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Preparation and Some Reactions of Thioacyl Diphenylthiophosphinoyl and Thioacyl Diphenylphosphino Sulfides

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The reaction of sodium or caesium dithiocarboxylates with diphenylthiophosphinic and diphenylselenophosphinic chlorides gives purple thioacyl diphenylthiophosphinoyl **5** and dark green thioacyl diphenylselenophosphinoyl sulfides **6**, which are useful thioacylating reagents under mild reaction conditions. Thioacyl diphenylphosphino sulfides **22**, which can be obtained by the similar method using diphenylphosphinous chlorides, react with methanol to yield the corresponding methyl dithiocarboxylates **15**, while the reactions of **22** with *N*-chlorosuccinimide leads to hitherto unknown *N*-(thioacylthio)succinimides **28**.

Darstellung und einige Reaktionen von Thioacyl(diphenylthiophosphinoyl)- und Thioacyl(diphenylphosphino)sulfiden

Durch Umsetzung von Natrium- oder Cäsium-dithiocarboxylaten mit Diphenylthiophosphinsäure- oder Diphenylselenophosphinsäurechloriden werden die rot-violetten Thioacyl(diphenylthiophosphinoyl)- **5** und tiefgrünen Thioacyl(diphenylselenophosphinoyl)sulfide **6**, die nützliche und unter milden Reaktionsbedingungen einsetzbare Thioacylierungsmittel sind, dargestellt. Die Thioacyl-(diphenylphosphino)sulfide **22**, die sich nach der gleichen Methode aus Chlor(diphenyl)-phosphan darstellen lassen, reagieren mit Methanol zu den entsprechenden Methyl-dithiocarboxylaten **15**. Die Reaktionen von **22** mit *N*-Chlorsuccinimid liefern bisher nicht bekannte *N*-(Thioacylthio)succinimide **28**.

Among potential reagents for thioacylation of nucleophiles, thiones[1] and dithioesters[2], dithiocarboxylic acids[3] and their salts[4], thioacyl chlorides[5], and imidazolides[6] have been employed with some disadvantages. Recently, bis(thioacyl) sulfides[7] **7** have been proven to be useful thioacylating agents under mild conditions, but their application still seems to be limited because of instability towards moisture. Thioacyl diphenylthiophosphinoyl sulfides **5** are expected to be more resistant towards moisture than **7**, because bis(diphenylthiophosphinoyl) sulfide is stable even in water. This paper deals with the preparation and some reactions of the diphenylthiophosphinoyl, diphenylselenophosphinoyl, and diphenylphosphino derivatives **5**, **6**, and **22**, respectively.

Results and Discussion

For the preparation of **5** and **6**, the reactions of piperidinium[8], sodium[9], and caesium 4-(methyl)dithiobenzoates[10] (**1**, **3**) with diphenylthiophosphinoyl or diphenylselenophosphinoyl chlorides (**2**, **4**) have been investigated in detail.

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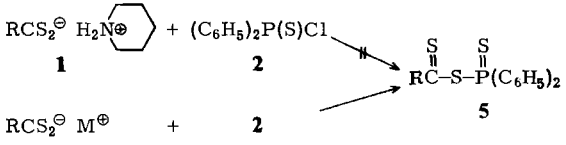
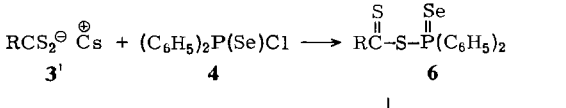


(1)

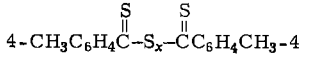
	M
3	Na
3'	Cs
3''	Li

	R
5a	C_6H_5
b	4-$CH_3C_6H_4$
c	4-$CH_3OC_6H_4$
d	2,4,6-$(CH_3)_3C_6H_2$
e	1-$C_{10}H_7$



(2)

	R
6a	C_6H_5
b	4-$CH_3C_6H_4$
c	4-$CH_3OC_6H_4$
d	1-$C_{10}H_7$



7b: x = 1
8b: x = 2

Depending on the reaction conditions, the unexpected bis[4-(methyl)thiobenzoyl] sulfide **7b** and the disulfide **8b** were obtained. Compounds **5a–e** and **6a–d** were prepared in good yields using sodium and caesium dithiocarboxylates **3**, **3'** in a solvent mixture such as methanol/*n*-hexane (5:7) (Table 1a).

The structures were established on the basis of UV/Vis, ^{1}H NMR, IR, and mass spectroscopic data, and microanalyses. For example, the IR spectrum of **5b** exhibits a characteristic absorption at 1240 cm^{-1} due to the thiocarbonyl stretching vibration. In the visible region of the electron spectra, an absorption maximum at 555 nm is observed, apparently due to the $n \rightarrow \pi^*$ transition of the thiocarbonyl group. The ^{1}H NMR spectrum shows a methyl singlet at δ = 2.30 and multiplet in the region of δ = 7.15–8.25 due to aromatic ring protons with the proton ratio of 3:14.

The mixed thioanhydrides **5** are purple while compounds **6** are green. They are readily dissolved in ether, dichloromethane, chloroform, and benzene, but their solubility in *n*-hexane and methanol is relatively low. As expected, they are stable towards heat and moisture. For example, **5a** and **6b** did not change on refluxing in benzene for one hour or when shaking dichloromethane solutions with water.

As expected, the compounds **5** and **6** were found to react readily with amines, sodium alkoxides[11], and thiolates[12] at room temperature to give the corresponding thioacylated products in good yields. The results are summarized in Tables 2–4. For example, **5b** reacted with aniline to give 4-(methyl)thiobenzanilide (**9d**) and anilinium diphenyldithiophosphinate (**10d**) in 78 and 84% isolated yields, respectively. **6b** gave analogous yields of the thioamides. In these reactions, the fact that no evolution of H_2S was detected, indicates the preferential attack of the amines at the thiocarbonyl carbon atom.

$$\mathbf{5}\text{ or }\mathbf{6} \xrightarrow{+\,R'_2NH} \underset{\mathbf{9}}{RC(S)NR'_2} + \underset{\mathbf{10}: E = S;\ \mathbf{11}: E = Se}{(C_6H_5)_2P(E)S^{\ominus}\ {}^{\oplus}NH_2R'_2} \qquad (3)$$

	R	R'_2N			R'_2N
9a	4-$CH_3C_6H_4$	*cyclo*-$C_6H_{11}NH$	**10a, 11a**		*cyclo*-$C_6H_{11}NH$
b	4-$CH_3C_6H_4$	$(C_2H_5)_2N$	**b**	**b**	$(C_2H_5)_2N$
c	4-$CH_3C_6H_4$		**c**	**c**	
d	4-$CH_3C_6H_4$	C_6H_5NH	**d**	**d**	C_6H_5NH
e	4-$CH_3C_6H_4$	4-$CH_3C_6H_4NH$	**e**		4-$CH_3C_6H_4NH$

5b also readily reacts with sodium alkoxides to give high yields of the thione esters **12** and sodium diphenyldithiophosphinate (**14a**). In the case of sodium phenolate, *O*-phenyl diphenylthiophosphinate (**13**) and the sodium dithioate **3b** were obtained, indicating direct attack of the phenolate anion at the phosphorus atom of **5b**. The reaction with potassium *tert*-butoxide affords the disulfide **8b** in appreciable yield, but the expected thione ester was not obtained possibly due to steric hindrance.

