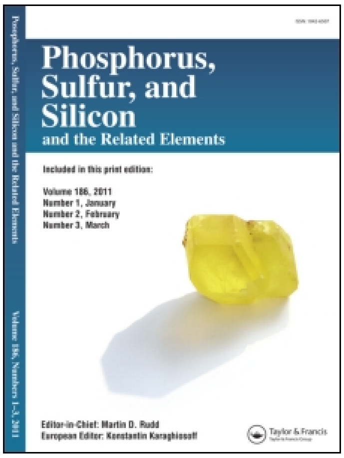

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Characterization of Benzylidene Bis-Dithiobenzoate

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To cite this Article Quintanilla, M Gloria , Guerra, Eva , Dotor, Jessica , Maresova, Jirina , Barba, Fructuoso and Martín, Avelino(2005) 'Synthesis and Characterization of Benzylidene Bis-Dithiobenzoate', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 7, 1691 — 1699

To link to this Article: DOI: 10.1080/104265090885138

URL: http://dx.doi.org/10.1080/104265090885138

Phosphorus, Sulfur, and Silicon, 180:1691–1699, 2005
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/104265090885138

Synthesis and Characterization of Benzylidene Bis-Dithiobenzoate

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Benzal chloride reacts with sodium sulfide in alcoholic solution to yield three main products: benzyl disulfide, benzyl dithiobenzoate, and a new interesting compound ***5***, *$C_{21}H_{16}S_4$, which was isolated and characterized as benzylidene bis-dithiobenzoate. The intermediates obtained from the autoxidation-reduction of the unisolable thiobenzaldehyde are implied in subsequent nucleophilic addition and substitution processes. NMR spectra and X-Ray structure analysis of* ***5*** *are discussed.*

Keywords Benzal chloride; benzyl dithiobenzoate; benzylidene bis-dithiobenzoate; dibenzyl disulfide; sodium sulfide; thiobenzaldehyde

Received March 25, 2004; accepted July 12, 2004.

This research was supported by the Spanish Ministry of Education and Culture, CTQ2004-05394/BQU.

The authors are very indebted to Jose Maria Arribas and Ana Albasanz for their help with the elemental analysis and mass spectra. Also we record with appreciation the help rendered by Luis Manuel Frutos by the Theoretical Studies.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-231178. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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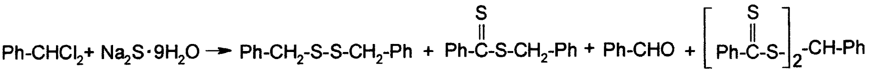
INTRODUCTION

The study of dithiocarboxylic acids and its esters is still a rather unexplored field in organic chemistry. Most of the work on this sulfur chemistry was done around 1900 and many of the described results are not coincident.[1] In 1882 Klinger[2] reported the reaction between benzal chloride **1** and potassium hydrogen sulfide, whereupon potassium dithiobenzoate and dibenzyl disulfide were obtained. Fromm and Schmoldt[3] tried to reproduce Klinger's results. When they treated benzal chloride with sodium sulfide, mainly β-thiobenzaldehyde (trithiobenzaldehyde) was produced. However, if sodium hydrogen sulfide was employed (similar as Klinger did), only dibenzyl disulfide was isolated. Therefore, those authors deduced that Klinger was wrong: *Gem*-dihalides do not lead to dithiocarboxylic salts; perhaps Klinger obtained it because of a contamination with trihalogenated compound (which is known as a source to obtain dithiocarboxylic salts[4]). Wood and Bost[5] asserted that benzal chloride and sodium sulfide react in alcoholic solution to form monomeric thiobenzaldehyde. This compound can not be isolated, but undergoes different reactions to yield β-trithiobenzaldehyde, benzyl mercaptan, sodium dithiobenzoate, small amounts of benzyl dithiobenzoate, and benzyl mercaptal of thiobenzaldehyde. The same authors described the reaction of benzaldehyde with H_2S in alcoholic solution either saturated with HCl or in alkaline medium. In both cases viscous pink oils are obtained, together with trithiobenzaldehyde or benzyl dithiobenzoate. Upon distillation, the pink oil decomposed to form mostly stilbene and sulfur. No more progresses concerning the study of this reaction have been found in the recent years. With this article, we intend to put some light on this process, with the isolation and identification of the obtained products and with a proposal of this formation route.

