

Bis(3-phenyl-1,4-benzodioxin-2-yl) Sulfide: Formation and Structure Elucidation

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Bis(3-phenyl-1,4-benzodioxin-2-yl)sulfid: Bildung und Strukturermittlung

Bei der Darstellung von 2-Phenyl-1,4-benzodioxin (2) durch Dehydratisierung von 2,3-Dihydro-2-hydroxy-2-phenyl-1,4-benzodioxin (1) mittels Thionylchlorid in Pyridin bei 120–130°C wird als Nebenprodukt Bis(3-phenyl-1,4-benzodioxin-2-yl)sulfid (3) gebildet. Dessen Struktur ist durch Röntgenstrukturanalyse und unabhängige Darstellung aus 2 und Schwefeldichlorid gesichert. Die Bildung des Sulfids 3 bei der Dehydratisierung von 1 mittels Thionylchlorid läßt sich vermeiden, wenn man die Reaktion unterhalb 90°C durchführt.

Following the procedure by *Katritzky et al.*¹⁾, we prepared 2-phenyl-1,4-benzodioxin (2) by dehydration of 2,3-dihydro-2-hydroxy-2-phenyl-1,4-benzodioxin (1) with thionyl chloride in pyridine at elevated temperatures (Eq. 1). While the expected benzodioxin 2 was the main product

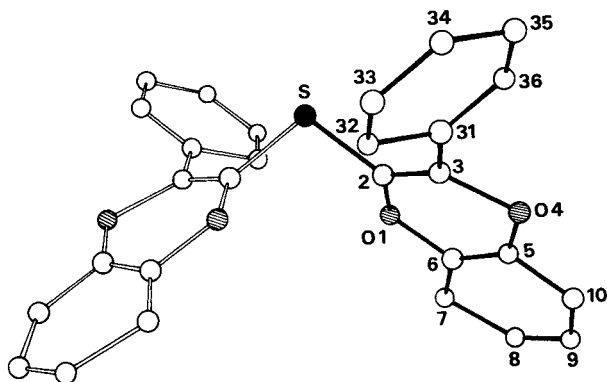
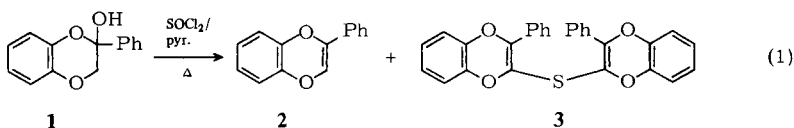


Fig. 1. Perspective drawing of bis(3-phenyl-1,4-benzodioxin-2-yl) sulfide (3), with the labeling of the atoms corresponding to Tables 1 and 2

Table 1. Positional and thermal parameters (\AA^2) of bis(3-phenyl-1,4-benzodioxin-2-yl) sulfide (3). U_{ij} is defined for $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$; the standard deviations are given in parentheses

Atom	Label	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S	4(e)	0	0.2270(2)	3/4	0.052(1)	0.054(1)	0.062(1)	0	0.027(1)	0
O(1)	8(f)	0.0282(1)	0.6082(5)	0.8553(1)	0.055(1)	0.075(1)	0.065(1)	-0.011(1)	0.031(1)	0.000(1)
C(2)	8(f)	0.0524(1)	0.4592(6)	0.8199(1)	0.053(1)	0.055(2)	0.052(1)	0.002(1)	0.025(1)	0.001(1)
C(3)	8(f)	0.1103(1)	0.4596(6)	0.8440(1)	0.053(1)	0.058(2)	0.051(1)	0.004(1)	0.025(1)	-0.002(1)
O(4)	8(f)	0.1532(1)	0.5933(5)	0.9118(1)	0.054(1)	0.080(1)	0.061(1)	-0.009(1)	0.027(1)	-0.005(1)
C(5)	8(f)	0.1301(1)	0.7666(6)	0.9437(1)	0.062(2)	0.063(2)	0.048(1)	0.005(1)	0.028(1)	-0.004(1)
C(6)	8(f)	0.0687(1)	0.7790(6)	0.9148(1)	0.066(2)	0.057(2)	0.049(1)	0.004(1)	0.029(1)	-0.000(1)
C(7)	8(f)	0.0464(1)	0.9595(7)	0.9461(2)	0.081(2)	0.072(2)	0.070(2)	0.004(2)	0.045(2)	0.003(2)
C(8)	8(f)	0.0861(2)	0.1269(8)	0.0074(2)	0.113(3)	0.078(2)	0.070(2)	-0.009(2)	0.057(2)	-0.003(2)
C(9)	8(f)	0.1474(2)	0.1113(8)	0.0371(2)	0.100(3)	0.086(2)	0.058(2)	-0.010(2)	0.043(2)	-0.024(2)
C(10)	8(f)	0.1693(1)	0.9311(7)	0.0050(2)	0.075(2)	0.080(2)	0.054(2)	0.001(2)	0.032(1)	-0.013(2)
C(31)	8(f)	0.1385(1)	0.3222(6)	0.8068(1)	0.052(1)	0.057(2)	0.060(2)	0.001(1)	0.031(1)	-0.006(1)
C(32)	8(f)	0.1157(1)	0.3722(7)	0.7308(2)	0.063(2)	0.083(2)	0.067(2)	0.009(2)	0.036(1)	0.005(2)
C(33)	8(f)	0.1418(1)	0.2366(8)	0.6961(2)	0.076(2)	0.103(3)	0.066(2)	0.000(2)	0.044(2)	-0.002(2)
C(34)	8(f)	0.1901(1)	0.0581(8)	0.7365(2)	0.072(2)	0.083(2)	0.084(2)	-0.009(2)	0.052(2)	-0.004(2)
C(35)	8(f)	0.2136(1)	0.0154(7)	0.8117(2)	0.063(2)	0.071(2)	0.090(2)	0.005(2)	0.045(2)	0.006(2)
C(36)	8(f)	0.1886(1)	0.1494(6)	0.8477(2)	0.057(2)	0.067(2)	0.063(2)	0.005(1)	0.033(1)	-0.002(1)

