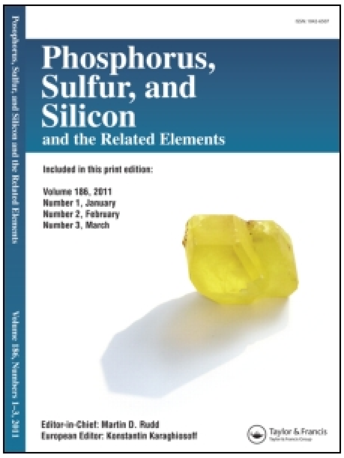

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CCl_4 AS MILD OXIDANT IN SULFUR CHEMISTRY. VIII.[1] ORGANYLTHIOLATION REACTIONS OF CH-ACIDIC COMPOUNDS WITH BIS(DIORGANYLTHIOPHOSPHINOYL)-DISULFIDES IN THE PRESENCE OF CCl_4/BASE

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CCl_4 AS MILD OXIDANT IN SULFUR CHEMISTRY. VIII.[1] ORGANYLTHIOLATION REACTIONS OF CH-ACIDIC COMPOUNDS WITH BIS(DIORGANYLTHIOPHOSPHINOYL)-DISULFIDES IN THE PRESENCE OF CCl_4/BASE

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Bis(diorganylthiophosphinoyl)-disulfides were studied as sulfenylation reagents in the presence of CCl_4, which gives rise to a more efficient utilization of disulfides. Five new ethers of diorganyldithiophosphinic acids are described and have been characterized by means of ^{31}P-NMR spectra. An X-ray structure analysis of 2-dicyclohexylthiophosphinoylthio-desoxybenzoine was performed.

Key words: Bis(diphenylthiophosphinoyl)-disulfide; bis(dicyclohexylthiophosphinoyl)-disulfide; CCl_4; CH-acidic compounds; X-ray crystal structure of 2-dicyclohexylthiophosphinoylthiodesoxybenzoine; ^{31}P-NMR data.

INTRODUCTION

CH-acid compounds can be sulfenylated by diorganyl-disulfides under basic conditions yielding thioethers and thiolate anions[2]; Equation (1).

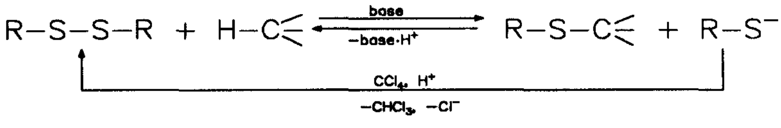
$$R{-}S{-}S{-}R + H{-}C< \xrightleftharpoons[-\text{base}\cdot H^{+}]{\text{base}} R{-}S{-}C< + R{-}S^{-} \qquad (1)$$

Because of simultaneous thiolate formation only 50% of the "disulfide sulfur" can be converted into the thioether. Additionally the thiolate anions attack the formed sulfur-carbon bond in a reverse reaction, which further decreases the yield or suppresses the sulfenylation reaction at all.

It has been already reported that CCl_4 is able to oxidize thiolate anions into their corresponding disulfides[3]; Equation (2).

$$2\ R{-}S{-}H + CCl_4 \xrightarrow[-\text{base}\cdot H^{+}]{\text{base}} R{-}S{-}S{-}R + CHCl_3 \qquad (2)$$

By combination of the organylthiolation and the thiolate oxidation by means of CCl_4, the yields of sulfenylated compounds can be increased and the disulfides are utilized to a higher degree, because the thiolate, generated in the sulfenylation step, is transformed into the starting disulfide; Equation (3).



