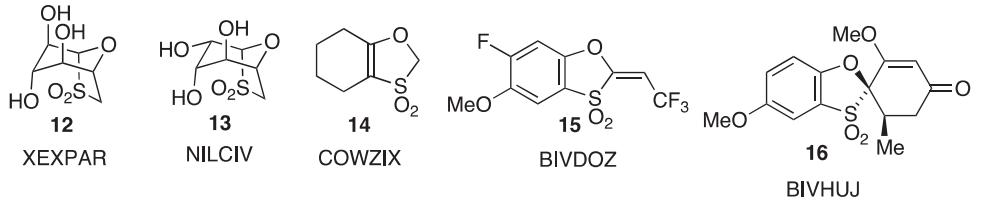


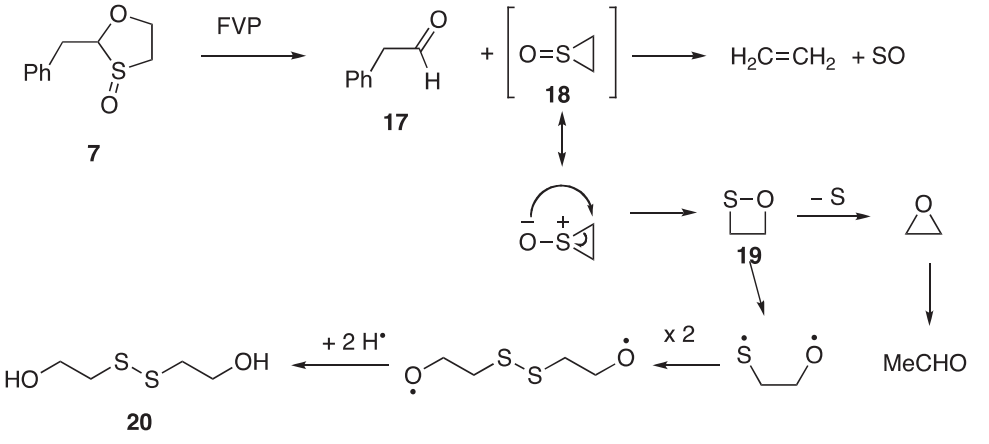
Figure 5. 1,3-Oxathiolane and 1,3-oxathiole *S,S*-dioxides previously characterized by X-ray crystallography with CCDC Reference Codes.

very similar envelope conformations and the bond lengths and angles within the ring are very similar to those observed for **8**. For the previous structures, the envelope conformation was attributed to the conformationally constrained bicyclic nature of the compounds, but it is interesting to observe that **8**, although freed of any such constraints, still prefers to adopt such a conformation. The values for the C(2)–S and S–C(4) bond lengths as well as the C(2)–S–C(4) angle also agree well with those observed for the few unsaturated 1,3-oxathiole *S,S*-dioxides **14** [18,19] and **15** and **16** [20] to be crystallographically characterized although in all these cases the oxathiole ring is planar (Figure 5).

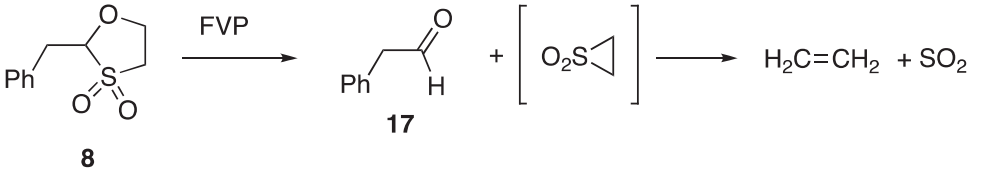
To obtain a sulfur-containing system more closely analogous to **1**, we examined the introduction of an exocyclic double bond at C-2. Attempted radical bromination of either **6** or **7** gave complex mixtures of products but the sulfone **8** was brominated in good yield to give the previously unknown compound **9** (Scheme 5). This proved to be rather unstable but was characterized spectroscopically and showed a distinctive AB pattern (δ_H 5.17, 4.71 $J = 9.6$ Hz) for the PhCHBr–CH(O)SO_2 function. There is some precedent for the formation of 2-alkylidene-1,3-benzoxathiole *S,S*-dioxides in the study of griseofulvin analogues such as **15** [20,21] and chlorination/dehydrochlorination was successful in some cases. When a crude sample of **9** was treated with triethylamine in diethyl ether at 0°C, the resulting product gave spectra which were dramatically simplified as compared to all the earlier compounds **6–9** and consistent with the completely planar structure **10**. In particular, there were two simple triplets for the ring CH_2 groups (δ_H 4.76, 3.36) and distinctive signals for PhCH = (δ_H 6.13; δ_C 103.6).

