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Studies on Organophosphorus Compounds. XXXVIII.* Synthesis of 2,3-Unsaturated *O*-Alkyl Thioesters, 2,3-Unsaturated Thioamides and Tetrahydro-2*H*-1,3,2-thiazaphosphorin-4-one 2-Sulfides

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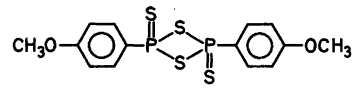
Ethyl 2-butenoate (ethyl crotonate), ethyl 3-phenyl-2-propenoate (ethyl cinnamate), methyl 2-cyano-3-phenyl-2-propenoate, and ethyl 2-cyano-3,3-diphenyl-2-propenoate, react wtih 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide, *1*, at 140 °C in xylene under formation of the corresponding *O*-alkyl thioesters. *N*-Unsubstituted, *N*-substituted, and *N*,*N*-disubstituted 3-phenyl-2-propenamides (cinnamamides) as well as *N*,*N*-disubstituted 2-butenamides (crotonamides) give the corresponding thioamides when treated with *1* in toluene at 60 °C. 2-Propenamide, 2-butenamide, and 3-methyl-2-butenamide give, however, 2*H*-1,3,2-thiazaphosphorin-4-ones, *10*–*12*, after reaction with *1* in HMPA at 60 °C. The 6-methyl derivative, *11*, was separated in the *cis* and *trans* forms and spectroscopic data of these isomers and X-ray crystallographic data of *trans-11* are given. The 2*H*-1,3,2-thiazaphosphorin-4-one, *10*, is readily transformed into the corresponding 4-thione by reaction with *1* at 90 °C in toluene.

To our knowledge very little has been published on 2,3-unsaturated *O*-alkyl thioates[1] although these compounds seem to be stable and readily available. 2,3-Unsaturated aromatic thioamides have been prepared by thiation with P_4S_{10}[2] and also 3-heterosubstituted 2-propenamides (vinylogous thioureas[3] and vinylogous dithiocarbamates[4]) have been prepared by this method. The preparation of an *N*,*N*-disubstituted 2-butenethioamide, from the corresponding *O*-alkyl thioate and amine, was published recently.[1]

Thiation of esters and amides with *1* is well established[5–9] and we therefore investigated the reactions between *1* and 2,3-unsaturated esters and 2,3-unsaturated amides, and this paper will report on our results.



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RESULTS AND DISCUSSION

A. 2,3-Unsaturated O-alkyl thioesters. The title compounds (Scheme 1) were isolated in reasonable yields after reaction of the appropriate ester with *1* for 2–24 h at 120–140 °C in xylene. 2-Cyano-2,3-unsaturated esters gave the thiocarbonyl compounds without side-reactions but in these cases total conversion of the ester could not be obtained, regardless of the amount of *1* used. The products were pale yellow, stable compounds which could be stored at room temperature without decomposition. The structures were established by ^1H and ^{13}C NMR spectroscopy, MS, UV, IR, and elemental analyses. When going from >C=O to >C=S the 2–C proton shifted approximately 0.5 ppm downfield. The 3–C proton was almost unaffected. Examples of the ^{13}C NMR shifts are given below (δ, $CDCl_3$).

* Part XXXVII, A. A. El-Barbary and S.-O. Lawesson. *Tetrahedron 37* (1981). *In press.*

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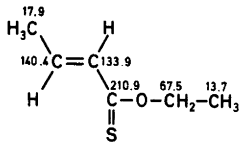

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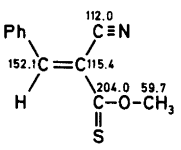

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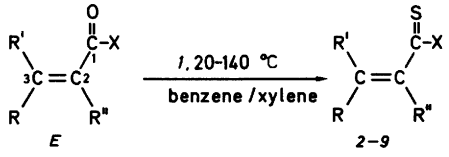
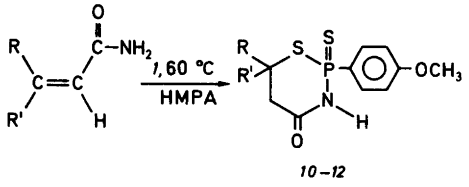
The assignments were confirmed by an off-resonance decoupled spectrum of *4* showing a doublet for 3−C and a small doublet for 2−C (splittings 45 Hz and 3 Hz, respectively) and a singlet for the CN carbon atom. In *2* it was found necessary to decouple the 2−C proton selectively to ensure correct assignment of 2−C and 3−C.