(3)

Some reactions only proceed in the presence of CCl_4 at all.[3] In general, the sulfenylation of protic nucleophiles with disulfides and CCl_4/base may be summarized according to Equation (4).

$$R{-}S{-}S{-}R + 2\ H{-}C\lessgtr + CCl_4 \xrightarrow[-\text{base}\cdot H^+]{\text{base}} 2\ R{-}S{-}C\lessgtr + CHCl_3 \quad (4)$$

Using this method we have already successfully carried out organylthiolations of CH-acidic compounds with disulfides like diaryl- or thiuramdisulfides.[3]

Recently we studied the behaviour of bis(diorganylthiophosphinoyl)-disulfides in sulfenylation reactions in the presence of CCl_4/base, where 2-carboxy-ethers of diorganyldithiophosphinic acids are formed. Till now only three examples of this type of compounds have been described.[4,5]

RESULTS AND DISCUSSION

Bis(diphenylthiophosphinoyl)-disulfide (**1**) was prepared from diphenyldithiophosphinic acid (**2**) and iodine.[6] Bis(dicyclohexylthiophosphinoyl)-disulfide (**3**) is obtainable from dicyclohexyldithiophosphinic acid (**4**) using the same procedure.

Sulfenylation reactions with disulfides in the presence of CCl_4/base are only reasonable, if the resulting thiolate ions could be oxidized by CCl_4; Equation (3).

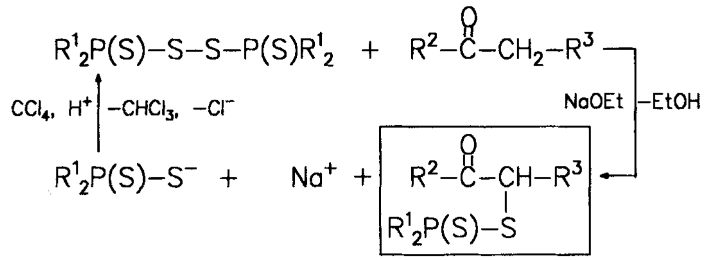
We were able to show that **2** and **4** generally are oxydizable by CCl_4/base to **1** and **3**, but in low yields; Equation (5).

$$2\ R_2P(S){-}S{-}H + CCl_4 \xrightarrow[-\text{EtOH},\ -\text{NaCl}]{\text{NaOEt}} \underset{\mathbf{1}\ R = \text{Ph}\ (40\%)\ ;\ \mathbf{3}\ R = \text{Cy}\ (7\%)}{R_2P(S){-}S{-}S{-}P(S)R_2} + CHCl_3 \quad (5)$$

Suitable bases are mainly NaOH and NaOEt, KOH decreases the yield, with amines no reaction takes place.

Organylthiolation reactions of pentane-2,4-dione, ethyl-2(acetyl)-acetate and desoxybenzoine with **1** and **3** were investigated. All reactions proceed according Scheme 1, the compounds obtained (**5–9**) are collected in Table I.

2-Diphenylthiophosphinoylthio-desoxybenzoine (**7**) was formed in only 13% yield, but 35% of a second compound (**7a**) could be isolated. **7** and **7a** were separated using different solvents. They are compared in Table II. **7a** probably represents



5–9

scheme 1

TABLE I

2-Carboxy-ethers of diorganyldithiophosphinic acids 5–9

R^1	R^2	R^3	yield	compound
Ph-	Me-	-C(O)-Me	80%	**5**
Ph-	Me-	-C(O)-O-Et	15%	**6**
Ph-	Ph-	-Ph	13%	**7**
Cy-	Me-	-C(O)-Me	36%	**8**
Cy-	Ph-	-Ph	49%	**9**

TABLE II

Reaction of bis(diphenylthiophosphinoyl)-disulfide with desoxybenzoine

compound	mass spectra m/z	^{31}P-NMR δ[ppm]	IR ν[cm^{-1}]	solvent
7	M^+ 444 (0.3%) B^+ 105 (Ph-CO) 201 (Ph_2P=O, 2%)	65.10 (S-ether)	1675 (CO)	diethylether
7a	M^+ 444(31%) B^+ 443 201 (Ph_2P=O, 40%)	82.84 (O-ether) (compare [7])	-	benzene