We now examined the pyrolysis behavior of the sulfur heterocycles prepared under FVP conditions. Thermal extrusion of SO_2 from five-membered ring heterocycles is well known [22], but we are only aware of one report describing such extrusion from 1,3-oxathiolane 3,3-dioxides [23]. In this, 4,4-dimethyl-1,3-oxathiolane 3,3-dioxide was found to fragment cleanly into SO_2, isobutene and formaldehyde. This allowed Gokel and coworkers to use the compound as a formyl anion equivalent [24], by deprotonation and alkylation with an alkyl halide, RX, at C-2 followed by thermal fragmentation to generate the corresponding aldehyde RCHO. However to our knowledge there have been no reports of thermal reactivity for 1,3-oxathiolane 3-oxides. When compound **7** was subjected to FVP, complete reaction was achieved at 500°C and the products in the cold trap were readily identified as phenylacetaldehyde **17**, ethene and acetaldehyde. At the furnace exit, there were several minor less volatile products. By lowering the reaction temperature to 450°C, some starting material was obtained but the proportion of one minor product was increased allowing it to be isolated by preparative TLC and identified as bis(2-hydroxyethyl) disulfide **20**. At both 450°C and at 400°C, the cold trap products were mainly phenylacetaldehyde **17**, ethene

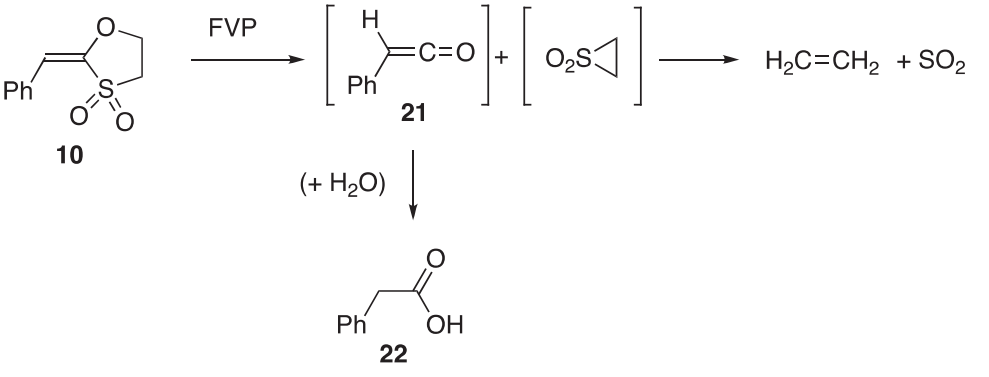
and acetaldehyde with increasing amounts of unreacted starting material recovered at the furnace exit. We propose that the unexpected disulfide product **20** is derived from thiirane *S*-oxide **18** (Scheme 6). Previous mechanistic studies have described formation of **20** from **18** in solution under acidic conditions [25,26] but under neutral gas-phase conditions a different explanation is required. We believe that ring expansion of **18** to give 1,2-oxathietane **19** may be followed either by loss of sulfur and isomerization, thus explaining the formation of acetaldehyde, or by homolysis of the O–S bond, dimerization of the diradicals and hydrogen atom abstraction to give **20** as shown (Scheme 6).



Scheme 6. FVP behavior of sulfoxide **7**.



Scheme 7. FVP behavior of sulfone **8**.



Scheme 8. FVP behavior of unsaturated sulfone **10**.

The corresponding sulfone **8** showed a simpler pattern of behavior with clean reaction upon FVP at 400°C to give phenylacetaldehyde **17**, SO_2 and ethene as the only products (Scheme 7). This is entirely analogous to the behavior of the 4,4-dimethyl compounds described by Gokel [23].

