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The Oxidative Coupling of Coumaranone with Disulfur Dichloride

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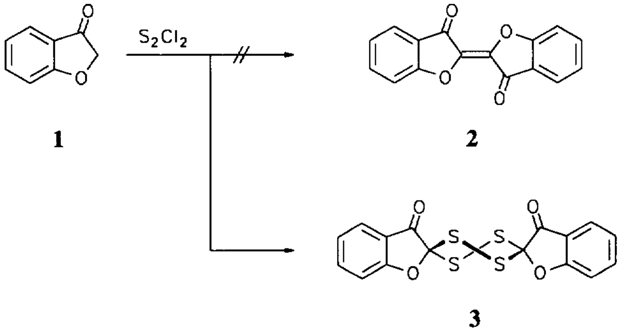
Abstract: The reaction of 3(2*H*)-benzofuranone (**1**) with S_2Cl_2 yields bis-2-spirocoumaranoylidenetetrathiane (**3**) instead of oxindigo (**2**). The structure of **3** is established by X-ray crystal structure analysis.

3(2*H*)-Benzofuranone (coumaranone, **1**) has been coupled oxidatively to oxindigo (**2**) by Fries[1] and Stoermer[2] via several steps. On the other hand, a very simple and more efficient (50% yield) one-step-coupling has been reported by Chovin[3] where **1** was heated with S_2Cl_2. However, there was a discrepancy of melting points: Fries found a m.p. of 272°C which corresponds to the 276-277°C of pure *trans*-oxindigo found by Guesten[4] whereas a m.p. of 336°C has been reported by Chovin.



Scheme 1.

We have carried out Chovin's reaction and obtained a solid material with a melting region below 93°C. Best results for purification are obtained by a crystallization from chloroform (40°C) yielding a yellow solid with a m.p. of 239°C. An X-ray crystal structure analysis[5] of this solid indicates the tetrathiane **3** instead of **2**. **2** could be detected neither in the isolated solid nor in the rough reaction product by TLC and a ^{13}C NMR analysis indicated **3** as the only detectable organic material. A transformation of **3** into **2** has not been successful yet. For example a thermolysis of **3** results in a complete decomposition. A distinction between **3** (1741, 1719 cm^{-1}) and **2** (1692;[4,6] *cis*-oxindigo: 1724, 1681) can be easily done by IR spectroscopy. The ^{1}H and ^{13}C NMR spectra of **2** and **3** exhibit characteristic small differences. The UV/Vis spectrum of **3** is hypsochromically shifted compared with **2** as one may expect. The tetrathiane ring of **3** has twist conformation and the two coumaranone rings are *syn*-oriented. The angle of twist between the two planar coumaranone units is 38° as determined from the coordinates of C-2, O-3, O-4 and C-10. Atom C-1 is in plane of its coumaranone ring, but C-9 lies well away from the plane of its ring.

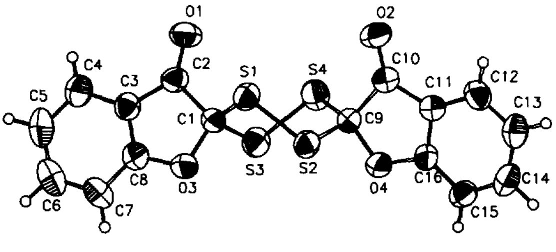
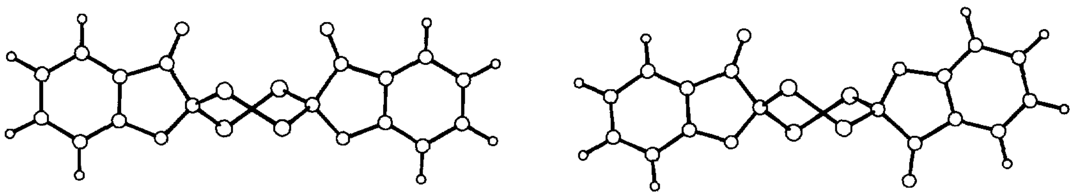


Figure 1. ORTEP-Plot of **3**.

The remarkable preference for the *syn*-orientation of **3** has been analyzed quantummechanically. The geometry of **3** and the corresponding *anti*-isomer **4** were roughly optimized with molecular mechanics calculations (MM2) and then refined with AM1 calculations. The structure of **3** is essentially correctly obtained: The calculated angle between the two aromatic ring systems is 38° and the distorsion of C-9 is also obtained (see Fig. 2). The calculated distance between the carbonyl oxygen atoms is slightly smaller (4.71 Å) than the experientally found (5.56 Å), whereas the distance of the heterocyclic oxygen atoms is longer (calcd. 5.60 Å, found 5.15 Å).