Table 2. Bond lengths (pm) and angles (deg) for bis(3-phenyl-1,4-benzodioxin-2-yl) sulfide (3); the standard deviations are given in parentheses

Bond lengths (pm)								
S	- C(2)	174.9(2)	C(3) - O(4)	140.2(3)	C(6) - C(7)	138.3(5)	C(31) - C(32)	139.1(4)
O(1)	- C(2)	139.9(4)	C(3) - C(31)	148.0(5)	C(7) - C(8)	138.4(4)	C(31) - C(36)	138.3(4)
O(1)	- C(6)	138.0(3)	O(4) - C(5)	138.4(4)	C(8) - C(9)	138.2(6)	C(32) - C(33)	139.4(6)
C(2)	- C(3)	132.2(4)	C(5) - C(6)	138.5(4)	C(9) - C(10)	138.4(6)	C(33) - C(34)	137.0(5)
			C(5) - C(10)	137.5(4)			C(34) - C(35)	136.6(5)
							C(35) - C(36)	139.0(6)
Angles (°)								
C(2) - S	- C(2')	103.2(2)	O(4) - C(5) - C(6)	121.6(2)	C(5) - C(10) - C(9)	119.9(3)		
C(2) - O(1) - C(6)		114.8(2)	O(4) - C(5) - C(10)	118.5(3)	C(3) - C(31) - C(32)	120.3(2)		
S - C(2) - O(1)		112.2(2)	C(6) - C(5) - C(10)	119.9(3)	C(3) - C(31) - C(36)	120.4(3)		
S - C(2) - C(3)		123.3(2)	O(1) - C(6) - C(5)	121.6(3)	C(32) - C(31) - C(36)	119.3(3)		
O(1) - C(2) - C(3)		123.7(2)	O(1) - C(6) - C(7)	117.7(3)	C(31) - C(32) - C(33)	119.7(3)		
C(2) - C(3) - O(4)		121.5(3)	C(5) - C(6) - C(7)	120.7(2)	C(32) - C(33) - C(34)	120.5(3)		
C(2) - C(3) - C(31)		126.6(2)	C(6) - C(7) - C(8)	119.1(3)	C(33) - C(34) - C(35)	119.8(4)		
O(4) - C(3) - C(31)		111.9(2)	C(7) - C(8) - C(9)	120.4(4)	C(34) - C(35) - C(36)	120.8(3)		
C(3) - O(4) - C(5)		115.5(2)	C(8) - C(9) - C(10)	120.1(3)	C(31) - C(36) - C(35)	119.8(3)		

of this dehydration, depending on the reaction temperature an unknown by-product was formed in variable amounts. Elemental composition and spectral data, especially ^1H NMR and mass spectrum (cf. Exp. Part), suggested that this by-product was the hitherto unknown bis(3-phenyl-1,4-benzodioxin-2-yl) sulfide (3). In view of the sensitive and labile nature of the dioxin moiety, chemical proof (e.g. oxidation or reduction) of the proposed structure was difficult. Fortunately good crystals of the sulfide 3 could be grown and X-ray analysis confirmed the assigned structure (Fig. 1). The structural parameters are summarized in Tables 1 and 2. In analogy to the reaction

of dihydropyran²), sulfide **3** could be prepared independently from dioxin **2** in 56% yield by treatment with purified³) sulfur dichloride.