The unsaturated sulfone **10** was mainly unreacted at 400°C but underwent complete reaction at 500°C to give phenylacetic acid **22** as well as ethene and SO_2 (Scheme 8). Since the sample **10** used contained some **8**, there was also some phenylacetaldehyde present from its pyrolysis. We interpret the formation of **22** as involving the expected extrusion to form phenylketene **21** which is hydrolyzed by adventitious moisture in the cold trap.

3. Conclusion

The previously reported thermal isomerization of 2-benzylidene-1,3-dioxolane to 3-phenylbutyrolactone proceeds well under FVP conditions. An analogous process was not observed for *S*-oxidized sulfur analogues, which instead underwent SO_n extrusion and fragmentation to give acyclic carbonyl products. A minor process observed for the cyclic sulfoxide **7** was the formation of bis(2-hydroxyethyl) disulfide, apparently via thermal ring-expansion of thiirane *S*-oxide. Conformational analysis of **7** by ^{1}H NMR showed it to be remarkably similar to the 2-*p*-nitrophenyl analogue, while X-ray structure determination of **8** showed a similar envelope conformation to that observed in previous bicyclic examples.

4. Experimental

4.1. General

Melting points were determined on a Reichert hot-stage microscope and are uncorrected. NMR spectra were recorded for ^{1}H at 300 or 400 MHz and for ^{13}C at 75 or 100 MHz on Bruker instruments. Spectra were obtained for solutions in $CDCl_3$ with Me_4Si as internal reference and coupling constants are given in Hz. FVP was conducted using a conventional flow system with the sample being volatilized from an electrically heated inlet tube through a horizontal quartz reactor tube (30 × 2.5 cm) heated externally by a laboratory tube furnace, and connected via a liquid nitrogen-cooled product collection trap to a rotary vacuum pump. The system was maintained at pressures in the range 10^{-3}–10^{-2} Torr corresponding to a contact time in the hot zone of 1–10 ms. Full details of the procedure are given in a recent publication [27]. CCDC 1570002 (**8**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.2. Synthesis and pyrolysis of 2-(phenylmethylene)-1,3-dioxolane 1

4.2.1. α-Bromophenylacetaldehyde dimethyl acetal

To a solution of β-methoxystyrene [5] (21.7 g, 161 mmol) in CH_2Cl_2 (100 mL) stirred at –50°C, a solution of bromine (8.3 mL, 25.8 g, 161 mmol) in CH_2Cl_2 (30 mL) was added dropwise over 30 min. Sodium (3.84 g, 167 mmol) was dissolved in methanol (50 mL) to give a solution of sodium methoxide. To the cold reaction mixture, methanol (7.5 mL) was

slowly added followed by the sodium methoxide solution. After 30 min, the resulting white suspension was added to water (200 mL) and the organic layer was separated, washed with water (2 × 100 mL), dried and evaporated to give the title product (36.0 g, 98%) as a brown oil. ^{1}H NMR (300 MHz): 7.43–7.29 (5 H, m, Ph), 4.93 (1 H, d, *J* 6.9, C*H*(OMe)$_2$), 4.74 (1 H, d, *J* 6.9, C*H*Br), 3.48, (3 H, s, OMe), 3.27 (3 H, s, OMe). ^{13}C NMR (100 MHz): 138.1 (C), 129.4 (CH), 128.51 (2CH), 128.47 (2CH), 105.9 (CH(OMe)$_2$), 55.0 (OMe), 54.8 (OMe), 52.9 (CHBr).

4.2.2. 2-(α-Bromobenzyl)-1,3-dioxolane

A mixture of α-bromophenylacetaldehyde dimethyl acetal (10.0 g, 41 mmol), ethane-1,2-diol (3.62 g, 58 mmol) and *p*-toluenesulfonic acid (20 mg) was distilled in a bath held at 180°C until evolution of methanol ceased. The residue was dissolved in CH_2Cl_2 (100 mL) and the solution was washed with aqueous sodium carbonate, dried and evaporated to give the title product (8.85 g, 89%) as a brown oil. ^{1}H NMR (400 MHz): 7.50–7.46 (2 H, m, Ph), 7.38–7.25 (3 H, m, Ph), 5.32 (1 H, d, *J* 4.4, OCHO), 4.91 (1 H, d, *J* 4.4, CHBr), 4.00–3.87 (4 H, m, CH_2). ^{13}C NMR (100 MHz): 137.1 (C), 128.8 (2CH), 128.7 (CH), 128.4 (2CH), 104.6 (OCHO), 65.84 (CH_2), 65.81 (CH_2), 54.4 (CHBr).