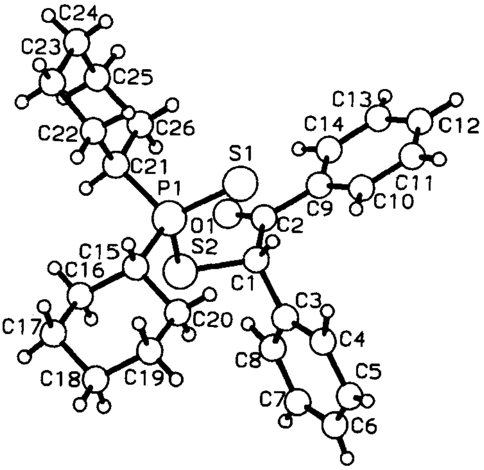


FIGURE 1 Molecular structure of **9** with atom labeling.

TABLE III

Selected bond lengths (Å), bond angles and torsion angles (°) for **9** (Standard deviations in parentheses)

Atoms	Distance	Atoms	Distance
P1 - S1	1.954(1)	P1 - S2	2.119(1)
P1 - C15	1.820(3)	P1 - C21	1.823(3)
C1 - S2	1.826(3)	C2 - O1	1.205(4)
C1 - C3	1.514(4)	C2 - C9	1.489(4)
C1 - C2	1.520(4)		
C-C (C3...C8)	1.37(2)	C-C (C9...C14)	1.37(2)
C-C (C15...C20)	1.519(11)	C-C (C21...C26)	1.512(14)

Atoms	Angle	Atoms	Angle
S1 - P1 - S2	114.09(4)	C15 - P1 - C21	107.70(12)
S1 - P1 - C15	113.20(9)	S2 - P1 - C15	102.97(9)
S1 - P1 - C21	113.35(9)	S2 - P1 - C21	104.62(9)
P1 - S2 - C1	102.09(9)		
S2 - C1 - C2	112.0(2)	O1 - C2 - C1	121.3(2)
S2 - C1 - C3	109.6(2)	O1 - C2 - C9	121.1(3)
C2 - C1 - C3	110.8(2)	C1 - C2 - C9	117.5(2)
C-C-C (C3...C8)	120.0(16)	C-C-C (C9...C14)	120.0(11)
C-C-C (C15...C20)	111.0(3)	C-C-C (C21...C26)	111.7(8)

Atoms	Torsion angle	Atoms	Torsion angle
S1 - P1 - S2 - C1	-6.45(10)	S2 - C1 - C2 - O1	-28.7(3)
P1 - S2 - C1 - C2	-102.0(2)	C3 - C1 - C2 - C9	-82.8(3)
C2 - C1 - C3 - C4	128.0(3)	C1 - C2 - C9 - C10	-3.8(4)
C-C-C-C (C15...C20)	56.1(8)	C-C-C-C (C21...C26)	54.0(16)

the isomeric O-ether $Ph_2P(S)O$-CH(Ph)-C(S)-Ph. **5**, **6** and **8** mainly exist as enoles, as deduced from the ^1H-NMR spectra.

Crystal and molecular structure of 2-dicyclohexylthiophosphinoylthiodesoxybenzoine (**9**)

The supposed constitution of **9** based on its synthesis (Scheme 1), and analytical and spectroscopic data (Tables IV and V) could be confirmed by the results of an X-ray analysis. The molecular structure of the compound with atom numbering is illustrated in Figure 1, selected bond lengths and angles, and torsion angles are given in Table III.

The coordination around the phosphorus atom is that of a slightly distorted tetrahedron. Bond angles at P1 in which S1 is included are all increased from ideal tetrahedral whereas the other three angles are decreased.

All bond lengths agree well with expectation. The two P-S bond lengths are clearly differentiated from each other and are correlated exactly with a single and a double bond, respectively.[8] The C2-O1 bond length corresponds to a C=O double bond, but is a little bit shorter than the mean value observed for a great number of ketones with an aryl substituent (1.112 Å).[9] The benzene and cyclohexane rings have normal dimensions.