RESULTS AND DISCUSSION

The reaction between benzal chloride **1** and sodium sulfide nonahydrate in ethanol under the experimental conditions described below led to the following products (Scheme 1): dibenzyl disulfide **2** (39%), benzyl dithiobenzoate **3** (6%), benzaldehyde **4** (8%), unreacted benzal chloride

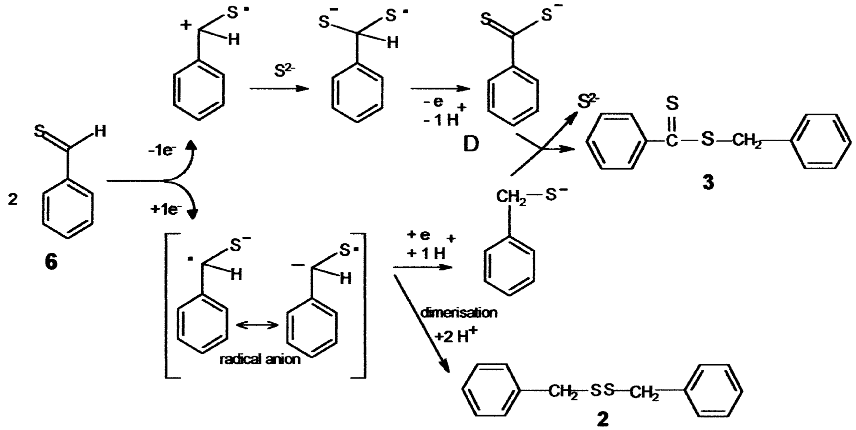


$$\underset{\mathbf{1}}{\mathrm{Ph\text{-}CHCl_2}} + \mathrm{Na_2S\cdot 9H_2O} \rightarrow \underset{\mathbf{2}}{\mathrm{Ph\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2\text{-}Ph}} + \underset{\mathbf{3}}{\mathrm{Ph\text{-}\overset{\overset{S}{\|}}{C}\text{-}S\text{-}CH_2\text{-}Ph}} + \underset{\mathbf{4}}{\mathrm{Ph\text{-}CHO}} + \underset{\mathbf{5}}{\left[\mathrm{Ph\text{-}\overset{\overset{S}{\|}}{C}\text{-}S\text{-}}\right]_2\mathrm{\text{-}CH\text{-}Ph}}$$

SCHEME 1

(9%), and a new red product **5** (38%) which was characterized by analytical and spectroscopic techniques as **benzylidene bis-dithiobenzoate** and its structure confirmed by X-Ray studies.

It has been reported in the literature[2] that the thiobenzaldehyde initially formed is not isolable and undergoes, under the slightly basic conditions of the process, a Cannizzaro-type reaction to yield benzyl mercaptan and dithiobenzoate. We propose for this reaction the redox process shown in the Scheme 2. The thiobenzaldehyde **6** disproportionates to the corresponding radical cation (which would immediately react with the anion S^{2-} and loses an electron and a proton to give the dithiobenzoate anion) and the radical anion, which takes up both an electron and a proton leading to the benzyl thiolate.



SCHEME 2

The formation of dibenzyl disulfide **2**, the most important of the side products, can be explained either as an air oxidation of benzyl thiolate or as an alternative of the reduction process: The radical anion, after taking up a proton, might also dimerise to give the benzyl disulfide.

The reaction between benzyl thiolate and the thiocarbonyl group of the dithiobenzoate would lead to the benzyl dithiobenzoate **3**.

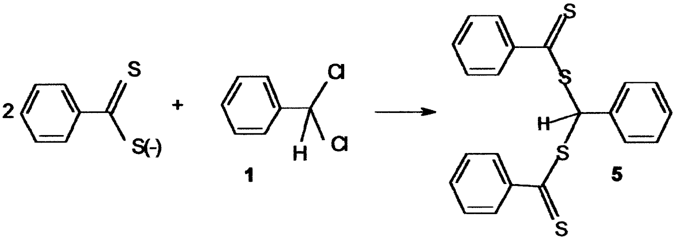
The amount of undesired benzaldehyde **4**, produced by hydrolysis of benzal chloride, was considerably reduced by improving the dryness method of hydrated sodium sulfide, as described in the Experimental.

The red crystals of the unknown compound **5** exhibited no carbonyl bands in its IR spectrum. EI mass spectra showed an apparent molecular peak at 332, which would not be in accordance with the molecular formula obtained from the elemental analysis: $C_{21}H_{16}S_4$.