4.2.3. 2-Benzylidene-1,3-dioxolane 1

A solution of potassium *tert*-butoxide (0.22 g, 2.0 mmol) in *tert*-butanol (1.5 mL) was added to 2-(α-bromobenzyl)-1,3-dioxolane (0.50 g, 2.0 mmol) and the mixture was heated under reflux for 2 h. A vacuum was applied and once all the *tert*-butanol was removed the residue was extracted with diethyl ether (5 mL) which was washed with water, dried and evaporated to afford the product (0.35 g, 96%) as a pale yellow oil. ^{1}H NMR (400 MHz): 7.37 (2 H, d, *J* 8.0, Ph), 7.23 (2 H, t, *J* 8.0, Ph), 7.00 (1 H, t, *J* 8.0, Ph), 4.86 (1 H, s, PhCH=), 4.40 (2 H, t, *J* 7.2, CH_2), 4.23 (2 H, t, *J* 7.2, CH_2). ^{13}C NMR (100 MHz): 159.7 (OCO), 136.3 (C), 128.2 (3CH), 125.8 (2CH), 123.4 (CH), 74.7 (PhCH=), 67.0 (CH_2), 64.8 (CH_2).

4.2.4. FVP of 1 to give 3-phenylbutyrolactone 3

FVP of 2-(phenylmethylene)-1,3-dioxolane (148 mg) at 600°C and 10^{-2} Torr gave at the furnace exit 3-phenylbutyrolactone **2** (56 mg, 38%). ^{1}H NMR (400 MHz): 7.38–7.25 (5 H, m, Ph), 4.43 (1 H, ddd, *J* 9.2, 8.4, 3.2, OCH_2), 4.30 (1 H, ddd, 9.2, 9.2, 6.8, OCH_2), 3.78 (1 H, dd, *J* 10.4, 9.2, PhCH–), 2.67, (1 H, dddd, *J* 12.4, 9.2, 6.8, 3.2, CH_2), 2.40 (1 H, dddd, *J* 12.4, 10.4, 9.2, 8.4, CH_2). ^{13}C NMR (100 MHz): 177.4 (CO), 136.6 (C), 128.7 (2CH), 127.8 (2CH), 127.5 (CH), 66.4 (CH_2O), 45.3 (PhCH), 31.4 (CH_2).

4.3. Synthesis of 2-(diphenylmethyl)-1,3-oxathiolane 5

A solution of diphenylacetaldehyde (2.19 g, 11.2 mmol), 2-mercaptoethanol (0.87 g, 11.1 mmol) and *p*-toluenesulfonic acid (0.02 g, 0.1 mmol) in toluene (35 mL) was heated under reflux under Dean–Stark azeotropic distillation conditions. After heating for 3 h, the solution was cooled to room temperature and most of the solvent was removed under reduced pressure. The resulting solid was filtered off to give the product (1.24 g, 43%) as a white solid, mp 75–78°C. HRMS (ESI) *m/z* calcd for $C_{16}H_{16}OSNa$: 279.0820, found: 279.0809 [M + Na]. ^{1}H NMR (300 MHz): 7.34-7.21 (10 H, m, Ph), 5.83 (1 H, d, *J* 9.0, OCHS), 4.39 (1 H, m, OCH_2), 4.25 (1 H, d, *J* 9.0, Ph_2CH), 3.87 (1 H, m, OCH_2) and

2.98 (2 H, m, SCH_2). ^{13}C NMR (75 MHz): 141.76 (C), 141.74 (C), 128.5 (2CH), 128.4 (2CH), 128.32 (2CH), 128.28 (2CH), 127.0 (CH), 126.7 (CH), 89.5 (OCS), 72.1 (CH_2O), 58.0 (CH_2S), 32.8 (Ph_2CH).