In the mass spectra a difference in fragmentation was observed when comparing *2* and *3* with *4* and *5*. In *2* and *3* loss of *O*-alkyl and *S*-alkyl was observed but in *4* and *5* a fairly abudant ion corresponding to M^+-alkyl was also observed.[10,11] The UV spectra showed absorptions at 325−335 nm for *3*−*5* and at 280 nm for *2*. The IR absorption band for the C≡N group was found at ~2240 cm^{-1} ($CHCl_3$) as in the starting compounds.[12] As the esters all products were pure *E*-isomers (^{1}H NMR[13] and IR[12]).

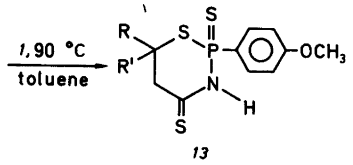


E 2–9

	R	R'	R"	X
2	Me	H	H	OEt
3	Ph	H	H	OEt
4	Ph	H	CN	OMe
5	Ph	Ph	CN	OEt
6	Ph	H	H	NH_2
7	Ph	H	H	NHPh
8	Ph	H	H	NEt_2
9	Me	H	H	NMe_2



10–12



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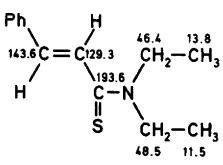
Scheme 1. Reactions of 2,3-unsaturated esters and amides with *1*. *10*, *13*, R=R'=H; *11*, R'=Me; *12*, R=R'=Me.

B. 2,3-Unsaturated thioamides. 3-Phenyl-2-propenamides (cinnamamides) react with *1* in benzene at 60 °C to give the corresponding thioamides *6*−*8* (Scheme 1) in high yields. *N,N*-Dimethyl-2-butenamide (dimethylcrotonamide) reacted exothermally with *1* within 0.5 h giving *9* in a quantitative yield. The products were identified as mentioned for the *O*-alkyl thioates. The ^{13}C NMR chemical shifts of *6* and *9* are given below (δ, $CDCl_3$).



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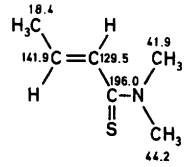

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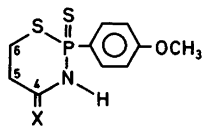
The assignments of the *N*-alkyl carbon atoms were made by comparison with other *N,N*-dialkyl thioamides.[7] 2−C and 3−C were assigned by comparison with *2*.

2-Propenamide, 2-butenamide, and 3-methyl-2-butenamide also react with *1* in benzene at 60 °C but in these cases very complex reaction mixtures (TLC) were obtained and no thioamides could be isolated. The use of HMPA as solvent in these reactions led to the formation of the 2*H*-1,3,2-thiazaphosphorin-4-ones *10*−*12* (Scheme 1) in low to moderate yields. To investigate the influence of HMPA also cinnamanilide was allowed to react under the same conditions but no phosphorus heterocycle was isolated. A few 2*H*-1,3,2-thiazaphosphorines have been reported[14,15] but very few data have been given. We characterized *10*−*13* by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, MS, IR and elemental analyses. Further proof of the structure was also found by treating *10* with *1* in toluene at 90 °C giving *13* in a quantitative yield. The ^{31}P NMR chemical shifts of *10*−*13* were found in the region δ 57.6−60.8. The ^{13}C NMR data of *10* and *13* are given in Table 1. The change in chemical

Table 1. ^{13}C NMR data of *10* and *13*, $(CD_3)_2SO$.



	X=O, *10*		X=S, *13*	
C	δ	$\lvert J_{PC}\rvert$ (Hz)	δ	$\lvert J_{PC}\rvert$ (Hz)
4	170.7	3.1	207.2	7.8
5	34.8	–	42.3	2.9
6	25.2	2.1	26.7	3.5

shift ($\Delta\delta$) of 5–6 and the $\lvert J_{PC}\rvert$ values proved the assignment.[7]

Two isomers of tetrahydro-2-(4-methoxyphenyl)-6-methyl-2*H*-1,3,2-thiazaphosphorin-4-one 2-sulfide, *cis-11* and *trans-11* were isolated by column chromatography.

The structure of one isomer was determined by *X*-ray diffraction methods; details of the analysis are given in Experimental. Fig. 1 is an ORTEP drawing of the molecule, showing the atomic labelling. Pertinent structural parameters are listed in Table 2.