The disulfide **8b** is considered to be formed by oxidation of the potassium salt. A similar oxidation of dithiocarboxylic acid salts by *tert*-butyl bromide has been described[8a].

$$\mathbf{5b} \xrightarrow{+\,R'ONa,\ R' = C_6H_5} \underset{\mathbf{12}}{4\text{-}CH_3C_6H_4C(S)OR'} + \underset{\mathbf{14a}}{(C_6H_5)_2PS_2^{\ominus}\ Na^{\oplus}} + \underset{\mathbf{13}}{(C_6H_5)_2P(S)OR'} + \underset{\mathbf{3b}}{4\text{-}CH_3C_6H_4CS_2^{\ominus}\ Na^{\oplus}} \qquad (4)$$

$$\mathbf{5b} \xrightarrow{+\,tert\text{-}BuOK} \mathbf{8b} + 4\text{-}CH_3C_6H_4CS_2^{\ominus}\ K^{\oplus} + \underset{\mathbf{14b}}{(C_6H_5)_2PS_2^{\ominus}\ K^{\oplus}} \qquad (5)$$

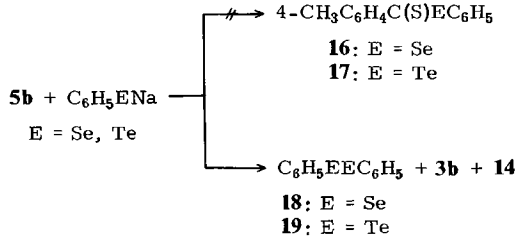
The reactions of **5b** and **6b** with lithium ethanethiolate and sodium thiophenolate under similar conditions gave the corresponding dithioesters **15b** and **15d** in good yields (Table 4).

$$\mathbf{5b} + R'SM \longrightarrow \underset{\mathbf{14}}{(C_6H_5)_2PS_2^{\ominus}\ M^{\oplus}} + \underset{\mathbf{15}}{4\text{-}CH_3C_6H_4CS_2R'} \qquad (6)$$

	M		R'
14a	Na	**15b**	C_2H_5
c	Li	**d**	C_6H_5

In order to extend the thioacylation reaction of **5** and **6**, reactions of **5b** and **6b** with sodium selenophenolate[13] and tellurophenolate[14] were carried out. Instead of the expected *Se*-phenyl thioseleno- and *Te*-phenyl thiotellurophenolates **16** and **17**, respect-

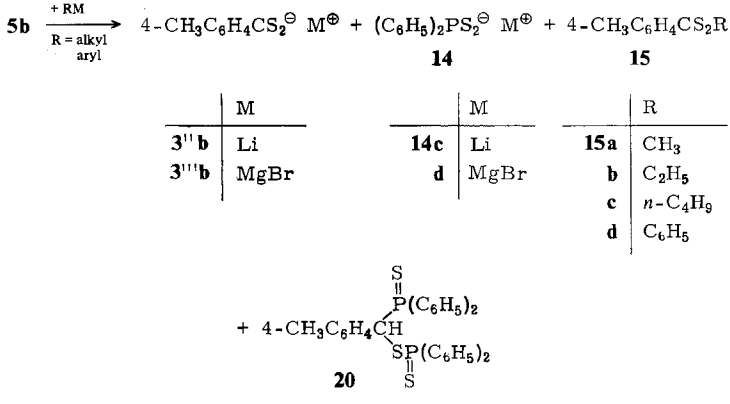
ively, the diselenide **18** and ditelluride **19** together with **3b** and **14a** were obtained in almost quantitative yields.



(7)

(8)

It is well known that aromatic dithioesters readily react with organolithium[15] and magnesium compounds to give both the products of thiophilic and carbophilic attack at the thiocarbonyl group. The results of the reaction of **5b** with organolithium and Grignard reagents are collected in Table 5.



	M
3'''b	Li
3'''b	MgBr

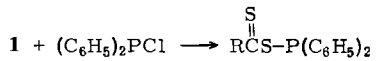
	M
14c	Li
d	MgBr

	R
15a	CH_3
b	C_2H_5
c	n-C_4H_9
d	C_6H_5

(9)

No formation of the expected thioketones was detected. Instead, dithioesters **15a – d** and crystalline diphenylthiophosphinoyl [(diphenylthiophosphinoyl)(4-methylphenyl)-methyl] sulfide (**20**) were obtained. Presumably, the dithioesters are formed by thiophilic attack of these nucleophiles at the thiocarbonyl sulfur. At the present state, no appropriate explanation for the mechanism of formation of **20** can be given.

To our best knowledge, the phosphinous esters of type **22** have not been described in the literature. In comparison with the mixed thioanhydride **5b**, it was thought to be of interest to synthesize **22** and to investigate the reactions with alcohols, alkoxides, and amines, etc.



	R
22a	C_2H_5
b	4-$CH_3C_6H_4$
c	4-ClC_6H_4
d	4-$CH_3OC_6H_4$

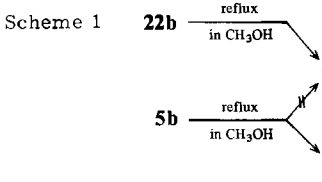
(10)

When diphenylphosphinous chloride (**21**) was added to a suspension of piperidinium 4-(methyl)dithiobenzoate in ether at room temperature, 4-(methyl)thiobenzoyl diphenylphosphino sulfide (**22b**) was obtained as reddish purple crystals in 72% yield. By analogous treatment of other piperidinium dithioates, the corresponding phosphinous esters (**22a, c, d**) were isolated in 20 – 90% yield (Table 7).

The structures of the phosphinous esters **22** were established by spectral (IR, UV/Vis, ^{1}H NMR) and analytical data as shown in Table 7. For example, the IR spectrum of **22b** exhibits a strong absorption at 1234 cm^{-1} due to the thiocarbonyl stretching vibration. A characteristic absorption maximum at 548 nm is observed in the visible region of the electron spectrum, apparently due to the $n \rightarrow \pi^*$ transitions of the thiocarbonyl group. The ^{1}H NMR spectrum shows a methyl singlet at $\delta = 2.34$ and a multiplet in the region of $\delta = 7.0 - 8.2$ due to aromatic ring protons. Moreover, the results of elemental analysis are consistent with the calculated values.