4.4. Synthesis of 2-benzyl-1,3-oxathiolane and its S-oxides

4.4.1. Synthesis of 2-benzyl-1,3-oxathiolane 6

Phenylacetaldehyde dimethyl acetal (5.8 g, 34.9 mmol), 2-mercaptoethanol (3.9 g, 3.5 mL, 49.9 mmol) and *p*-toluenesulfonic acid (0.01 g) were heated to 100°C. Once the methanol produced had boiled off, the residual oil was dissolved in CH_2Cl_2 (15 mL) and the solution was washed with water, dried and evaporated to afford the product (5.64 g, 90%) as a brown oil. ^1H NMR (400 MHz): 7.32–7.22 (5 H, m, Ph), 5.28 (1 H, t, *J* 6.2, OCHS), 4.35 (1 H, m, OCH_2), 3.79 (1 H, m, OCH_2), 3.23 (1 H, m, SCH_2), 3.02 (3 H, m, SCH_2 and CH_2Ph). ^{13}C NMR (100 MHz) 137.4 (C), 129.1 (2CH), 128.3 (2CH), 126.7 (CH), 87.3 (OCHS), 71.4 (CH_2O), 42.9 ($PhCH_2$), 32.7 (CH_2S). The NMR data reported agree with the literature values [8,9].

4.4.2. Synthesis of 2-benzyl-1,3-oxathiolane 3-oxide 7

To a stirred solution of 2-benzyl-1,3-oxathiolane (1.00 g, 5.6 mmol) in methanol (10 mL), a solution of sodium metaperiodate (1.24 g, 5.8 mmol) in water (5 mL) was added dropwise. The reaction mixture was stirred overnight then filtered and the filtrate extracted with CH_2Cl_2 (20 mL) which was dried and evaporated to yield the product (0.81 g, 74%) as an orange oil. HRMS (ESI) *m/z* calcd for $C_{10}H_{12}SO_2Na$: 219.0456, found: 219.0444 [M + Na]. ν_{max}/cm^{-1} 1213, 1055, 1030 (S=O), 747, 540. *m/z* (ESI) 219.04 (M + Na, 100%).

Trans diastereomer ^1H NMR (400 MHz): 7.33–7.24 (5 H, m, Ph), 4.68 (1 H, dd, *J* 6.4, 5.6, OCHS), 4.54 (1 H, m, OCH_2), 4.30 (1 H, m, OCH_2), 3.38–3.22 (2 H, m, $PhCH_2$), 2.99–2.90 (1 H, m, SCH_2), 2.46 (1 H, m, SCH_2). ^{13}C NMR (100 MHz): 135.3 (C), 128.6 (2CH), 128.5 (2CH), 127.1 (CH), 110.4 (OCS), 68.9 (CH_2O), 52.5 (CH_2S), 36.7 ($PhCH_2$).

Cis diastereomer ^1H NMR (400 MHz): 7.33–7.24 (5 H, m, Ph), 4.64 (1 H, m, OCH_2), 4.41 (1 H, dd, *J* 6.8, 6.0, OCHS), 3.87 (1 H, m, OCH_2), 3.38–3.22 (3 H, m, $PhCH_2$ and SCH_2), 2.99–2.90 (1 H, m, SCH_2); ^{13}C NMR (100 MHz) 135.9 (C), 129.4 (2CH), 129.3 (2CH), 127.0 (CH), 100.2 (OCS), 67.8 (CH_2O), 54.2 (CH_2S), 32.8 ($PhCH_2$).