The molecular packing is shown in Figure 2. It is characterized by isolated molecules without interactions. The molecules are arranged in sheets parallel to the ab-plane.

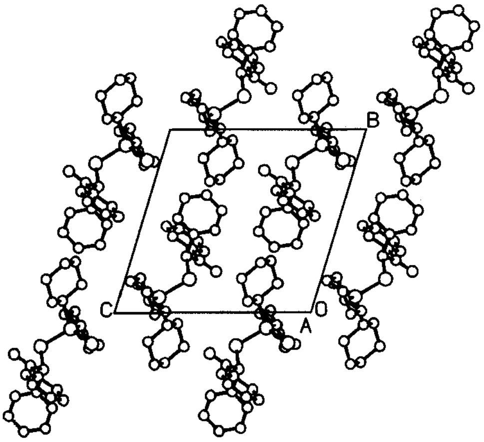


FIGURE 2 Packing of the molecules of **9** within the crystal packing viewed along the a-axis of the unit cell.

TABLE IV

Analytical data of **5–9**

compound	m.p. [°C]	molecular formula	M [g/mol]	analysis (calcd.) found [%] C	H	P	S
5	86-87	$C_{17}H_{17}O_2PS_2$	348	(58.60)	(4.92)	(8.90)	(18.40)
				58.49	4.90	8.95	18.51
6	oil	$C_{18}H_{19}O_3PS_2$	378.4	(57.12)	(5.06)	(8.19)	(16.94)
				56.89	5.12	8.31	17.18
7	128-130	$C_{26}H_{21}OPS_2$	444.5	(70.25)	(4.76)	(6.97)	(14.42)
				70.05	4.80	7.12	14.26
8	86-91	$C_{17}H_{29}O_2PS_2$	360.4	(56.63)	(8.11)	(8.59)	(17.78)
				56.64	8.09	8.55	17.62
9	143	$C_{26}H_{33}OPS_2$	456.6	(68.38)	(7.28)	(6.78)	(14.04)
				68.78	7.40	7.05	14.28

TABLE V

Spectroscopic data of 5–9

compound	mass spectra M$^+$ (%)	B$^+$ (100%)	IR [cm^{-1}] C=O	^{31}P-NMR [ppm]	^{1}H-NMR [ppm]
5	348 (5.2)	43		64.9	2.06 (6H, s, Me); 7.40-8.07 (10H, m, Ph); 17.44 (1H, s, OH from enol)
6	378 (2.0)	43		66.0	0.98 (3H, t, CH_3-CH_2); 2.24 (3H, s, COMe); 3.88 (2H, q, -CH_2-); 7.46-8.08 (10H, m, Ph); 14.0 (1H, s, OH from enol)
7	444 (0.3)	105	1675	64.94	6.5 (1H, d, CH-CO); 7.0-8.2 (20H, m, Ph)
8	360 (8.4)	55	1676	97.24	1.26-2.26 (22H, m, Cy); 2.32 and 2.39 (6H, 2s, Me); 17.31 (0.6H, s, OH from enol)
9	456 (3.0)	55	1690	96.10	1.15-1.95 (22H, m, Cy); 6.34 (1H, d, CH-CO); 7.18-8.15 (10H, m, Ph)

TABLE VI

^{31}P-NMR data of dicyclohexylthiophosphinoyl-compounds in $CHCl_3$

compd.	$[Cy_2P(S)S]_2$ (3)	$Cy_2P(S)SH$ (4)	$Cy_2P(S)S^-$ (4a)	$Cy_2P(S)S$-$CH[C(O)$-$Me]_2$ (8)	$Cy_2P(S)S$-$CH(Ph)$-$C(O)$-Ph (9)	$[Cy_2P(S)]_2O$ (10)
δ [ppm]	101	88	86	97	96	115