The aromatic phosphinous esters **22** are fairly stable compounds. They are readily dissolved in ether, dichloromethane, benzene, and methanol, etc. In general, crystallization is more difficult than with **5**. Interestingly, when **22b** was refluxed in methanol for 24 h, methyl 4-(methyl)dithiobenzoate (**15a**) was obtained in 73% yield (eq. 11), while similar refluxing of **5b** afforded no **15a**. The dithioester **15a** could be formed by the reaction of the dithioacid with excess methanol[16].

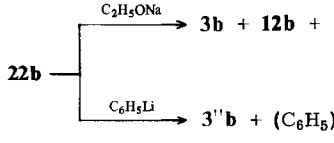
Scheme 1



(11)

(12)

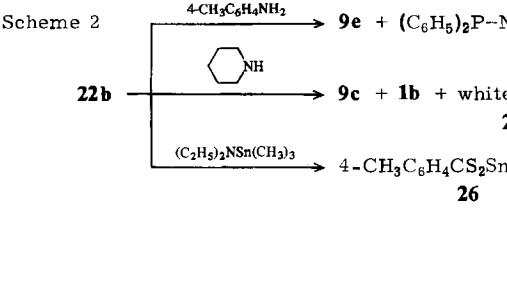
A similar remarkable effect of the phosphorus atom can be observed in the reaction with sodium ethoxide, giving only 7% of the expected thione ester **12b** (eq. 13). In addition, the reaction with phenyllithium[15] afforded lithium 4-(methyl)dithiobenzoate (**3''b**) and triphenylphosphane in 77 and 93% yield, respectively.



(13)

(14)

Scheme 2



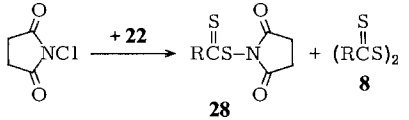
(15)

(16)

(17)

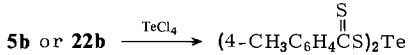
The reaction of **22b** with 4-toluidine at room temperature yields 37% of the thiocarboxamide **9e** and 25% of the phosphane **24a** with evolution of hydrogen sulfide (Scheme 2). The similar reaction with piperidine yields **9c**, piperidinium 4-(methyl)-dithiobenzoate (**1b**), and an unidentified colourless solid **25**. During this reaction, no evalution of hydrogen sulfide was observed. The stoichiometric reaction of **22b** with (diethylamino)trimethylstannane[17] yielded trimethylstannyl 4-(methyl)dithiobenzoate (**26**) in good yields.

In contrast, the reaction of **22** with *N*-chlorosuccinimide under analogous conditions was found to give 10–20% of the corresponding *N*-(thioacylthio)succinimide[18] **28** together with bis(thioacyl) disulfides **8** and tetraphenyldiphosphane (**27**). No (diphenylphosphino)succinimide was detected.



8,28	R
a	C_6H_5
b	4-$CH_3C_6H_4$
c	4-$CH_3OC_6H_4$
d	4-ClC_6H_4

(18)



(19)

Reactions of **5b** and **22b** with tellurium tetrachloride afford tellurium bis[4-(methyl)-dithiobenzoate] (**29**) in moderate yields.

Experimental Part

The melting points were obtained by using a Yanagimoto micromelting-point apparatus and are uncorrected. – The IR spectra were measured with a JASCO grating IR spectrophotometer IR-G and A-302. – The UV/Vis spectra were taken from a Hitachi 124 spectrometer. – The ^1H NMR spectra were recorded on a Hitachi R-24 (60 MHz) and R-22 (90 MHz) spectrometer with TMS as internal standard. The mass spectra were taken from a Hitachi RMU-6 M mass spectrometer (70 eV, 180–190 °C). – Elemental analyses were performed by the Elemental Analyses Center of Kyoto University and Alfred Bernhardt, Analytical Laboratory, Engelskirchen (Germany).

Materials: Diphenylthiophosphinoyl chloride (**2**) and chloro(diphenyl)phosphane (**21**, = diphenylphosphinous chloride) were of commercial grade and distilled before use. Amines were dried by refluxing with potassium hydroxide and distilled before use. *N*-Chlorosuccinimide was of reagent grade and used without further purification. The solvents were dried with sodium metal or calcium chloride and distilled before use.

Thiobenzoyl diphenylthiophosphinoyl sulfide (**5a**): Diphenylthiophosphinoyl chloride (**2**) (253 mg, 1.0 mmol) was added dropwise to a solution of caesium dithiobenzoate[10] (286 mg, 1.0 mmol) in methanol (5 ml) at 0 °C and the reaction mixture was stirred for 2 min, followed by adding *n*-hexane (5 ml) and by stirring at ca. 15 °C for additional 30 min. The color of the solution changed from red to light purple. The mixture was concentrated to ca. 1 ml under reduced pressure (10 °C/20 Torr) and the concentrate was extracted with *n*-hexane (30 ml). Evaporation of the *n*-hexane under reduced pressure afforded a dark purple oil which was purified by

Table 1a. Yields and physical properties of thioacyl diphenylthiophosphinoyl- and diphenylselenophosphinoyl sulfides **5** and **6**

	... sulfide	Yield[a] (%)	Dithio salt[b]	m. p. [°C]	IR (KBr) [cm^{-1}] νC=S	νP=S	νP=Se	UV/Vis [nm][c] λ_{max} (lg ε)	^1H NMR[d] (δ values)
5a	Thiobenzoyl diphenylthiophosphinoyl ...	0 45	A, B C	111–112	1236	738 660		297 (4.22) 558 (2.03)	7.25–8.25 (m, 15H, Ar)
b	4-(Methyl)thiobenzoyl diphenylthiophosphinoyl ...	73 80	B C	135–138	1240	735 660		330 (4.24) 555 (2.13)	2.30 (s, 3H, CH_3), 7.15–8.25 (m, 14H, Ar)
c	4-(Methoxy)thiobenzoyl diphenylthiophosphinoyl ...	55 78	B C	140–142	1240	735 658		353 (4.39) 547 (2.26)	3.82 (s, 3H, CH_3O), 6.80–8.20 (m, 14H, Ar)
d	2,4,6-Trimethylthiobenzoyl diphenylthiophosphinoyl ...	68	C	109–111	1240	735 655		288 (3.91) 313 (3.82) 545 (1.80)	2.20 (s, 3H, 4-CH_3), 2.27 (s, 6H, 2,6-CH_3), 6.80–8.20 (m, 12H, Ar)
e	1-Thionaphthoyl diphenylthiophosphinoyl ...	64	C	126–129	1240	735 660		277 (4.12) 285 sh (4.10) 551 (1.91)	7.20–8.30 (m, 17H, Ar)
6a	Thiobenzoyl diphenylselenophosphinoyl ...	0 80	B C	98.5–101	1223		508 565	299 (3.92) 583 (1.91)	7.6–8.14 (m, 15H, Ar)
b	4-(Methyl)thiobenzoyl diphenylselenophosphinoyl ...	52	B	105–106	1228		508 565	309 (4.22) 584 (1.98)	2.47 (s, 3H, CH_3), 7.15–8.25 (m, 14H, Ar)
c	4-(Methoxy)thiobenzoyl diphenylselenophosphinoyl ...	31 56	B C	116–118	1240		510 563	345 (4.14) 565 (2.31)	3.76 (s, 3H, CH_3O), 6.85–8.10 (m, 14H, Ar)
d	1-Thionaphthoyl diphenylselenophosphinoyl ...	14 46	B C	104–105	1234		508 565	279 (4.15) 552 (2.18)	7.25–8.35 (m, 17H, Ar)

[a] Isolated yield. – [b] The starting dithio salt: A = piperidinium dithiocarboxylate, B = sodium dithiocarboxylate, C = caesium dithiocarboxylate. – [c] Ether. – [d] $CDCl_3$.

silica gel column chromatography (*n*-hexane/ether, 6:1). The purple eluant was concentrated to ca. 5 ml and allowed to stand at room temperature for 12 h to give 166 mg (45%) of **5a** as purple columns. The spectral and microanalytical data together with those of **5b–e** and **6** are collected in Tables 1a and b.