The *X*-ray analysis led to the *trans* isomer, as the sulfur atom (S2) was in an axial orientation and the C4 methyl group was in an equatorial one, on the heterocyclic pseudo chair-formed six-membered ring. This heterocyclic ring was somewhat flattened on the carbonyl side; the coordination about C3 was planar and the phosphorus atom was also only slightly displaced from this plane. One would not expect a large energy barrier for an inversion of this type of ring. However, inversion would orient both C4 and C5 axially and would bring the two atoms close to each other and lead to steric repulsion.

The observed P–S2 bond length was close to the value calculated from the covalent double bond radii

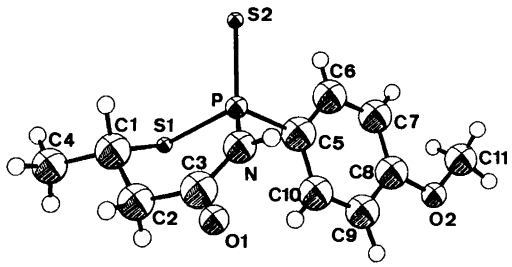


Fig. 1. ORTEP plot of compound *trans-11*.

of the two atoms (1.94 Å). The P–C, P–N and P–S1 bonds were all shorter than the corresponding sums of the covalent single bond radii. This may be explained by an electron transfer from the phosphorus atom to the ligands caused by differences in their electronegativity (resonance forms). In accordance with the valence shell electron pair repulsion model the S2–P–N, S2–P–S1 and S2–P–C5 angles were large (ranging from 112.9 to 116.8°), whereas the S1–P–N, N–P–C5 and C5–P–S1 angles were small (ranging from 102.7 to 104.8°).

The nitrogen atom was sp^2 hybridized with its hydrogen atom situated in the plane of atoms P, N and C3. This resulted in a shortening of the N–C3 bond. All intermolecular contacts were of the normal van der Waals type; no intermolecular hydrogen bonding was observed.

From the 270 MHz ^1H NMR spectrum (Table 3) it is also clear that 6–H was in an axial position in both forms as the 6–H–5–H coupling constants were 12.2 and 11.3 Hz, respectively.[16] The origin of the isomerism must, therefore, be the spatial positions of the ligands on the phosphorus atom. A significant difference between the two forms was found in the chemical shift values of 6–H (δ4.03 in *11t* and δ 3.18 in *11c*) and it was therefore concluded that the axial sulfur atom shielded the axial 6–H less than did the axial methoxyphenyl group. A pronounced effect was also found in the chemical shifts of the NH hydrogens ($\Delta\delta$ 2.31) and in both cases the ring current effect is assumed to account for the shielding/deshielding. 5–C absorbs at relatively low field (Tables 3 and 4) when compared with 5–C in *10* (Table 1), but the assignment is in agreement with an off-resonance decoupled spectrum which shows a triplet for 5–C. The IR spectra show absorptions for the C=O in the region 1665–95 cm^{-1}.

The transformation of *10* into *13* in a smooth reaction is in accordance with earlier findings.[8] Diethyl fumarate and diethyl maleate did not lead to the corresponding thiocarbonyl compounds after reaction with *1* at 140 °C for 6 hours.

EXPERIMENTAL

^1H, ^{13}C and ^{31}P NMR, IR, UV and mass spectra were obtained as earlier described.[8,9] Spectra of *11* were recorded at 270 MHz on a Bruker HX-270. Coupling constants are given as $\lvert J\rvert$. ^{31}P NMR shift data are rel. to ext. H_3PO_4. Elemental analyses

Table 2. Structural data for *trans-11*. The numbering of the atoms is given Fig. 1. Estimated standard deviations (in parantheses) are calculated from the correlation matrix.