TABLE VII

Selected parameters of X-ray structure analysis for **9**

Empirical formula	$C_{26}H_{33}OPS_2$
Molecular weight (g·mol^{-1})	456.61
Crystal system	triclinic
Space group	$P\overline{1}$
Lattice parameters: a (Å)	9.790(3)
b (Å)	11.565(4)
c (Å)	11.816(4)
α (°)	106.74(2)
β (°)	90.55(2)
γ (°)	101.13(2)
V (Å^3)	1254.1
Z	2
F(000)	488
μ(MoK$_\alpha$) (cm^{-1})	2.8
Temperature (K)	293
ρ_x (g·cm^{-3})	1.209
Crystal size (mm)	0.46 x 0.23 x 0.11
Wave length (MoK$_\alpha$) (Å)	0.71073
No. of reflections: measured	8864 (3° $<$ 2Θ $<$ 50°)
unique	4238 (R_{int} = 0,023)
observed (F_o > 3,92 $\sigma(F_o)$)	2934 (= 69.2%)
Min./max. h, k, l (unique)	$\overline{11},\overline{13},0/11,13,14$
Standards: hkl	$\overline{3}32$ $0\overline{3}4$ $\overline{14}3$
max. deviation (%)	±3.1 ±2.3 ±2.3
Max. Δ/σ in final l.s. cycle	0.08
No. of reflections/parameter	7.3
Weighting scheme	$w = 2.03/(\sigma^2(F_o)+0.0002F^2)$
Min./max. $\Delta\rho$ (e·Å^{-3}) in final difference-Fourier synthesis	-0.202 / 0.355
R / wR / S	0.046 / 0.039 / 2.406
Scattering factors and f' and f" from	SHELX-76[11]

EXPERIMENTAL

All experiments were carried out under nitrogen atmosphere with dry CCl_4 and DMF.

Bis(dicyclohexylthiophosphinoyl)-disulfide (**2**). 0.01 mol (**4**) was added to 0.01 mol NaOH in 250 ml of H_2O. Into the stirred solution 0.01 mol KI_3 in 200 ml of H_2O were dropped; (**3**) precipitates. After reduction of excess iodine with $Na_2S_2O_3$ it is filtered off and recrystallized from benzene. yield: 96%; m.p.: 163–165°C; ^{31}P-NMR: 101 ppm; Mass spectrum: M^+ 522 (0.7%), B^+ 55
Anal. calcd. for $C_{24}H_{44}P_2S_4$ (522.8 g/mol) C, 55.14; H, 8.48; P, 11.85; S, 24.53% Found: C, 54.77; H, 8.26; P, 12.02; S, 23.66%.

[Cy₂P(S)]₂O (**10**). Sometimes is isolable in small amounts, also in the sulfenylation reactions. m.p.: 152°C; ^{31}P-NMR: 115.3 ppm; Mass spectrum: M^+ 474 (12.8%), B^+ 55
Anal. calcd. for $C_{24}H_{44}OP_2S_2$ (474.7 g/mol) C, 60.73; H, 9.34, P, 13.05; S, 13.51% Found C, 60.93; H, 9.43; P, 12.89; S, 13.73%.

Oxydation of diorganyldithiophosphinic acids with CCl_4. A solution of 0.01 mol diorganyldithiophosphinic acid (**2** or **4**), 0.01 mol NaOEt and 20 ml CCl_4 in 50 ml DMF was stirred and heated 6 hours at 60°C, cooled to r.t., mixed with 100 ml of H_2O and extracted three times with $CHCl_3$. The crude product (**1** or **3**) was recrystallized from benzene.