Table 1b. Elemental analyses of the mixed thioanhydrides **5** and **6**

	Summation formula (Mol. mass)		C	H
5a	$C_{19}H_{15}PS_3$ (370.5)	Calc.	61.60	4.08
		Found	61.81	4.31
5b[a]	$C_{20}H_{17}PS_3$[b] (384.4)	Calc.	62.48	4.46
		Found	62.52	4.31
5c	$C_{20}H_{17}OPS_3$ (400.5)	Calc.	59.97	4.28
		Found	60.01	4.33
5d	$C_{22}H_{21}PS_3$ (412.6)	Calc.	64.05	5.13
		Found	64.11	5.30
5e	$C_{23}H_{17}PS_3$ (420.6)	Calc.	65.69	4.07
		Found	65.93	4.21
6a	$C_{19}H_{15}PS_2Se$ (417.4)	Calc.	54.68	3.62
		Found	54.74	3.64
6b[a]	$C_{20}H_{17}PS_2Se$[c] (431.5)	Calc.	55.68	3.97
		Found	54.84	3.74
6c	$C_{20}H_{17}OPS_2Se$ (447.5)	Calc.	53.69	3.83
		Found	53.80	3.80
6d	$C_{23}H_{17}PS_2Se$ (467.5)	Calc.	59.10	3.67
		Found	58.97	3.93

[a] By Analytisches Laboratorium (Germany). – [b] Calc. P 8.05 Found P 8.21; Calc. S 25.01 Found S 24.87. – [c] Calc. P 7.18 Found P 7.31; Calc. Se 18.30 Found Se 18.15.

4-(Methyl)thiobenzoyl diphenylthiophosphinoyl sulfide (**5b**): The reaction of diphenylthiophosphinoyl chloride (**2**) (253 mg, 1.0 mmol) with sodium 4-(methyl)dithiobenzoate (190 mg, 1.0 mmol) in methanol (15 ml) at 0°C, followed by chromatographic purification on silica gel (chloroform/*n*-hexane, 5:1) gave 280 mg (73%) of **5b** as purple prisms.

4-(Methoxy)thiobenzoyl diphenylthiophosphinoyl sulfide (**5c**): The reaction of diphenylthiophosphinoyl chloride (**2**) (235 mg, 1.0 mmol) with caesium 4-(methoxy)dithiobenzoate (316 mg, 1.0 mmol) followed by chromatographic purification on silica gel (*n*-hexane/ether, 5:1) gave 312 mg (78%) of **5c** as light purple plates.

2,4,6-Trimethylthiobenzoyl diphenylthiophosphinoyl sulfide (**5d**): Diphenylthiophosphinoyl chloride (**2**) (253 mg, 1.0 mmol) was reacted with caesium 2,4,6-trimethyldithiobenzoate [m. p. 217–227°C, IR (KBr): 1005 cm^{-1} (νC=S)] (328 mg, 1.0 mmol) at 0°C for 2 h, then purified on silica gel (*n*-hexane/ether, 6:1). On standing, the purple eluant at ca. 15°C gave 292 mg (68%) of **5d** as light purple prisms.

1-Thionaphthoyl diphenylthiophosphinoyl sulfide (**5e**): Diphenylthiophosphinoyl chloride (**2**) (127 mg, 0.5 mmol) and caesium 1-dithionaphthoate[10] (168 mg, 0.5 mmol) were stirred in methanol (3 ml) at 0°C for 40 min. Recrystallization of the resulting purple precipitates from ether gave 123 mg (64%) of **5e** as light purple needles.

Thiobenzoyl diphenylselenophosphinoyl sulfide (**6a**): A benzene solution (5 ml) of diphenylselenophosphinoyl chloride[19] (**4**) (1.0 mmol), freshly prepared from diphenylphosphinous

chloride (**21**) and selenium, was added dropwise to caesium dithiobenzoate (429 mg, 1.5 mmol) in methanol (5 ml) at 0 °C. After stirring for 2 min, *n*-hexane (7 ml) was added, followed by stirring at ca. 18 °C for 30 min. The resulting precipitate (black) was filtered and extracted with chloroform. The combined extracts were concentrated to ca. 3 ml under reduced pressure. *n*-Hexane (5 ml) was added to the concentrate. After 2 d in a refrigerator (−20 °C) 340 mg (80%) of **6a** were obtained as dark green prisms.

4-(Methyl)thiobenzoyl diphenylselenophosphinoyl sulfide (**6b**): The reaction of diphenylselenophosphinoyl chloride (**4**) (1.0 mmol) with sodium 4-(methyl)dithiobenzoate (190 mg, 1.0 mmol) according to **6a** gave 224 mg (52%) of **6b** as dark green prisms.

4-(Methoxy)thiobenzoyl diphenylselenophosphinoyl sulfide (**6c**): The reaction of diphenylselenophosphinoyl chloride (**4**) (1.0 mmol) with sodium 4-(methoxy)dithiobenzoate (206 mg, 1.0 mmol) gave 138 mg (31%) of **6c** as green microfine crystals.

1-Thionaphthoyl diphenylselenophosphinoyl sulfide (**6d**): The reaction of diphenylselenophosphinoyl chloride (**4**) (1.0 mmol) and sodium 1-dithionaphthoate (226 mg, 1.0 mmol), followed by recrystallization from ether/*n*-hexane (6:1) gave 66 mg (14%) of **6d** as dark-green microfine prisms.

For the reaction of **5b** and **6b** with amines, sodium alkoxides and thiolates, and organolithium and Grignard reagents general or typical procedures are described. Details of the reaction conditions are shown in Tables 2–5. The physical properties and microanalyses of the products are collected in Table 6a, b.