This latter fact suggested that also in the thionyl chloride-pyridine reaction, sulfur dichloride must have been the reagent responsible for the formation of sulfide **3**. Since thionyl chloride dissociates on standing or at elevated temperatures into a complex mixture containing sulfur dichloride⁴), the thionyl chloride was carefully purified by treatment with triphenyl phosphite⁵) and used immediately after distillation. Again at 130 °C both dioxin **2** and sulfide **3** were formed in 52 and 23% yields, respectively. However, when the dehydration temperature of **1** with freshly purified and distilled thionyl chloride was kept between 80–90 °C, instead of the prescribed 130 °C, an 81% yield of the desired dioxin **2** was obtained. Only traces of sulfide **3** could be detected by TLC on silica gel. Consequently, to avoid side reactions with thionyl chloride, it is recommended to conduct such dehydrations at carefully controlled conditions, i. e. at temperatures below 90 °C to minimize decomposition of thionyl chloride.

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Experimental Part

Bis(3-phenyl-1,4-benzodioxin-2-yl) sulfide (3)

a) *From the dehydration of 2,3-dihydro-2-hydroxy-2-phenyl-1,4-benzodioxin (1) with thionyl chloride in pyridine:* 9.4 g (41.2 mmol) of **1**⁶) and 6.0 g (50.4 mmol) of freshly distilled thionyl chloride, which was previously purified with triphenyl phosphite⁵), in 30 ml of dry pyridine are heated with stirring at 120–130 °C for 6 h. After cooling to room temperature, the reaction mixture is poured into 200 ml of ether, washed with 3 × 35 ml of 2 N HCl and with 1 × 30 ml of water. After drying over sodium sulfate and roto-evaporation (ca. 20 °C at 20 torr) of the solvent, the residue is chromatographed on silica gel, eluting with a petroleum ether (30–50 °C)/methylene chloride (95:5). As first fraction the benzodioxin **2** is eluted, 4.5 g (21.4 mmol, 52%), m. p. 73–75 °C (lit.¹) 73 °C), and as second fraction the sulfide **3**, 2.13 g (4.73 mmol, 23%). Sulfide **3** was further purified by recrystallization from petroleum ether (30–50 °C)/methylene chloride, m. p. 132–134 °C (colorless prisms). – IR (CCl₄): 3060, 1605, 1495, 1270, 1250, 1055, 690 cm⁻¹. – ¹H NMR (CDCl₃) at 400.13 MHz: δ = 6.71–6.79 (m, 4H), 6.82–6.87 (m, 4H), 7.26–7.33 (m, 6H), 7.57–7.63 (m, 4H). – ¹³C NMR (CDCl₃) at 100.61 MHz: δ = 115.86 (d), 115.96 (d), 124.19 (d), 124.36 (d), 126.94 (s), 127.85 (d), 128.79 (d), 129.09 (d), 131.75 (s), 141.44 (s), 142.82 (s), 143.37 (s). – MS (70 eV): *m/e* = 450 (M⁺, 63%), 417 (4), 345 (11), 342 (17), 197 (100), 105 (43), 89 (16), 77 (35).

C₂₈H₁₈O₄S (450.5) Calc. C 74.65 H 4.03 Found C 74.50 H 3.87

b) *From 2-phenyl-1,4-benzodioxin (2) and sulfur dichloride:* The mixture of 3.0 g (14.3 mmol) of **2** and 0.93 g (9.0 mmol) of freshly distilled sulfur dichloride³) in 10 ml pyridine is heated at 130 °C for 4 h while stirring magnetically. After cooling the contents are poured into 70 ml of ether, washed with 3 × 10 ml of 2 N HCl, 10 ml of water, and dried over sodium sulfate. After roto-evaporation (ca. 20 °C at 20 torr) of the solvent and chromatography on silica gel (30:1 ratio of adsorbent to substrate) eluting with petroleum ether/methylene chloride (4:1), 1.8 g (4.0 mmol, 56%) of the sulfide **3** is obtained. The spectral data matched that obtained in the above preparation.

X-Ray crystallography of 3⁴): The orientation matrix and the cell parameters were determined from a clear colorless crystal of dimensions 0.7 × 0.4 × 0.25 mm on a SYNTEX P3 four-circle diffractometer. Measurement of intensities: ω-scan, 1° range, Mo-K_α, 2θ maximum = 55°. The

intensities of 2283 reflections were measured, 1974 of them with $F > 3\sigma(F)$ were applied for the structure determination. The phases of 193 strong reflections were determined, and on the resulting E -map approximate positions of all non-hydrogen atoms were determined. Positional and thermal parameters were refined by anisotropic least squares cycles to $R = 0.049$. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements. We have omitted the presentation of the structure factors, which can be obtained upon request.

Sulfide **3** crystallizes monoclinically in the space group $C2/c$ (No. 15) with $a = 2629.2(9)$, $b = 468.1(2)$, $c = 2100.8(8)$ pm, and $\beta = 122.51(2)^\circ$. The unit cell contains $Z = 4$ formula units, the density was calculated to be $1.372 \text{ Mg} \cdot \text{m}^{-3}$. All atomic parameters are listed in Table 1. Bond distances and bond angles are summarized in Table 2.

*¹) Further details and basic data concerning the X-ray analysis may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen (W. Germany) by specifying registry number CSD 50 278, author, and source.

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⁴) Ref. ³), p. 347.

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