TABLE VIII

Final fractional coordinates and equivalent isotropic displacement parameters ($Å^2$) for non-H atoms of **9**

$U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$

Atom	x/a	y/b	z/c	U_{eq}
P1	.52149(7)	.08461(6)	.79863(6)	.043(5)
S1	.42049(8)	.16672(7)	.92959(6)	.059(5)
S2	.56833(8)	.18137(7)	.67176(7)	.060(5)
O1	.3252(2)	.2229(2)	.5464(2)	.083(9)
C1	.4757(3)	.3077(2)	.7224(2)	.05(1)
C2	.3396(3)	.2846(3)	.6487(3)	.06(1)
C3	.5695(3)	.4275(3)	.7204(3)	.05(1)
C4	.6248(4)	.5140(4)	.8236(3)	.09(1)
C5	.7119(5)	.6255(5)	.8205(5)	.13(1)
C6	.7433(5)	.6421(4)	.7137(7)	.14(1)
C7	.6890(5)	.5572(5)	.6110(5)	.11(1)
C8	.6020(4)	.4503(3)	.6156(3)	.08(1)
C9	.2273(3)	.3467(2)	.7057(3)	.05(1)
C10	.2379(3)	.4175(3)	.8226(3)	.06(1)
C11	.1292(3)	.4729(3)	.8702(3)	.08(1)
C12	.0114(4)	.4577(4)	.8013(4)	.09(1)
C13	-.0003(4)	.3885(4)	.6869(4)	.10(1)
C14	.1062(3)	.3334(3)	.6387(3)	.08(1)
C15	.6924(3)	.0683(2)	.8459(2)	.05(1)
C16	.7748(3)	.0065(3)	.7451(3)	.06(1)
C17	.9128(3)	-.0092(3)	.7937(3)	.08(1)
C18	.9978(3)	.1134(3)	.8689(4)	.09(1)
C19	.9172(3)	.1732(3)	.9686(3)	.08(1)
C20	.7791(3)	.1905(3)	.9226(3)	.06(1)
C21	.4260(3)	-.0679(2)	.7132(2)	.05(1)
C22	.4112(3)	-.1572(3)	.7869(3)	.07(1)
C23	.3225(5)	-.2819(3)	.7188(3)	.10(1)
C24	.1835(4)	-.2724(4)	.6697(4)	.11(1)
C25	.2022(3)	-.1852(4)	.5964(3)	.09(1)
C26	.2842(3)	-.0603(3)	.6636(3)	.07(1)

2-Carboxy-ethers of diorganyldithiophosphinic acids (**5**–**9**). Common procedure: 0.01 mol **1** or **3** resp. and 20 ml CCl_4 were added to a stirred solution of 0.02 mol of the CH-acidic compound and 0.02 mol NaOEt in 50 ml DMF. After heating 6 hours to 60°C the mixture was cooled, mixed with 100 ml of H_2O and extracted three times with $CHCl_3$. Crude products were recrystallized from ethanol.

The analytical and spectroscopic data of the compounds **5**–**9** are summarized in Tables IV and V.

31P-NMR data of dicyclohexylthiophosphinoyl-compounds unpublished till now were collected during the work. They are summarized in Table VI.

X-ray crystal structure analysis of 2-dicyclohexylthiophosphinoylthio-desoxybenzoine. An optical clear, colorless crystal suitable for X-ray analysis was mounted on a Stoe four-circle diffractometer Stadi4 and investigated using graphite monochromatized MoKα radiation. Lattice parameters were derived by a least-squares treatment of the setting angels for 72 reflections. Intensity data were measured by ω/Θ-scanning mode. Data reduction was carried out applying Lorentz and polarization correction but neglecting absorption and extinction effects. The structure was solved by direct methods and refined by full-matrix least squares refinement on F. Non-H atom positions were refined with anisotropic displacement parameters, H atoms located in a difference Fourier map with isotropic ones. Relevant crystal data and parameters of structure solution and refinement are summarized in Table VII, final atomic parameters in Table VIII. All calculations were done on a RISC/6000-320 workstation using the programs SHELXS-86,[10] SHELX-76,[11] EDIT,[12] and PLUTO.[13]

Further details of the crystal structure analysis are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-W-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-56742, the names of the authors, and the journal citation.

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