It was necessary to use two *soft ionization methods* to find the correct molecular weight of our compound: ESI (Electro Spray Ionization) and APCI (Atmospheric Pressure Chemical Ionization).[6] The EI might be too aggressive, breaking the molecule and losing elementary sulfur, which displays peaks at 64 and 128 in the spectrum. Both techniques confirmed what we were expecting: a molecular weight of 396 for the molecular formula $C_{21}H_{16}S_4$ as the elemental analysis predicted.

These results and the ^1H and ^{13}C NMR spectra led us to assign to compound **5** the structure of benzylidene bis-dithiobenzoate, which was confirmed by X-ray structural analysis. In the ^1H-NMR spectrum **5** showed peaks which correspond to the presence of three phenyl rings of two different types: two of them are more unshielded than the benzaldehyde protons, and the third one appears at a lower frequency: 7.94 ppm (d, 4H (o-)); 7.61 ppm (d, 2H (o′-)); 7.51 ppm (t, 2H (p-)); a multiplet from 7.37 ppm to 7.30 ppm, with a predominant triplet at 7.35 ppm (7H (m-), (m′-), (p′-)); 6.97 ppm (s, 1H*, methynic proton). From the proton-coupled ^{13}C-NMR spectra, we could emphasize the following signals: 223.98 ppm, corresponding to two equivalent thiocarbonyl carbons (q, $^3J = 3.3$ Hz, by coupling with two aromatic and the methynic proton); 144.16 ppm corresponding to two equivalent ipso carbons of the A, A′ rings (td, $^3J_{C-Hm} = 8$ Hz, $^4J_{C-Hp} = 1.48$ Hz); 136.14 ppm corresponding to the ipso carbon of the B ring (td, $^3J_{C-Hm'} = 7.5$ Hz, $^2J_{C-H*} = 4.5$ Hz); 127.14–132.88 ppm (aromatic carbons); 62.11 ppm corresponding to the methynic group (dt, $^1J_{C-H*} = 158.43$ Hz, $^3J_{C-Ho'} = 4.72$ Hz). (It has been described that in aromatic systems the coupling constants C—H at two bond is smaller than at three bonds.)[7]

Compound **5** would be produced by a nucleophilic substitution of the benzalchloride (Scheme 3) by the dithiobenzoate anion (see Scheme 2).



