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Synthesis and Structure of Anhydroindanone-1 Disulfide

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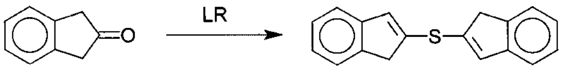
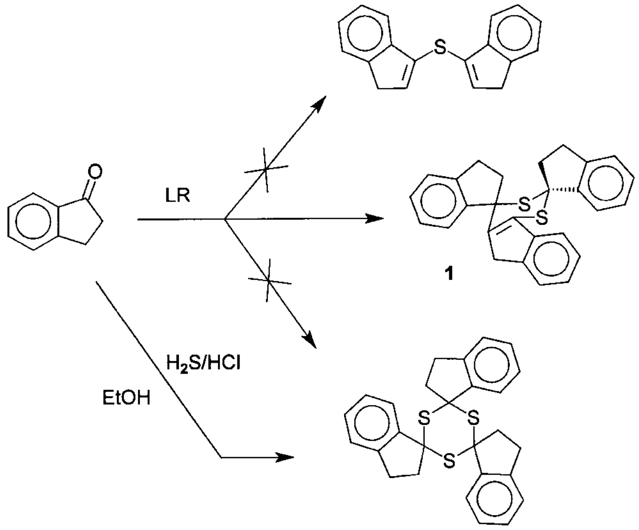
ABSTRACT: *An unexpectedly high yield of anhydroindanone-1 disulfide* (**1**) *was obtained by reaction of Lawesson's reagent with indanone-1. The molecular structure of* **1** *was established by X-ray diffraction. A possible mechanism of the reaction is discussed.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 369–371, 1999



RESULTS AND DISCUSSION

The formation of anhydroketone disulfides in the reaction of the appropriate ketone with H_2S or P_4S_{10} was reported in 1895 by E. Baumann and E. Fromm [1]. Different thiating agents have been applied in the thione synthesis, but one of the most powerful is Lawesson's reagent (LR) [2]. Searching for a synthesis of bis-(1-indenyl)-sulfide, a potential ligand for metallocene chemistry, which could not be obtained by the H_2S/HCl reaction [3], we investigated the reaction of LR with indanone-1. It had previously been



SCHEME 1

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TABLE 1 Crystal Data, Data Collection, and Refinement Parameters for **1**

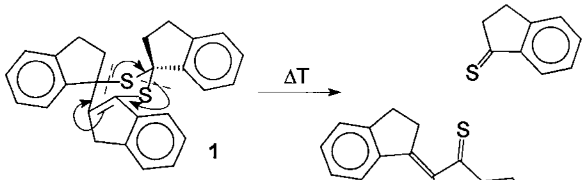
Empirical formula	$C_{27}H_{22}S_2$
Formula weight	410.57
Crystal size (mm)	0.7 × 0.8 × 0.4
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	14.419(8)
b (Å)	12.943(4)
c (Å)	11.767(5)
β (deg)	106.02(4)
V (Å^3)	2111.0(2.0)
Z	4
D_{calc} (g/cm^3)	1.292
F(000)	864
μ (cm^{-1})	2.63
Diffractometer	Enraf-Nonius CAD4
Radiation	Mo-Kα, graphite monochromator
λ, Å	0.71069
Temperature (K)	293
θ range (deg)	$2.15 < \theta < 27.96$
Scan type	ω
Scan range	$0.8 + 0.35 \tan\theta$
Measured reflections	2935
Unique reflections	2830
R_{int}	0.0353
Solution method	direct
Refinement method	full-matrix least-squares on F^2
Hydrogen atoms	isotropic approximation
Number of variables	351
Final *R* indices [$I > 2s(I)$]	$R1 = 0.0593$, $wR2 = 0.1450$
Final *R* indices (all data)	$R1 = 0.1034$, $wR2 = 0.1675$
Goodness-of-fit	1.107
Min./max. residual electron density, eÅ^{-3}	−0.383/0.456

The structure of **1** was refined using SHELX-93 software [5].

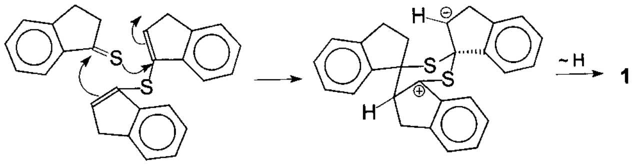
found that indanone-2 reacts with LR to form bis-(2-indenyl)-sulfide [4]. Under the same conditions, we had obtained from indanone-1 a light-yellow crystalline solid in more than 95% yield (see Scheme 1). According to the EI mass spectrum, the product was believed to be $(C_9H_7)_2S$, but EA and nuclear magnetic resonance (NMR) data have shown that this was incorrect. A proposed structure for 1 could be that of Fromm's anhydroketone disulfide.

Different attempts to assign the complex spectra were unsuccessful; however, a single-crystal X-ray analysis verified our prior assumption (see Figure 1).

Additional evidence of the structure of 1 was in comparison of EI and FD mass spectra. The fragments with m/e 262 and 148 most likely result from a retro Diels-Alder transformation of the molecular ion of 1 M^+ (410), which could be observed only under conditions of FD ionization (see Scheme 2).