3 **4**

Figure 2. Calculated structures of **3** and **4**.

The calculations indicate that the isomer **4** is energetically more stable than **3** as is expected: 1.07 kcal/mol by MM2 and 0.75 cal/mol by AM1 calculations. The preference of the formation of the less stable isomers must thus be attributed to a kinetic control of the reaction. The coupling reaction may proceed via an enol of **1** where the carbonyl oxygen atoms are held together with a hydrogen bond.

The formation of **3** from **1** by treatment with S_2Cl_2 is typical for the reaction of C-H acid compounds;[7-9] and it can be expected that the reaction from **1** to **3** could be extended to further derivatives.

Table 1. Coordinates, bond lengths and bond angles of **3**.

	x	y	z	U(eq)		x	y	z	U(eq)
S(1)	7689(1)	1821(1)	4635(1)	53(1)	C(5)	2232(5)	2461(4)	5138(5)	75(1)
S(2)	8568(1)	749(1)	4328(1)	54(1)	C(6)	2407(5)	1667(4)	5689(5)	76(2)
S(3)	5663(1)	940(1)	2289(1)	60(1)	C(7)	3430(5)	1174(3)	5602(5)	65(1)
S(4)	7076(1)	1300(1)	1384(1)	61(1)	C(8)	4286(4)	1510(3)	4917(4)	54(1)
O(1)	5500(3)	3011(2)	3087(3)	66(1)	C(9)	8520(4)	784(2)	2445(4)	48(1)
O(2)	9946(3)	1942(2)	2206(4)	72(1)	C(10)	9766(4)	1203(3)	2221(4)	51(1)
O(3)	5380(3)	1086(2)	4761(3)	62(1)	C(11)	10603(4)	512(2)	2061(4)	50(1)
O(4)	8611(3)	-82(2)	2121(3)	55(1)	C(12)	11897(4)	464(3)	1983(5)	58(1)
C(1)	5964(4)	1588(2)	3888(4)	51(1)	C(13)	12431(5)	-300(3)	1868(5)	67(1)
C(2)	5193(4)	2415(2)	3671(4)	48(1)	C(14)	11675(5)	-1013(3)	1833(5)	66(1)
C(3)	4135(4)	2288(3)	4321(4)	50(1)	C(15)	10392(5)	-994(3)	1895(4)	56(1)
C(4)	3090(4)	2791(3)	4447(5)	61(1)	C(16)	9876(4)	-217(2)	2013(4)	46(1)

S(1)-C(1)	1.805(4)	O(2)-C(10)	1.201(5)	C(3)-C(8)	1.371(6)	C(10)-C(11)	1.451(6)
S(1)-S(2)	2.013(2)	O(3)-C(8)	1.379(5)	C(3)-C(4)	1.394(6)	C(11)-C(12)	1.384(6)
S(2)-C(9)	1.850(4)	O(3)-C(1)	1.432(5)	C(4)-C(5)	1.374(7)	C(11)-C(16)	1.390(5)
S(3)-C(1)	1.847(4)	O(4)-C(16)	1.379(5)	C(5)-C(6)	1.378(7)	C(12)-C(13)	1.365(6)
S(3)-S(4)	2.012(2)	O(4)-C(9)	1.435(5)	C(6)-C(7)	1.356(5)	C(13)-C(14)	1.388(7)
S(4)-C(9)	1.800(4)	C(1)-C(2)	1.540(5)	C(7)-C(8)	1.372(6)	C(14)-C(15)	1.367(6)
O(1)-C(2)	1.205(5)	C(2)-C(3)	1.439(6)	C(9)-C(10)	1.539(6)	C(15)-C(16)	1.377(6)