4.4.3. Synthesis of 2-benzyl-1,3-oxathiolane 3,3-dioxide 8

2-Benzyl-1,3-oxathiolane (1.00 g, 5.6 mmol), benzoic acid (0.68 g, 5.6 mmol) and benzyltriethylammonium chloride (0.21 g, 0.94 mmol) were stirred in CH_2Cl_2 (30 mL). A solution of potassium permanganate (2.00 g, 12.7 mmol) in water (50 mL) was added and the mixture was stirred vigorously overnight. Sodium metabisulfite was added until the reaction mixture turned colorless and the suspension was filtered through celite. The CH_2Cl_2 layer was separated and the aqueous layer extracted with CH_2Cl_2 (30 mL). The combined organic phase was washed with aqueous hydrazine dihydrochloride, aqueous sodium hydroxide and then dried and evaporated to yield the product (0.36 g, 31%) as colorless crystals, mp 98–99.5°C, (lit. [8] 95–96.5°C). HRMS (ESI) *m/z* calcd for $C_{10}H_{12}SO_3Na$: 235.0405, found: 235.0398 [M + Na]. ^1H NMR (400 MHz): 7.36–7.28 (5 H, m, Ph), 4.53 (1 H, ddd, *J* 10.4, 6.0, 4.0, OCH_2), 4.30 (1 H, dd, *J* 8.4, 4.4, OCHS), 4.13 (1 H, ddd, *J* 10.4, 9.6, 7.2, OCH_2), 3.27–3.21 (3 H, m, $PhCH_2$ and SCH_2), 3.05 (1 H, dd, *J* 14.8, 8.4, SCH_2). ^{13}C

NMR (100 MHz): 134.6 (C), 129.3 (2CH), 128.7 (2CH), 127.3 (CH), 91.7 (OCHS), 64.6 (CH_2O), 48.9 (CH_2S), 34.1 ($PhCH_2$). *m/z* (ESI) 235.04 (M + Na, 100%). The NMR data reported are in agreement with those in the literature [8].

4.4.4. X-ray structure determination of 2-benzyl-1,3-oxathiolane 3,3-dioxide 8

Data were collected on a Rigaku Saturn 724 diffractometer using graphite monochromated Mo–K_α radiation, $\lambda = 0.71075$ Å. Crystal data for $C_{10}H_{12}O_3S$, M 212.26, colorless platelet $0.20 \times 0.10 \times 0.010$ mm. Monoclinic, space group $P2_1/n$, $a = 12.535(5)$, $b = 5.7368(16)$, $c = 15.205(5)$ Å, $\beta = 112.539(7)°$, $V = 1009.9(6)$ Å^3, $Z = 4$, $D_c = 1.396$ g/cm^3, $T = 125$ K, $R = 0.0344$, $R_w = 0.0780$ for 1387 data with $I > 2\sigma(I)$ and 127 parameters.

4.5. Preparation of 2-benzylidene-1,3-oxathiolane 3,3-dioxide

4.5.1. Synthesis of 2-(α-bromobenzyl)-1,3-oxathiolane 3,3-dioxide 9

A solution of 2-benzyl-1,3-oxathiolane 3,3-dioxide (0.10 g, 0.47 mmol), *N*-bromosuccinimide (0.08 g, 0.47 mmol) and AIBN (0.008 g) in CH_2Cl_2 (5 mL) was heated under reflux. After 4 hours the reaction mixture was filtered, washed with water, dried and evaporated to yield the product (0.10 g, 72%) as an unstable white solid which still contained some starting material and succinimide but was used without further purification for the next step. HRMS (ESI) *m/z* calcd for $C_{10}H_{11}O_3{}^{79}BrSNa$: 312.9510 and $C_{10}H_{11}O_3{}^{81}BrSNa$: 314.9490, found 312.9499 [^{79}Br–M + Na] and 314.9477 [^{81}Br–M + Na]. ν_{max}/cm^{-1} 1314 (S=O), 1117 (S=O), 1076 (C–O), 1055 (C–O), 754 (C–S), 692 (C–Br). ^{1}H NMR (400 MHz): 7.51–7.26 (5 H, m, Ph), 5.17 (1 H, d, *J* 9.6, OCHS), 4.71 (1 H, d, *J* 9.6, PhCHBr), 4.66–4.61 (1 H, m, OCH_2), 4.30–4.23 (1 H, m, OCH_2), 3.35-3.31 (2 H, m, SO_2CH_2). ^{13}C NMR (100 MHz): 134.5 (C), 130.0 (CH), 129.0 (2CH), 128.6 (2CH), 92.7 (OCHS), 64.1 (CH_2O), 50.6 (CH_2S), 47.8 (PhCHBr). *m/z* (ESI) 314.95 (^{81}Br-M + Na, 100%), 312.95 (^{79}Br-M + Na, 98%).