Bond lengths (Å)

P	S2	1.931(1)
P	C5	1.796(3)
P	N	1.696(3)
P	S1	2.077(1)
N	C3	1.369(4)
C3	O1	1.224(4)
C3	C2	1.504(4)
C2	C1	1.507(4)
C1	C4	1.528(4)
C1	S1	1.844(3)
C5	C6	1.390(4)
C6	C7	1.387(5)
C7	C8	1.387(5)
C8	C9	1.395(4)
C9	C10	1.375(5)
C5	C10	1.395(4)
C8	O2	1.362(4)
O2	C11	1.435(4)
N	H	0.85
C–H	(mean)	0.95(5)

Bond angles (°)

S1	P	S2	116.8(1)
S1	P	C5	103.9(1)
S1	P	N	102.7(1)
S2	P	C5	114.3(1)
S2	P	N	112.9(1)
C5	P	N	104.8(1)
P	N	C3	133.0(2)
N	C3	O1	120.1(3)
N	C3	C2	120.1(3)
O1	C3	C2	119.8(3)
C3	C2	C1	116.7(2)
C2	C1	C4	111.8(3)
C2	C1	S1	108.9(2)
C4	C1	S1	108.0(2)
C1	S1	P	95.9(1)
P	P	C6	121.0(2)
P	C5	C10	120.0(2)
C6	C5	C10	119.1(3)
C5	C6	C7	121.1(3)
C6	C7	C8	119.1(3)
C7	C8	C9	120.3(3)
C8	C9	C10	120.1(3)
C9	C10	C5	120.3(3)
C9	C8	O2	115.1(3)
C7	C8	O2	124.6(3)
C8	O2	C11	117.9(2)

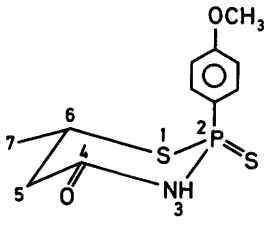
Torsion angles (°)

S2	P	N	C3	117.3(3)	N	P	C5	C10	35.5(3)
S2	P	S1	C1	−83.4(1)	P	N	C3	O1	175.2(2)
S2		P	C5	−18.3(3)	P	N	C3	C2	−5.9(4)
S2	P	C5	C10	159.6(2)	N	C3	C2	C1	−22.4(4)
C5	P	N	C3	−117.7(3)	O1	C3	C2	C1	156.5(3)
C5	P	S1	C1	149.7(1)	C3	C2	C1	C4	−174.9(3)
S1	P	N	C3	−9.4(3)	C3	C2	C1	S1	65.8(3)
S1	P	C5	C6	110.1(2)	C4	C1	S1	P	168.2(2)
S1	P	C5	C10	−71.9(2)	C2	C1	S1	P	−70.2(2)
N	P	S1	C1	40.8(1)	C7	C8	O2	C11	−2.9(4)
N	P	C5	C6	−142.4(2)	C9	C8	O2	C11	176.8(3)

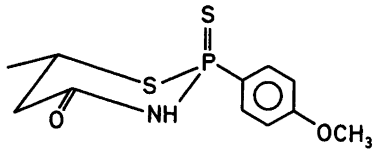
were carried out by NOVO Microanalytical Laboratory, Novo Industri A/S, Novo Allé, DK-2880 Bagsværd, supervised by Dr. R. E. Amsler. Silica gel 60 (Merck) was used for column chromatography. *1* is commercially available as Lawesson reagent (Fluka AG, Buchs, Switzerland).

X-Ray data. Crystals of *trans-11* were formed by recrystalization from a 1:1 (v/v) mixture of CH_2Cl_2 and Et_2O. The specimen used for the X-ray diffraction measurements had dimensions $0.2 \times 0.4 \times 0.4$ mm. Data were collected on a SYNTEX $P\bar{1}$ four-circle diffractometer using graphite crystal monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). The temperature at the crystal site was −150 °C. Cell parameters were determined by a least-squares fit to the diffractometer settings for 15 general reflections. Intensity data were recorded using the $\theta/2\theta$ scanning mode with a scan speed (2θ) of 3° min^{-1} and a scan range from 1.0° below $2\theta(\alpha_1)$ to 1.1° above $2\theta(\alpha_2)$. The background counts were taken for 0.35 times the scan time at each end of the scan. Reflections in one hemisphere of reciprocal space

Table 3. NMR data for *cis-* and *trans-11*, 270 MHz ^{1}H NMR in $CDCl_3$.



cis - 11
(11c)



trans - 11
(11t)

^{1}H	(δ, ppm) *cis/trans*	6−H *cis/trans*	Coupling constant (Hz) to 5−H_a	5−H_e	5−H_e	P
6−H	3.18/4.03	−	11.3/12.2	3.1/2.8	7.2/7.9	7.3/7.9
5−H_a	2.67/2.65		−	17.7/17.7	[a]	[a]
5−H_e	2.89/2.99			−	[a]	0.9/0.9
7−CH_3	1.39/1.54				−	1.6/1.6
NH	7.39/9.70					very br.