Table 2. Reactions of **5** and **6** with amines
Molar ratio **5** or **6**: amine = 1:2. Solvent: ether

$RCS_2P(E)Ph_2$ **5** or **6**	Amines	Temp. [°C]	Time [h]	Products (%) Thioamide **9**	Salt **10/11**
5b	cyclohexylamine	r. t.[a]	4	88 (**9a**)	85 (**10a**)
	diethylamine	r. t.[a]	2	82 (**9b**)	94 (**10b**)
	diphenylamine	r. t.[a]	48	no reaction	
	piperidine	r. t.[a]	4	82 (**9c**)	90 (**10c**)
	aniline	r. t.[a]	4	78 (**9d**)	84 (**10d**)
	4-toluidine	r. t.[a]	4	70 (**9e**)	64 (**10e**)
6b	cyclohexylamine	r. t.[b]	6	70 (**9a**)	80 (**11a**)
	diethylamine	r. t.[b]	6	93 (**9b**)	91 (**11b**)
	piperidine	r. t.[b]	6	77 (**9c**)	83 (**11c**)
	aniline	r. t.[b]	24	60 (**9d**)	68 (**11d**)

[a] Room temperature (17–22 °C). – [b] 20–25 °C.

Reactions with amines: The amine (2 mmol) was added dropwise to a solution of **5b** or **6b** (0.5 mmol) in ether (20 ml) and the mixture was stirred at ca. 20 °C. The precipitates were filtered off, followed by washing with *n*-hexane (5 ml) to give the corresponding ammonium diphenyldithiophosphinate (**10**) or diphenylselenothio-*S*-phosphinate (**11**), which were confirmed by IR, ^1H NMR, and microanalysis. The combined filtrates and washings were concentrated under reduced pressure. The concentrate was chromatographed on silica gel (*n*-hexane/ether, 1:1) to give the corresponding thioamide **9** as pale yellow to yellow crystals. The IR spectra were consistent with those of authentic samples[7c].

Reactions with sodium ethoxide: To a solution of **5b** (1.0 mmol) in ether (10 ml) sodium ethoxide (1.0 mmol) in ethanol (5 ml) was added and the mixture was stirred. The solvent was

evaporated under reduced pressure and the residue was kept in a refrigerator (−20 °C). Filtration of the precipitate gave 107 mg (79%) of sodium diphenyldithiophosphinate with m. p. 260–270 °C which was confirmed by conversion with methyl iodide into methyl diphenyldithiophosphinate; m. p. 83 °C. – IR (KBr): 660 cm^{-1} (νP=S). – ^1H NMR ($CDCl_3$): δ = 2.29 (3H, CH_3), 7.2–8.3 (10H, Ar). The filtrate was evaporated under reduced pressure to give a yellow oil which was purified by column chromatography (silica gel, *n*-hexane/ether, 4:1) to give 42 mg (47%) of *O*-ethyl 4-(methyl)thiobenzoate (**12b**). Its structure was confirmed by comparison of IR and ^1H NMR spectra with those of an authentic sample.

Table 3. Reactions of **5b** with alkoxides R'OM
Molar ratio **5b**: R'OM = 1:2. Temp. 16–22 °C

R'OM R'	M	Solvent	Time [h]	Products (%) RC(S)OR' **12**	RCS_2M **3**	$(RCS_2)_2$ **8**	$Ph_2P(S)OR'$ **13**	Ph_2PS_2M **14**
CH_3	Na	CH_3OH	2	38 (**12a**)				65 (**14a**)
C_2H_5	Na	C_2H_5OH	2	47 (**12b**)				79 (**14a**)
tert-C_4H_9	K	C_2H_5OH	24		trace	21 (**8b**)		57 (**14b**)
C_6H_5	Na	C_6H_5OH	4	83 (**12c**)	15 (**3b**)		14 (**13**)	73 (**14a**)

Reaction with potassium tert-butoxide: The reaction of potassium *tert*-butoxide (224 mg, 2 mmol) with **5b** (384 mg, 1.0 mmol) in ether (30 ml) gave 35 mg (21%) of bis[4-(methyl)thiobenzoyl] disulfide (**8b**) from the ether layer and potassium diphenyldithiophosphinate (**14b**) and 4-(methyl)dithiobenzoate, which can be confirmed by conversion into the methyl esters.

Reaction with sodium phenolate: A solution of sodium phenolate (1.0 mmol) and **5b** (192 mg, 0.5 mmol) in ether (30 ml) was stirred at ca. 20 °C. The mixture was poured into water (30 ml) and extracted with ether (30 ml). The extract was dried with anhydrous sodium sulfate and concentrated to give ca. 1 ml, followed by adding *n*-hexane (3 ml) and by allowing to stand in a refrigerator (−20 °C) for about 12 h. Filtration of the precipitate gave 42 mg (14%) of *O*-phenyl diphenylthiophosphinate (**13**). The filtrate was evaporated under reduced pressure and the residue was chromatographed on silica gel (column, *n*-hexane, yellow eluant) to give 94 mg (83%) of *O*-phenyl 4-(methyl)thiobenzoate (**12c**) as pale yellow plates (m. p. 56–58 °C)[7c]. The aqueous layer containing **1a** and **14a** was evaporated under reduced pressure below 10 °C and the residue was treated with methyl iodide (25 ml) at 20 °C for 3 h. The mixture was dissolved in a solvent mixture (20 ml) of ether/*n*-hexane (20:1), followed by chilling below −20 °C. Filtration of the precipitate gave 92 mg (73%) of methyl diphenyldithiophosphinate. Chromatographic purification of the filtrate on silica gel (column, *n*-hexane) gave 14 mg (15%) of methyl 4-(methyl)dithiobenzoate[7c] (**15a**). The structures of **12c** and **15a** were confirmed by comparison of m. p. and IR spectra with those of authentic samples.

Reaction with lithium ethanethiolate: A solution of **5b** (192 mg, 0.5 mmol) and lithium ethanethiolate (1.0 mmol) in ether (30 ml) was stirred. The mixture was concentrated to ca. 2 ml, diluted with *n*-hexane (5 ml) and kept in a refrigerator (−20 °C) for about 12 h. The precipitate was filtered off to give lithium diphenyldithiophosphinate (**14c**) which can be confirmed by conversion with methyl iodide into methyl diphenyldithiophosphinate. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography (silica gel, *n*-hexane/ether, 3:1) to give 72 mg (74%) of ethyl 4-(methyl)dithiobenzoate (**15b**) which was confirmed by comparison of IR and ^1H NMR spectra with those of an authentic sample[7c].

Table 4. Reactions of **5b** with metal thiolates R'SM
Molar ratio **5b**: R'SM = 1:2. Solvent: ether

R'SM R'	M	Temp. [°C]	Time [h]	Products (%) RCS_2R' **15**	RCS_2M **3**	Ph_2PS_2M **14**
C_2H_5	Li	r. t.[a]	4	74 (**15b**)		82 (**14c**)
C_2H_5	Na	22	4			
tert-C_4H_9	Na	r. t.[a]	72			9 (**14a**)
C_6H_5	Na	r. t.[a]	4	90 (**15d**)	5 (**3b**)	89 (**14a**)

[a] Room temperature (16 – 22 °C).