SCHEME 3

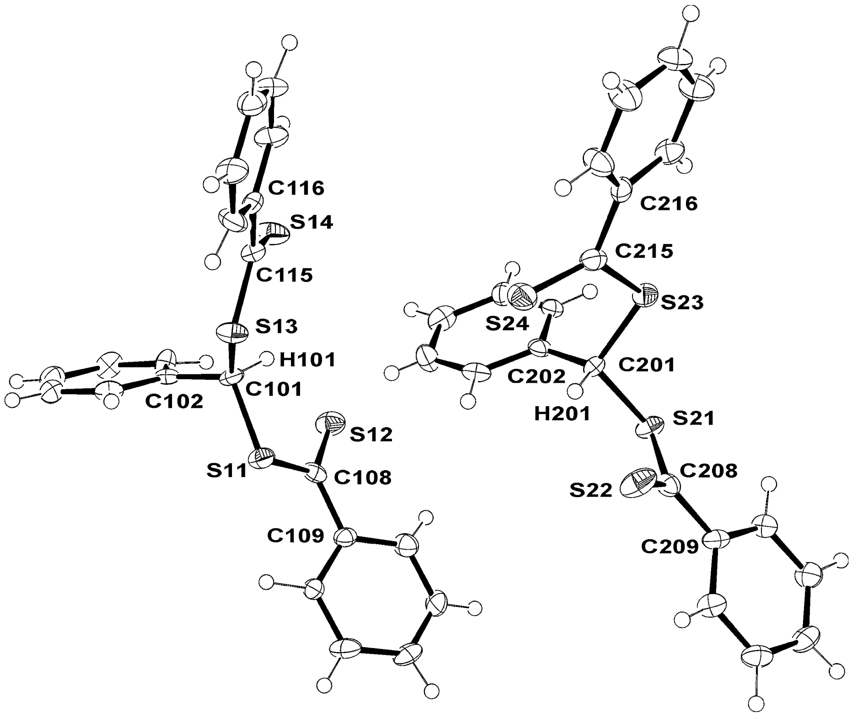


FIGURE 1

X-Ray Structural Analysis

Compound **5** crystallizes in the monoclinic space group $P2_1/c$. Selected bond distances, interactions and angles are presented in Table 1. Two independent molecules were found in the asymmetric unit. As can be seen in Figure 1, the tetrahedral environment of C101 and C201 is slightly distorted with angles in the range 105.0(3)–114.8(3)°. Distances from H101 and H201 to the nearest sulfur atoms H101· · ·S12 = 2.53 (4) Å and H201· · ·S22 = 2.43 (4) Å are shorter than the sum of the Van der Waals radii, which could indicate some interaction and hindrance of the free rotation around the C101–H101 or C201–H201 bonds. At the same time, the distance between S12 and the S11 of the nearest molecule in the unit cell is 3.516 (2) Å, again shorter than the sum of the Van der Waals radii. This interaction does not appear in the second molecule (distance S21 to S22 of the nearest molecule 3.861 (2)Å) and could be responsible for the spatial arrangement and the existence for the two different molecules.

TABLE I Selected Bond Lengths (Å), Interactions (Å) and Angles (°) of 5

C101-S11	1.821 (5)	C201-S21	1.816 (5)
C101-S13	1.813 (5)	C201-S23	1.817 (5)
C101···S12	3.174 (5)	C201···S22	3.146 (5)
C101-H101	1.00 (4)	C201-H201	1.06 (4)
H101···S12	2.53 (4)	H201···S22	2.43 (4)
C108-S12	1.627 (5)	C208-S22	1.626 (5)
S13-C101-S11	105.0 (3)	S23-C201-S21	108.5 (3)
S11-C108-C109	110.4 (3)	S21-C208-C209	111.1 (3)
C109-C108-S12	123.5 (4)	C209-C208-S22	122.7 (4)
S12-C108-S11	126.0 (3)	S22-C208-S21	126.1 (3)
H101-C101-S11-C108	−26 (3)	H201-C201-S21-C208	−19 (3)
H101-C101-S13-C115	38 (3)	H201-C201-S23-C215	−44 (2)
S11-C108-C109-C110	30.3 (6)	S21-C208-C209-C210	32.7 (6)

At sight of these results, theoretical calculations were made in order to find out whether the apparent absence of free-rotation could imply the existence of two real enantiomers.

Theoretical Predictions

The HF (Hartree-Fock)[8] method with B3Lyp hybrid exchange-correlation energy functional, using 3-21G* basis set, were used in order to determine the structures of the molecular conformations predicted by X-Ray technique. All the structures were optimized, in order to identify them as stationary points in the potential energy surface (PES), and analysis of approximate Hessian of the energy confirms them as a minimum in the PES. The results show that the two conformers found have the same energy, in fact, the structures are enantiomers. The structures are in equilibrium through a transition state, which has energy around 1 kcal/mol over the minima, so the interconversion is very fast in solution at room temperature, and it is not expected to detect any optical activity.

EXPERIMENTAL

Benzal chloride, absolute ethanol (99.9%), and sodium sulfide nonahydrated were obtained commercially. IR measurements were performed on a Perkin-Elmer Model 583 spectrophotometer; liquid samples were measured neat on NaCl plates; solid samples as KBr pellets. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (300 MHz and 500 MHz) spectra were recorded on Varian Unity 300 and Unity Plus 500 spectrometers; the chemical shifts are given in ppm. Melting points were determined on a Reichert Thermovar microhot stage apparatus. Elemental analysis was performed on a LECO CHNS-932 analyzer. Mass Spectra (EI, ionizing voltage 70 eV) were determined using a Hewlett Packard Model 5988A mass selective detector equipped with a Hewlett Packard MS Chem Station. APCI and ESI[6] were performed on an Automass Multi of ThermoQuest, font Aqua, and solvent systems: MeOH (AcOH 5%) for ESI and H_2O/MeOH for APCI.

The study of the stoichiometry has been very important in this process, since the proportional amount of both starting materials causes a big influence in the results.

After several attempts the best results were obtained starting the reaction with a mixture of 3 moles of benzal chloride and 4 moles of sodium sulfide.

From the procedure we could remark the following steps:

A carefully drying process of the $Na_2S \cdot 9H_2O$ is necessary, where it is previously crashed and then heated in a wide plate at 105°C for 20 hours to evaporate the water of hydration.

It is also of deciding importance how the reagents are added. To the mixture of dried sodium sulfide in ethanol the benzal chloride is added in two portions (see below).

The water of hydration of the $Na_2S \cdot 9H_2O$ must be removed because of the undesirable production of benzaldehyde as a consequence of the benzal chloride hydrolysis under basic conditions.