[a] No coupling observed.

up to sin $\theta/\lambda = 0.6$ Å^{-1} were measured. Out of the 2288 reflections recorded, 2113 with $I > 2.5\ \sigma(I)$ were retained fot the structure analysis. Corrections were made for Lorentz and polarization effects, but not for absorption. Scattering factors used were those of Ref. 17 for *S*, *P*, *O*, *N* and *C*, and of Ref. 18 for *H*. Descriptions of the computer programmes applied are given in Refs. 19 and 20.

Crystal data. *trans*-Tetrahydro-2-(4-methoxyphenyl)-6-methyl-2*H*-1,3,2-thiazaphosphorin-4-one 2-sulfide, triclinic. $a = 11.082(1)$ Å; $b = 6.192(1)$ Å; $c = 12.199(2)$ Å; $\alpha = 87.29(2)°$; $\beta = 129.39(1)°$; $\gamma = 91.82(2)°$; $V = 646.2(2)$ Å^3, (t = −150 °C). $M = 287.32$; $Z = 2$; F (000) = 300 μ(MoKα) = 5.13 cm^{-1}, $Dx = 1.477$ g cm^{-3}. Space group $P\bar{1}$ (No. 2).

Structure determination. The structure was determined by direct methods[19] and refined by standard Fourier and least-squares calculations. The non-hydrogen atoms were assigned anisotropic temperature factors while the hydrogen atoms were assumed to vibrate isotropically.

The refinement converged to a convential *R*-value of 0.037, $R_w = 0.066$ and $S = (\Sigma w \Delta F^2/(n-m))^{\frac{1}{2}} = 3.2$. The final atomic parameters are listed in Table 5. A list of observed and calculated structure factors is available from the authors.

Table 4. NMR data for *cis* and *trans-11*, 20 MHz ^{13}C NMR in $(CD_3)_2SO$, $\delta(|J_{PC}|$, Hz).

C	*cis*	*trans*
4	170.6(2.2)	170.5([a])
5	43.0([a])	43.5([a])
6	36.7(2.8)	36.6([a])
7	21.1(10.5)	21.7(9.6)

[a] No coupling observed.

A. 2,3-Unsaturated O-*alkyl thioates.* All starting materials were commercially available. Ethyl 2-cyano-3,3-diphenyl-propenoate (Uvinyl-*N*-35) was kindly placed at our disposal by Gafdan, Energivej 33, DK-2750 Ballerup. All starting materials were pure *E*-isomers as determined by ^{1}H NMR and IR (see text).

General procedure for the preparation of 2,3-unsaturated O-*alkyl thioates*, 2 − 5. The appropriate ester (10.0 mmol) was dissolved in anhydrous xylene (10 ml) and *1* (2.45 g, 6.00 mmol) was added. The reaction mixture was heated (oil bath) with stirring. Reaction times and temperatures are given below. After cooling to room temperature the reaction mixture was evaporated on silica gel and applied to a column using ether/ligroin (5:95 v/v) as eluent. In the case of *2* the reaction mixture was placed on the column without stripping off the xylene (*2* is low boiling). The products were distilled or recrystallized (diisopropyl ether).

O-*Ethyl (*E*)-2-butenethioate*, *2* (ethyl thionocrotonate). Reaction temp.: 135 °C. Reaction time: 2 h. Yield: 46 %. B.p. 60 °C/10 Torr.[6] ^{1}H NMR ($CDCl_3$): δ 7.00 (dq, 3−CH, *J* 16 Hz, *J* 7 Hz), 6.33 (dq, 2−CH, *J* 16 Hz, *J* 1.5 Hz), 4.43 (q, CH_2),

Table 5. Fractional atomic coordinates and thermal parameters with estimated standard deviations for compound *trans-11*. The anisotropic temperature factor is given by exp-$2\pi^2$ ($U11a^*h^2+\ldots+2U12a^*b^*hk+\ldots$).