Reaction with sodium thiophenolate: A solution of **5b** (96 mg, 0.25 mmol) and sodium thiophenolate (66 mg, 0.5 mmol) in ether (20 ml) was stirred. To the reaction mixture ether (30 ml) and then water (30 ml) were added. The ether layer was evaporated under reduced pressure, followed by recrystallization from *n*-hexane, to give 52 mg (90%) of phenyl 4-(methyl)dithiobenzoate (**15d**) as red plates with m. p. 77 – 79 °C. The IR spectrum was consistent with that of an authentic sample[7c]. The aqueous solution was evaporated under reduced pressure to give sodium diphenyldithiophosphinate (**14a**) which was confirmed by conversion with methyl iodide into methyl diphenyldithiophosphinate.

Reaction with sodium selenophenolate: To an ethanol solution (10 ml) of freshly prepared selenophenolate (2.6 mmol) using diphenyl diselenide (**18**) (406 mg, 1.3 mmol) and sodium tetrahydroborate (106 mg, 2.8 mmol), **5b** (192 mg, 0.5 mmol) was added and the mixture was stirred at 0 °C for 6 h, followed by adding water (30 ml) and then ether (30 ml). The ether layer was dried with sodium sulfate and evaporated in a rotary evaporator. Recrystallization of the residue from ether/*n*-hexane (7:1) at −20 °C gave 340 mg (83%) of **18**. The aqueous phase was evaporated under reduced pressure below 10 °C to give a mixture of sodium 4-(methyl)dithiobenzoate (**3b**) and sodium diphenyldithiophosphinate (**14a**) which were confirmed by conversion with phenacyl bromide or methyl iodide into phenacyl 4-(methyl)dithiobenzoate with m. p. 101 – 103 °C[20] and methyl diphenyldithiophosphinate, respectively.

Reaction with sodium tellurophenolate: To an ethanol solution (10 ml) of freshly prepared sodium tellurophenolate (2.6 mmol) using diphenyl ditelluride (**19**) (525 mg, 1.3 mmol) and sodium tetrahydroborate (106 mg, 2.8 mmol), **5b** (192 mg, 0.5 mmol) was added and the reaction mixture was left standing at 0 °C for 6 h. Work-up in analogy to the procedure mentioned above gave 457 mg (86%) of **19**, 67% of sodium 4-(methyl)dithiobenzoate (**3b**) and 58% of sodium diphenyldithiophosphinate (**14a**).

Table 5. Reactions of **5b** with organolithium compounds and Grignard reagents R'M
Molar ratio **5b**: R'M = 1:2. Solvent: ether. Temp. 14 – 20 °C. Time 24 h

R'M	Products (%) Ester **15**	Salt **3**	Salt **14**	**20**
CH_3Li	19 (**15a**)	12 (**3'b**)	39 (**14c**)	9
n-C_4H_9Li	15 (**15c**)	8 (**3''b**)	40 (**14c**)	trace
C_6H_5Li	15 (**15d**)	5 (**3''b**)	54 (**14c**)	
C_2H_5MgBr	57 (**15b**)		36 (**14d**)	
C_6H_5MgBr	21 (**15d**)		29 (**14d**)	

Reaction with methyllithium: An ether solution (0.53 ml) containing methyllithium (1.0 mmol) was added dropwise to a solution of **5b** (384 mg, 1.0 mmol) in ether (30 ml) at ca. 17 °C under argon. After stirring for about 12 h water (30 ml) and ether (30 ml) were added. The aqueous phase was concentrated in a rotary evaporator and esterified with methyl iodide (3 ml), followed by thin-layer chromatography, to yield 98 mg (39%) of methyl diphenyldithiophosphinate and 30 mg (12%) of methyl 4-(methyl)dithiobenzoate (**15a**). *n*-Hexane (3 ml) was added to the ether layer. Filtration of the resulting solid, followed by recrystallization from *n*-hexane, yielded 48 mg (9%) of diphenylthiophosphinoyl [(diphenylthiophosphinoyl)(4-methylphenyl)methyl] sulfide (**20**). The filtrate was concentrated to give ca. 0.5 ml and chromatographed on silica gel (*n*-hexane) to yield 25 mg (19%) of **15a** and 50 mg of an intractable yellow oil.

Thioacyl diphenylphosphino sulfides **22**. – *General procedure:* A solution of diphenylphosphinous chloride (**21**) (10 mmol) in ether (10 ml) is added to a suspension of piperidinium dithiocarboxylate (**1**) (10 mmol) in ether (30 ml) and the reaction mixture is stirred at ca. 12 °C for 2 h. The white precipitate (piperidinium chloride) is filtered off and the filtrate is evaporated under reduced pressure. Recrystallization of the resulting residue from ether in a refrigerator (ca.

Table 6a. Physical properties of the compounds **9**, **10**, **11**, **20**, **24**, **27**, and **29**. IR: characteristic bands [cm^{-1}] in KBr unless otherwise indicated. – ^1H NMR: δ values. – UV/Vis: λ_{max} (lg ε) [nm] in CH_2Cl_2