General Procedure: 7.25 g ($4.5 \cdot 10^{-2}$ moles) of benzal chloride were added to a solution of 7.21 g ($3 \cdot 10^{-2}$ moles) of previously dried sodium sulfide and 100 mL of absolute ethanol in a double neck round bottomed flask. The reaction mixture was heated and stirred for 2 h, after which $3 \cdot 10^{-2}$ moles of the previously dried sodium sulfide were again added to complete the proportion 3:4.

After filtration of the white solid precipitated at the bottom of the flask, (NaCl) and evaporation of solvent 4.56 g of a red oil was obtained. A steam distillation was carried out of that red mixture to remove the benzaldehyde **4** (0.37 g, 8%).

The distillate was extracted with ether; the organic layer was separated, concentrated, and dried over anhydrous $MgSO_4$. After solvent evaporation a red amorphous mass was obtained where an important amount of red crystals was included. The crude, product was separated by column chromatography (hexane/chloroform, 29:1) leading to 0.45 g benzal chloride **1** (9%), 1.81 g benzyl disulfide[3,9] **2** (39%), 0.26 g benzyl dithiobenzoate[5] **3** (6%), 1.65 g benzal bis-dithiobenzoate **5** (36%).

Benzyl dithiobenzoate[5,10](3): (0.26 g, 6% yield). ^{1}*H-NMR* (300 MHz, $CDCl_3$)δ: 8.02 (d, 2H, J = 6.10 Hz); 7.54 (t, 1H, J = 6.32 Hz); 7.42–7.30 (m, 7H); 4.61 (s, 2H). ^{13}*C-NMR* (300 MHz, $CDCl_3$) δ: 227.64, 144.74, 134.96, 132.39, 129.28, 128.7, 128.52, 128.34, 127.74, 126.90. *MS (EI)* m/e (%): 244 (M^+, 35), 121 (100), 91 (88), 77 (43).

Benzylidene bis-dithiobenzoate (5): (1.65 g, 36.% yield, red crystals, m.p. 73–75°C).^{1}*H-NMR* (300 MHz, $CDCl_3$) δ: 7.945 (d, 4H, J = 7.3Hz), 7.61 (d, 2H, J = 7.8 Hz), 7.51 (t, 2H, J = 7.3 Hz), 7.37–7.30 (m, 7H), 6.97 (s, 1H); ^{13}*C-NMR* (500 MHz, $CDCl_3$) δ: 223.98 (q, J = 3.3Hz); 144.6 (td,$^3J_{C-Hm} = 8$ Hz, $^4J_{C-Hp} = 1.48$ Hz); 136.14 (td, $^3J_{C-Hm'} = 7.5$ Hz, $^2J_{C-H*} = 4.5$ Hz); 127.14–132.88 (aromatic carbons), 62.11 (dt, $^1J_{C-H*} = 158.43$ Hz, $^3J_{C-Ho'} = 4.72$ Hz). *IR* υ_{max} (KBr/cm^{-1}): 3058.68; 3027.75; 2919.40; 1674.15; 1589.45; 1493.63; 1444.37; 1236.52; 1043.22; 872.68; 760.05. *MS (EI)* m/e(%): 332(M^+–64, 18), 274(14) 210(20), 121(100), 77(26). *Anal.Calc.* for $C_{21}H_{16}S_4$: C, 63.636; H, 4.040; S, 32.327. *Found*: C, 63.630; H, 4.013; S, 33.77. *ESI:* Peaks corresponding to Molecule + H^+: 397.0; Molecule + Na^+: 419.0; Molecule + K^+: 435.1; Dimer + Na^+: 815.0; Dimer + K^+: 830.0, *APCI:* Molecule + H^+: 397.0.

X-ray data were collected on a Bruker-Nonius Kappa CCD difractometer at 150°K. Crystal data: monoclinic, $C_{21}H_{16}S_4$ (M_w:396.58), space group $P2_1/c$ with $a = 15.637(2)$, $b = 6.329(1)$ and $c = 37.846(6)$ Å, $\beta = 95.06(1)^\circ$, $V = 3730(1)$Å^3, $Z = 8$, and $D_{calc} = 1.412$ gcm^{-3}. Of the 44006 measured reflections for **5**, 7966 [$R(int) = 0.258$] were independent; $R1 = 0.078$, $wR2 = 0.134$ (for 3292 reflections with $F > 4\sigma(F)$). The structure was solved, using the WINGX package,[11] by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97).[12] All nonhydrogen atoms were anisotropically refined, while the hydrogen atoms were located in the difference Fourier map and isotropically refined with a fixed thermal factor of 0.03.

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