Atom	X	Y	Z	U11	U22	U33	U12	U13	U23
S1	.61917(8)	−.01626(11)	.92841(7)	.0144(4)	.0206(4)	.0165(4)	−.0022(3)	.0105(3)	−.0005(3)
S2	1.00683(9)	−.09668(12)	1.20465(8)	.0189(4)	.0239(4)	.0199(4)	.0098(3)	.0136(4)	.0064(3)
P	.83733(8)	.10756(11)	1.09170(7)	0.125(4)	.0165(4)	.0123(4)	.0022(3)	.0088(3)	.0020(3)
O1	.8291(2)	.5067(3)	.8310(2)	.0175(10)	.0217(11)	.0163(10)	−.0003(8)	.0115(9)	.0023(8)
O2	.7334(3)	.6371(4)	1.4177(2)	.0285(12)	.0289(12)	.0177(10)	.0097(9)	.0171(10)	.0022(8)
N	.8667(3)	.2980(4)	1.0061(3)	.0146(12)	.0190(12)	.0136(12)	−.0025(10)	.0089(10)	−.0007(9)
C1	.6516(3)	−.0190(5)	.7989(3)	.0159(14)	.0206(14)	.0186(14)	−.0001(12)	.0117(13)	−.0016(11)
C2	.6554(4)	.2106(5)	.7533(3)	.0164(15)	.0238(15)	.0148(14)	.0017(12)	.0099(13)	.0018(11)
C3	.7888(3)	.3494(5)	.8656(3)	.0147(14)	.0195(14)	.0160(13)	.0030(11)	.0116(12)	.0001(11)
C4	.5196(4)	−.1494(6)	.6723(4)	.0237(17)	.0259(17)	.0243(16)	−.0058(13)	.0137(15)	−.0067(13)
C5	.8023(3)	.2584(5)	1.1913(3)	.0134(14)	.0193(14)	.0160(14)	−.0005(11)	.0106(12)	−.0003(11)
C6	.8595(4)	.1873(5)	1.3263(3)	.0170(14)	.0233(15)	.0178(14)	.0059(12)	.0117(13)	.0046(12)
C7	.8384(3)	.3078(5)	1.4060(3)	.0188(15)	.0251(15)	.0145(14)	.0045(12)	.0107(12)	.0050(11)
C8	.7597(3)	.5030(5)	1.3495(3)	.0146(14)	.0242(15)	.0166(14)	−.0003(11)	.0112(12)	−.0020(11)
C9	.6999(4)	.5745(5)	1.2134(3)	.0213(15)	.0226(15)	.0184(14)	.0063(12)	.0131(13)	.0039(12)
C10	.7211(4)	.4533(5)	1.1352(3)	.0190(14)	.0219(15)	.0139(14)	.0053(12)	.0107(12)	.0040(11)
C11	.7845(4)	.5678(6)	1.5552(3)	.0252(17)	.0315(18)	.0149(14)	.0005(14)	.0136(14)	−.0020(12)

Atom	X	Y	Z	B	Atom	X	Y	Z	B
HN	.950(6)	.369(8)	1.060(5)	2.5(6)	H1	.749(5)	−124(7)	.843(5)	2.5
H21	.568(5)	.285(6)	.723(4)	1.2(5)	H22	.662(4)	.215(6)	.680(4)	1.2
H41	.536(6)	−.169(8)	.602(5)	3.0(5)	H42	.421(6)	−.080(8)	.627(5)	3.0
H43	.514(6)	−.296(9)	.703(5)	3.0	H6	.916(5)	.069(7)	1.364(4)	2.0(4)
H7	.876(5)	.257(7)	1.493(5)	2.0	H9	.647(5)	.720(7)	1.177(4)	2.0
H10	.685(5)	.502(6)	1.047(5)	2.0	H11	.763(5)	.687(8)	1.586(5)	2.5(5)
H112	.893(6)	.546(7)	1.618(5)	2.5	H113	.728(5)	.434(8)	1.544(5)	2.5

1.90 (dd, 4−CH_3, *J* 7 Hz, *J* 1.5 Hz), 1.40 (t, CH_2-CH_3). ^{13}C NMR given in the text. MS: *m/e* (% rel.int.): 130 (M^+, 95), 85 (100, $M^+-EtO^·$), 69 (61, $M^+-EtS^·$).

O-*Ethyl (*E*)-3-phenyl-2-propenethiate*, *3* (ethyl thionocinnamate). Reaction temp.: 120 °C. Reaction time: 10 h. Yield: 72 %. B.p. 140 °C/12 Torr.[6] ^{1}H NMR ($CDCl_3$): *δ* 7.68 (d, 3−CH, *J* 16 Hz), 7.34 (m, Ph), 6.95 (d, 2−CH, *J* 16 Hz), 4.59 (q, CH_2), 1.41 (t, CH_3). ^{13}C NMR ($CDCl_3$): *δ* 210.4 (C=S), 140.3 (3−C, 134.8 (quart. C), 130.1 (p−C), 129.0 (2−C), 128.9 and 128.3 (*o*- and *m*−C), 67.7 (CH_2), 13.7 (CH_3). MS: *m/e* (% rel.int.): 192 (M^+, 69), 147 (39, $M^+-EtO^·$), 131 (46, $M^+-EtS^·$), 115 (100). Anal. $C_{11}H_{12}OS$: C, H, S.