C(1)-S(1)-S(2)	102.2(1)	S(1)-C(1)-S(3)	113.1(2)	C(7)-C(8)-O(3)	122.5(4)	C(11)-C(10)-C(9)	104.2(3)
C(9)-S(2)-S(1)	103.5(1)	O(1)-C(2)-C(3)	131.6(4)	C(7)-C(8)-C(3)	123.6(4)	C(12)-C(11)-C(16)	119.4(4)
C(1)-S(3)-S(4)	103.9(1)	O(1)-C(2)-C(1)	123.6(4)	O(3)-C(8)-C(3)	113.9(4)	C(12)-C(11)-C(10)	132.9(4)
C(9)-S(4)-S(3)	102.5(1)	C(3)-C(2)-C(1)	104.9(3)	O(4)-C(9)-C(10)	106.3(3)	C(16)-C(11)-C(10)	107.7(4)
C(8)-O(3)-C(1)	107.1(3)	C(8)-C(3)-C(4)	119.5(4)	O(4)-C(9)-S(4)	114.3(3)	C(11)-C(12)-C(13)	119.0(4)
C(16)-O(4)-C(9)	107.0(3)	C(8)-C(3)-C(2)	107.8(4)	C(10)-C(9)-S(4)	109.4(3)	C(12)-C(13)-C(14)	119.9(4)
O(3)-C(1)-C(2)	105.9(3)	C(4)-C(3)-C(2)	132.7(4)	O(4)-C(9)-S(2)	102.1(2)	C(15)-C(14)-C(13)	123.0(4)
O(3)-C(1)-S(1)	114.5(3)	C(3)-C(4)-C(5)	117.2(5)	C(10)-C(9)-S(2)	111.2(3)	C(16)-C(15)-C(14)	116.1(4)
C(2)-C(1)-S(1)	108.2(3)	C(6)-C(5)-C(4)	121.1(5)	S(4)-C(9)-S(2)	113.2(2)	C(15)-C(16)-O(4)	123.9(4)
O(3)-C(1)-S(3)	101.4(3)	C(5)-C(6)-C(7)	122.6(5)	O(2)-C(10)-C(11)	130.7(4)	C(15)-C(16)-C(11)	122.6(4)
C(2)-C(1)-S(3)	113.7(3)	C(8)-C(7)-C(6)	115.9(5)	O(2)-C(10)-C(9)	125.1(4)	O(4)-C(16)-C(11)	113.4(3)

EXPERIMENTAL

***Z*-1,2,4,5-Tetrathiane-3,6-bis-spiro-2',2''-bis-3(2*H*)-benzofuranone** (**3**): 3(2*H*)-Benzofuranone[10] (2.18 g, 16.3 mmol) and distilled S_2Cl_2 (4.39 g, 32.5 mmol) in xylene (1.25 ml) react for 2 h at 20°C. The solvent is removed in vacuo and the remaining gold-yellow crystals are collected by vacuum filtration: 2.58 g (82%) **3** ; higher reaction temperatures (170°C) decrease the yield (73% in 10 min reaction time and 51% in 1 h). M.p. 239°C (from chloroform) - R_f (silica gel/$CHCl_3$) = 0.58. - IR (KBr) ν = 1741 m (C=O) cm^{-1}, 1719 s (C=O), 1610 s, 1597 s, 1474 s, 1459 s, 1323 m, 1296 m, 1191 m, 972 s, 968 s, 865 s, 759 m. - UV ($CHCl_3$): λ_{max} = 262.8, 335.2. - ^1H NMR ($CDCl_3$): δ = 7.81 (dd, ^3J = 7.7, ^4J = 0.8 Hz, 1H), 7.74 (m, 1H),7.26 (m, 1H), 7.20 (dd, ^3J = 8.4, ^4J = 0.8 Hz, 1H). - ^{13}C NMR ($CDCl_3$): δ = 168.93 (C=O), 168.93 (Cq), 139.12 (C-H), 125.83 (C-H), 124.21 (C-H), 118.59 (Cq), 113.71 (Cq), 113.60 (C-H). - MS (70 eV): m/z (%) = 328 (11), 228 (2), 256 (1), 224 (1), 192 (1), 164 (100), 160 (1), 128 (1), 120 (1), 104 (37), 96 (1), 76 (48), 64 (34).

Crystal structure (diffractometer: ENRAF-Nonius CAD4, radiation: MoK_α, monochromator: highly oriented graphite crystal): $C_{16}H_8O_4S_4$ - M_r = 392.5, a = 10.506(2), b = 16.046(3), c = 9.888(3), β = 105.44(2)°, volume = 1.606(1) nm^3, Z = 4, density (calcd.) = 1.62 Mg/m^3, μ = 0.548, crystal system monoclinic, space group $P2_1/c$ (Nr. 14). - Data collection: single crystal 0.13 x 0.27 x 0.47 mm^3 (yellow), ω scan, measured 2 Θ range: 4-48°, in $\pm$hkl, scan width: 0.80 + 0.35 tan Θ; 3 standard reflexes every 3600 s measuring time, index range: $-12 \leq h \leq 11$, $0 \leq k \leq 18$, $0 \leq l \leq 11$, collected reflexes: 2621, independent and observed: 2621, observed ($I > 2\sigma(I)$): 1710, no corrections for absorption, structure determination: direct method, anisotropic refinement of non-hydrogen atoms, isotropic refinement of hydrogen atoms, 217 parameters, R1 = 0.040, wR2 = 0.1203 (F^2), $w^{-1} = [\sigma^2F_o^2+(0.1207\ P)^2+7.7270\ P]$ where $P = (F_o^2+2Fc^2)/3$, minimal and maximal residual electron density 10^6 e/pm^3) 0.25 - 0.24.

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