SCHEME 2



SCHEME 3

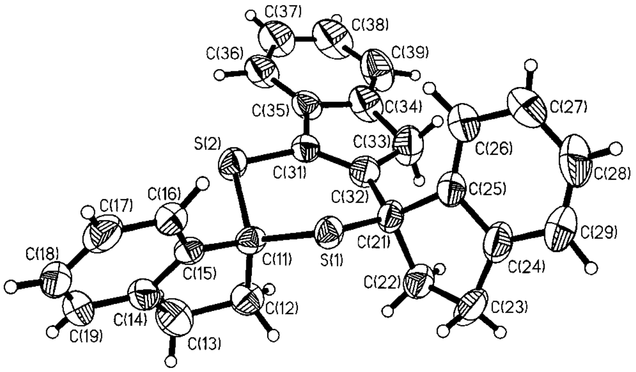


FIGURE 1 Molecular structure of **1.** Displacement ellipsoids are shown at 50% probability level.

A similar retrodiene splitting of the 1,3-dithiin ring is known and was confirmed by a PE spectroscopic investigation of the diallyl sulfide decomposition by pyrolysis [6]. A possible mechanism of the formation of 1 might include rapid interaction of bis-(1-indenyl)-sulfide with its precursor—1-thioindanone (see Scheme 3).

Our studies of sulfur-containing indenyl-type ligands and metallocenes are now in progress.

EXPERIMENTAL

Toluene was purified by distillation over potassium–sodium alloy; indanone-1 and Lawesson's reagent were used as supplied (Aldrich).

Synthesis of 1. To the boiled solution of indanone-1 (13.2 g, 100 mmol) in dry toluene (200 mL), Lawesson's reagent (20.5 g, 50 mmol) was slowly added. The mixture was refluxed under continuous stirring for 8 hours and then at room temperature

TABLE 2 Selected Bond Lengths (Å) for **1**

S(1)-C(11)	1.808(4)
S(1)-C(21)	1.838(5)
S(2)-C(31)	1.725(5)
S(2)-C(11)	1.828(4)
C(11)-C(15)	1.516(6)
C(11)-C(12)	1.521(7)
C(21)-C(32)	1.497(7)
C(21)-C(25)	1.518(7)
C(21)-C(22)	1.560(7)
C(31)-C(32)	1.343(6)
C(31)-C(35)	1.468(6)
C(32)-C(33)	1.525(7)

TABLE 3 Selected Bond Angles (deg) for **1**

C(11)-S(1)-C(21)	104.6(2)	C(31)-S(2)-C(11)	101.3(2)
C(15)-C(11)-C(12)	103.5(4)	C(15)-C(11)-S(1)	110.3(3)
C(12)-C(11)-S(1)	116.0(3)	C(15)-C(11)-S(2)	104.0(3)
C(12)-C(11)-S(2)	111.2(3)	S(1)-C(11)-S(2)	110.9(2)
C(32)-C(21)-C(25)	114.5(4)	C(32)-C(21)-C(22)	114.2(4)
C(25)-C(21)-C(22)	100.9(4)	C(32)-C(21)-S(1)	112.3(3)
C(25)-C(21)-S(1)	101.9(3)	C(22)-C(21)-S(1)	111.8(4)
C(32)-C(31)-C(35)	110.1(4)	C(32)-C(31)-S(2)	130.9(4)
C(35)-C(31)-S(2)	119.0(4)	C(31)-C(32)-C(21)	129.7(5)
C(31)-C(32)-C(33)	110.0(4)	C(21)-C(32)-C(33)	120.2(4)

overnight. After that, toluene was removed under reduced pressure and the residue chromatographed (Celite, hexane/ethylacetate, 4:1) to give 1 (13.1 g, >95%), mp 205–207°C. $C_{27}H_{22}S_2$ (410.57). Calcd: C, 78.98, H, 5.40. Found: C, 77.42; H, 5.40.

Crystallographic data (excluding structure factors) for the structure reported in this article (Table 1) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-111961. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int.code +44(1223)336033; E-mail: deposit@ccdc.cam.ac.uk].

Selected bond lengths and bond angles of the heterocyclic fragment of 1 are given in Tables 2 and 3, respectively.

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REFERENCES

[1] Baumann E., Fromm E.. Chem Ber.1895; 28, 895.
[2] Scheibye, S.; Shabana, R.; Lawesson, S.-O.; Rømming, C. Tetrahedron 1982, 38(7), 993.
[3] Campaigne, E.; Moss, Rodney D. J Am Chem Soc 1954, 76, 1269.
[4] Baierweck, P.; Simmoross, U.; Müllen, K. Chem Ber 1988, 121, 2195.
[5] Sheldrick, G. M. SHELXL-93: Program for Refinement of Crystal Structure; University of Göttingen, Göttingen, Germany, 1993.
[6] Bock, H.; Mohmand, S.; Hirabayashi, T.; Semkov, A. Chem Ber 1982, 115, 1139.