9e	m. p. 172 – 174 °C. – IR: 1520 (Thioamide B). – ^1H NMR[a]: 2.33 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 3.20 (s, 1H, NH), 7.2 – 7.8 (m, 8H, Ar).
10a	m. p. 207 – 213 °C. – IR: 665 (P=S). – ^1H NMR[a]: 0.7 – 2.2 (m, 11H, *cyclo*-C_6H_{11}), 6.5 – 7.8 (3H, $^{\oplus}NH_3$), 7.1 – 8.3 (m, 10H, Ar).
10b	m. p. 152 – 155 °C. – IR: 665 (P=S). – ^1H NMR[a]: 1.21 (t, 6H, CH_3), 2.82 (q, 4H, CH_2), 7.2 – 8.6 (m, 10H, Ar), 7.5 (?) (2H, $^{\oplus}NH_2$).
10c	m. p. 207 – 212 °C. – IR: 665 (P=S). – ^1H NMR[a]: 1.65 (m, 6H, CH_2), 3.06 (m, 4H, CH_2N), 7.2 – 8.2 (m, 10H, Ar), 7.0 – 9.0 (2H, $^{\oplus}NH_2$).
10d	m. p. 142 – 150 °C. – IR: 665 (P=S). – ^1H NMR[a]: 7.8 – 8.4 (m, 15H, Ar), 8.5 – 9.0 (3H, $^{\oplus}NH_3$).
10e	m. p. 140 – 144 °C. – IR: 665 (P=S). – ^1H NMR[a]: 2.36 (s, 3H, CH_3), 7.0 – 8.4 (m, 15H, Ar), 8.5 – 9.0 (br. s, 3H, $^{\oplus}NH_3$).
11a	m. p. 160 – 164 °C. – IR: 525 (P=Se). – ^1H NMR[b]: 0.7 – 2.1 (m, 11H, *cyclo*-C_6H_{11}), 6.3 – 7.1 (br. s, 3H, $^{\oplus}NH_3$), 7.1 – 8.4 (m, 10H, Ar).
11b	m. p. 120 – 124 °C. – IR: 530 (P=Se). – ^1H NMR[b]: 1.28 (t, 6H, CH_3), 3.05 (q, 4H, CH_2), 5.9 – 6.3 (br. s, 2H, $^{\oplus}NH_2$), 7.1 – 8.4 (m, 10H, Ar).
11c	m. p. 191 – 195 °C. – IR: 530 (P=Se). – ^1H NMR[b]: 1.62 (m, 6H, CH_2), 3.1 – 4.2 (m, 4H, $CH_2N^{\oplus}$), 6.4 – 7.1 (m, 2H, $^{\oplus}NH_2$), 7.1 – 8.5 (m, 10H, Ar).
11d	m. p. 137 – 140 °C. – IR: 525 (P=Se). – ^1H NMR[b]: 5.6 – 5.9 (s, 3H, $^{\oplus}NH_3$), 7.0 – 8.3 (m, 15H, Ar).
20	m. p. 185 – 187 °C. – MS (180 °C, 70 eV): *m/e* = 571 ($M^{\oplus}$). – IR: 664 (P=S). – ^1H NMR[a]: 2.38 (s, 3H, CH_3), 4.58 (s, 1H, CH), 6.8 – 8.1 (m, 24H, Ar).
24a	m. p. 180 – 181 °C. – IR: 3350 (NH). – ^1H NMR[a]: 2.16 (s, 3H, CH_3), 5.31 (s, 1H, NH), 6.4 – 7.5 (m, 14H, Ar).
24b	Oil. – IR (neat): 3100, 2800 – 2600, 1590, 1435, 940, 760, 710, 506. – ^1H NMR[a]: 0.92 (t, 6H, CH_3), 3.16 (q, 4H, CH_2), 7.4 – 7.6 (m, 10H, Ar).
27	m. p. 123 – 125 °C. – IR: 1470, 1400, 1147, 1110, 760, 710, 570, 560, 504.
29	m. p. 210 °C. – MS (180 °C, 20 eV): *m/e* = 462. – IR: 1238 (C=S). – UV/Vis: 258 (4.73), 313 (4.62), 451 (4.72).

[a] $CDCl_3$. – [b] $CDCl_3$/[D_6]DMSO (1:1).

−20°C) for about 12 h gave **22**. The yields, physical properties, and elemental analyses are summarized in Tables 7 and 6b.

Table 6b. Elemental analyses of compounds **20**, **22**, **28**, and **29**

	Summation formula (Mol. mass)		C	H
20	$C_{32}H_{28}P_2S_3$ (570.7)	Calc.	67.35	4.95
		Found	67.61	4.88
22a	$C_{19}H_{15}PS_2$ (338.4)	Calc.	67.43	4.47
		Found	67.26	4.53
22b	$C_{20}H_{17}PS_2$ [a] (352.5)	Calc.	68.16	4.86
		Found	67.88	4.86
22c	$C_{19}H_{14}ClPS_2$ (372.8)	Calc.	61.20	3.78
		Found	61.39	3.82
22d	$C_{20}H_{17}OPS_2$ (368.5)	Calc.	65.20	4.65
		Found	65.22	4.77
28a	$C_{11}H_9NO_2S_2$ [b] (251.3)	Calc.	52.58	3.61
		Found	52.78	3.63
28b	$C_{12}H_{11}NO_2S_2$ (265.3)	Calc.	54.33	4.18
		Found	54.43	4.21
28c	$C_{12}H_{11}NO_3S_2$ (281.3)	Calc.	51.23	3.94
		Found	51.40	2.98
28d	$C_{11}H_8ClNO_2S_2$ (285.8)	Calc.	46.23	2.82
		Found	45.90	2.76
29	$C_{16}H_{14}S_4Te$ (462.1)	Calc.	41.58	3.05
		Found	41.62	3.10

[a] Calc. P 8.79, Found 8.70. – [b] Calc. N 5.57 Found 5.69; Calc. S 25.51 Found 25.70.

Table 7. Yields and physical properties of thioacyl diphenylphosphino sulfides **22**

	... diphenylphosphino sulfide	% Yield[a] (m. p. [°C])	IR[b] [cm^{-1}] $\nu_{as}C{=}S$	UV/Vis [nm][c] λ_{max} (lg ε)	^1H NMR[d] (δ values)
22a	Thiobenzoyl ...	36 (74 – 76)	1224	294 (4.11) 548 (2.35)	7.0 – 8.2 (m, 15H, Ar)
22b	4-(Methyl)thiobenzoyl ...	72 (92 – 93)	1234	316 (4.23) 548 (2.34)	2.34 (s, 3H, CH_3), 7.0 – 8.2 (m, 14H, Ar)
22c	4-(Chloro)thiobenzoyl ...	22 (75 – 77)	1228	305 (4.15) 551 (2.30)	7.2 – 8.2 (m, 14H, Ar)
22d	4-(Methoxy)thiobenzoyl ...	93 (87 – 89)	1233	349 (4.28) 542 (2.36)	3.78 (s, 3H, CH_3O), 6.8 – 8.2 (m, 14H, Ar)

[a] Isolated yield. – [b] KBr. – [c] **22a, b**: In CH_2Cl_2; **22c, d**: In *cyclo*-C_6H_{12}. – [d] $CDCl_3$.

Refluxing of **22b** *in methanol:* A solution of **22b** (352 mg, 1.0 mmol) in methanol (20 ml) was refluxed for 24 h. The reaction mixture was concentrated in a rotary evaporator to afford a dark red oil which was purified by chromatography (silica gel, *n*-hexane/ether, 9:1) to give 132 mg (73%) of methyl 4-(methyl)dithiobenzoate (**15a**) as a red oil. The structure was confirmed by IR, ^1H NMR, and mass spectra.

Reaction of **22b** *with sodium ethoxide:* A solution of sodium ethoxide (1.2 mmol) in ethanol (1 ml) was added to **22b** (352 mg, 1.0 mmol) in ether (5 ml) and the mixture was stirred at room temperature for 2 h. The solvent was evaporated under reduced pressure to afford a reddish brown solid. This solid was dissolved in ether (5 ml) and the resulting precipitate was filtered off to give 156 mg (82%) of sodium 4-(methyl)dithiobenzoate (**3b**) which can be confirmed by conversion into phenacyl 4-(methyl)dithiobenzoate. The filtrate was concentrated in a rotary evaporator to afford a slightly orange oil which was purified by chromatography (silica gel, *n*-hexane/ether, 9:1) to give 20 mg (7%) of *O*-ethyl 4-(methyl)thiobenzoate (**12b**) and 80 mg of an unidentified colorless oil (**23**)[21] [^{1}H NMR: δ = 1.50 (t, CH_3), 2.36 (q, CH_2), 6.4 – 7.5 (m, Ar)].