4.5.2. Preparation of 2-benzylidene-1,3-oxathiolane 3,3-dioxide 10

A solution of 2-(α-bromobenzyl)-1,3-oxathiolane 3,3-dioxide (0.24 g, 0.82 mmol) in diethyl ether (5 mL) was stirred at 0°C. Triethylamine (0.12 g, 1.20 mmol) was added slowly and the reaction mixture left to stir for 1 h. Addition of CH_2Cl_2 (10 mL) gave a clear solution which washed with water (2×10 mL), dried and evaporated to yield the product. This was then recrystallized from hexane/diethyl ether (3:1) to obtain the pure product (22.5 mg, 13%) as colorless crystals. ^{1}H NMR (400 MHz): 7.60–7.29 (5 H, m, Ph), 6.13 (1 H, s, PhCH=), 4.76 (2 H, t, *J* 6.6, OCH_2), 3.35 (2 H, t, *J* 6.6, SO_2CH_2). ^{13}C NMR (100 MHz) (obtained from a mixture containing **8**): 147.4 (OCS), 131.9 (C), 129.2 (2CH), 128.6 (2CH), 128.4 (CH), 103.6 (PhCH=), 65.9 (CH_2O), 46.4 (CH_2S).

4.6. FVP of 1,3-oxathiolane S-oxides

4.6.1. FVP of 2-benzyl-1,3-oxathiolane 3-oxide 7

FVP of **7** (49.5 mg) at 500°C gave, in the cold trap, a mixture of phenylacetaldehyde **17** ^{1}H NMR (300 MHz): 9.75 (1 H, t, *J* 2.4, CHO), 7.42–7.22 (5 H, m, ArH), 3.70 (2 H, d, *J* 2.4, CH_2) (agrees with lit. [28]); ethene ^{1}H NMR (300 MHz): 5.40 (s); and acetaldehyde ^{1}H NMR (400 MHz): 9.79 (1 H, q, *J* 2.8, CHO), 2.20 (3 H, d, *J* 2.8). At the furnace exit, there

was a small amount of material consisting of bis(2-hydroxyethyl) disulfide **20** and other unidentified components.

FVP of **7** (103 mg) at 450°C gave, in the cold trap, a mixture of phenylacetaldehyde, ethene and acetaldehyde as described above. At the furnace exit, there was an oil consisting of unchanged **7**, bis(2-hydroxyethyl) disulfide and other unidentified components. Preparative TLC (SiO_2, EtOAc) yielded bis(2-hydroxyethyl) disulfide **20** ^{1}H NMR (400 MHz): 3.92 (2 H, t, *J* 5.8, CH_2OH), 2.89 (2 H, t, *J* 5.8, SCH_2), 1.25 (1H, br s, –OH). ^{13}C NMR (100 MHz): 60.3 (CH_2O), 41.2 (CH_2S) (agrees with lit. [29]).

4.6.2. FVP of 2-benzyl-1,3-oxathiolane 3,3-dioxide 8

FVP of **8** (38.1 mg) at 400°C gave, in the cold trap, a mixture of phenylacetaldehyde, ^{1}H NMR as above; ^{13}C NMR (100 MHz) 199.5 (CO), 129.6 (2CH), 129.0 (2CH), 127.4 (CH), 50.6 (CH_2) (agrees with lit. [28]) and ethene ^{1}H NMR as above.

4.6.3. FVP of 2-benzylidene-1,3-oxathiolane 3,3-dioxide 10

FVP of **10** (46.8 mg, containing some **8**) at 500°C gave, in the cold trap, a mixture of phenylacetaldehyde **17**, ^{1}H NMR as above, ethene, ^{1}H NMR as above, and phenylacetic acid **22** ^{1}H NMR (400 MHz) 7.40–7.22 (5 H, m, ArH), 3.72 (2 H, s, CH_2); ^{13}C NMR (100 MHz) 178.5 (CO), 134.5 (C), 129.3 (2CH), 128.6 (2CH), 127.3 (CH), 40.8 (CH_2) (agrees with lit. [30]).

Disclosure statement

No potential conflict of interest was reported by the authors.

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