Reaction of **22b** *with phenyllithium:* Phenyllithium (1.0 mmol) in ether (12 ml) was added dropwise to a solution of **22b** (352 mg, 1.0 mmol) in ether (30 ml) at −10 °C and the mixture was stirred at −10 to 0 °C for 2 h, followed by adding ether (30 ml) and then water (50 ml). The ether layer was evaporated under reduced pressure to yield 244 mg (93%) of triphenylphosphane as a colorless solid (m. p. 79 °C). The IR spectrum was consistent with that of an authentic sample. The aqueous phase was concentrated in a rotary evaporator to give 77% of lithium 4-(methyl)dithiobenzoate which can be confirmed by conversion into phenacyl 4-(methyl)dithiobenzoate.

Reaction of **22b** *with 4-toluidine:* 4-Toluidine (214 mg, 2 mmol) was added to a solution of **22b** (352 mg, 1.0 mmol) in ether (15 ml) and the mixture was stirred at room temperature for 4 h. The color changed from purple to yellow and evolution of hydrogen sulfide was detected using lead acetate paper. The mixture was concentrated to ca. 1 ml in a rotary evaporator. Chromatographic purification of the concentrate on silica gel (*n*-hexane/ether, 4:1) afforded 100 mg (37%) of 4-methyl-*N*-(4-methylphenyl)thiobenzamide (**9e**) (the pale yellow eluant) and 73 mg (25%) of [(4-methylphenyl)amino]diphenylphosphane (**24a**) as colorless crystals with the spectral data shown in Table 6a.

Reaction of **22b** *with piperidine:* Piperidine (214 mg, 2.0 mmol) and **22b** (352 mg, 2.0 mmol) was stirred in ether (20 ml) at room temperature for 1 h. Filtration of the resulting reddish precipitates yielded 150 mg (60%) of piperidinium 4-(methyl)dithiobenzoate[8a] (**1b**). The filtrate was concentrated to ca. 1 ml in a rotary evaporator. The concentrate was chromatographed on silica gel (*n*-hexane/ether, 9:1) to yield 56 mg (26%) of **9c** and colorless crystals of an unidentified compound with m. p. 143 – 145 °C. – ^{1}H NMR ($CDCl_3$): δ = 0.6 – 2.9 (m, piperidine ring H?), 6.8 – 8.0 (m, Ar). – Analysis: Found C 67.72, H 6.75, N 4.44, P 6.59.

Reaction of **22b** *with (diethylamino)trimethylstannane:* (Diethylamino)trimethylstannane (471 mg, 2.0 mmol) was added dropwise to a solution of **22b** (704 mg, 2.0 mmol) in ether (20 ml) and the mixture was stirred at 20 °C for 3 h. The solvent was evaporated under reduced pressure. The residue was dissolved in *n*-hexane (20 ml). Filtration of the white precipitate and washing with *n*-hexane (2 × 1 ml) gave 121 mg (17%) of tetraphenyldiphosphane[22] (**27**). The filtrate was concentrated to ca. 1 ml in a rotary evaporator to afford a red oil which was purified by chromatography (silica gel, *n*-hexane/ether, 4:1) to give 420 mg (79%) of trimethylstannyl 4-(methyl)-dithiobenzoate[23] (**26**) as a red oil, 40 mg (8%) of (diethylamino)diphenylphosphane[24] (**24b**) and an intractable light brown oil (140 mg). The structures of **24b**, **26**, and **27** were identified by comparison with IR and ^{1}H NMR spectra of authentic samples prepared according to the literature.

For the reactions of **22** with *N*-chlorosuccinimide (NCS), a typical example is described below. The structures of **28** were established by comparison of IR and ^{1}H NMR spectra with those of authentic samples prepared from the corresponding sodium or caesium dithiocarboxylates with NCS. Their yields, spectral data, and microanalyses are collected in Tables 8 and 6b.

Table 8. Yields and physical properties of *N*-(thioacylthio)succinimides **28**

	... succinimide	Yield[a] (%)	m. p. [°C]	IR (KBr) νC=S	[cm^{-1}] νC=O	UV/Vis [nm][b] λ_{max} (lg ε)	^{1}H NMR (δ values)
28a	*N*-(Thiobenzoylthio)...	16	124–125	1142	1732	303 (4.20) 496 (2.04)	2.98 (s, 4H, CH_2), 7.1–8.1 (m, 5H, Ar)
b	*N*-[4-(Methyl)thiobenzoylthio]...	7	184–185	1145	1695 sh 1735	315 (4.23) 493 (2.11)	2.39 (s, 3H, CH_3), 3.00 (s, 4H, CH_2), 7.1–8.0 (m, 4H, Ar)
c	*N*-[4-(Methoxy)thiobenzoylthio]...	9	120–122	1170	1698 1738	298 (4.13) 489 (2.14)	3.00 (s, 4H, CH_2), 3.84 (s, 3H, CH_3O), 6.2–8.1 (m, 4H, Ar)
d	*N*-[4-(Chloro)thiobenzoylthio]...	19	119–121	1138	1695 sh 1730	312 (4.19) 498 (1.16)	3.02 (s, 4H, CH_2), 7.3–8.0 (m, 4H, Ar)

[a] Isolated yield. – [b] CH_2Cl_2. – [c] $CDCl_3$.

Reaction of **22b** *with NCS:* A solution of **22b** (352 mg, 1.0 mmol) and NCS (133 mg, 1.0 mmol) in tetrahydrofuran (15 ml) was stirred at ca. 16°C for 3 h. The solvent was evaporated in a rotary evaporator to afford a red solid, which was purified by column chromatography on silica gel (*n*-hexane/ether, 1:1) to yield four fractions in the following order: 147 mg (44%) of **8b**, 170 mg (45%) of **27**, 60 mg (7%) of *N*-[4-(methyl)thiobenzoylthio]succinimide (**28b**) as reddish orange crystals, and an intractable oily substance (40 mg). The IR and ^{1}H NMR spectra of **28b** were consistent with those of an authentic sample prepared by the reaction of **3b** with NCS.

Reaction of **22b** *with tellurium tetrachloride:* A solution of **22b** (352 mg, 1.0 mmol) and tellurium tetrachloride (68 mg, 0.25 mmol) in chloroform (20 ml) was stirred at 0°C for 3 h. The mixture was concentrated in a rotary evaporator to ca. 1 ml which was chromatographed on silica gel (column; dichloromethane/ether, 4:1) to give 51 mg (44%, based on $TeCl_4$) of tellurium bis[4-(methyl)dithiobenzoate] (**29**). The m. p., spectral data, and elemental analyses are shown in Table 6a and 6b. The IR spectrum was consistent with that of an authentic sample[25].

Reaction of **5b** *with tellurium tetrachloride:* A solution of **5b** (384 mg, 1.0 mmol) and tellurium tetrachloride (68 mg, 0.25 mmol) was stirred at 0°C for 3 h. Chromatographic purification of the reaction mixture on silica gel using dichloromethane gave 60 mg (52%) of **29**.

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