O-*Methyl (*E*)-2-cyano-3-phenyl-2-propenethioate*, 4. Reaction temp.: 140 °C. Reaction time: 24 h. Yield: 40 %. M.p. 68−70 °C. Starting material (45 %) was regenerated. ^{1}H NMR ($CDCl_3$): *δ* 8.30 (s, 3−CH), 7.86 (m, *o*−H), 7.40 (m, *m*- and *p*−H), 4.18 (s, CH_3). ^{13}C NMR given in the text. MS: *m/e* (% rel.int.): 203 (M^+, 98), 202 (100, M^+-H), 188 (13, $M^+-Me^·$), 172 (23, $M^+-EtO^·$), 140 (49). Anal. $C_{11}H_9NOS$: C, H, N, S.

O-*Ethyl 2-cyano-3,3-diphenyl-2-propenethioate*, 5. Reaction temp.: 140 °C. Reaction time: 12 h. Yield: 39 %. M.p. 126−128 °C. Starting material (48 %) was regenerated. ^{1}H NMR ($CDCl_3$): *δ* 7.27 (m, Ph_2), 4.23 (q, CH_2), 0.89 (t, CH_3). ^{13}C NMR ($CDCl_3$): *δ* 205.9 (C=S), 162.0 (3−C), 139.5 and 138.5 (quart. C's), 131.1 and 129.9 (*p*-C's), 130.4, 129.3, 128.4 and 128.2 (*o*- and *m*-C's), 117.5 (2−C), 113.5 (CN), 68.8 (CH_2), 12.7 (CH_3). MS: *m/e* (% rel.int.): 293 M^+, 81), 54, $M^+-Et^·$), 232 (31, $M^+-EtS^·$), 216 (100). Anal. $C_{18}H_{15}NOS$: C, H, N, S.

B. 2,3-Unsaturated thioamides. The starting materials were commercially available or prepared from the appropriate acid chloride and the amine.

General procedure for the preparation of 2,3-unsaturated thioamides, 6−9. As above using toluene as solvent.

*(*E*)-N,N-Dimethyl-2-butenethioamide*, *9* (dimethylthiocrotonamide). Slightly exothermic. Reaction time: 0.5 h. Yield: 80 %. B.p.: 133 °C/12 Torr. ^{1}H NMR ($CDCl_3$): *δ* 7.03 (dq, 3−CH, *J* 15 Hz, *J* 7 Hz), 6.50 (dq, 2−CH, *J* 15 Hz, *J* 1.5 Hz), 3.51 (s, *syn* NCH_3), 3.37 (s, *anti* NCH_3), 1.93 (dq, CH_3, *J* 7 Hz, *J* 1.5 Hz). ^{13}C NMR given in text. MS: *m/e* (% rel.

int.): 129 (M^+, 100), 114 (46), 96 (14), 88 (21), 85 (39), 81 (29). Anal. $C_6H_{11}NS$: C, N, S.

(E)-*3-Phenyl-2-propenethioamide*, *6* (thiocinnamamide). Reaction temp.: 60 °C. Reaction time: 2 h. Yield: 60 %. M.p. 146 °C.[2] ^1H NMR ($(CD_3)_2CO$): δ 9.60 (br.s, *syn* NH), 9.32 (br.s, *anti* NH), 7.83 (d, 3−CH, *J* 15 Hz), 7.35 (m, Ph), 6.94 (d, 2−CH, *J* 15 Hz). ^{13}C NMR ($CDCl_3+(CD_3)_2CO$): 198.7 (C=S), 142.5 (3−C), 135.5 (quart. C), 130.2 (2−C), 129.3, 128.4 (*o*- and *m*-C), 127.3 (*p*-C). MS: *m/e* (% rel. int.): 163 (M^+, 62), 162 (100), 130 (20).

(E)-N,*3-Diphenyl-2-propenethioamide*, 7 (thiocinnamanilide). Reaction temp.: 60 °C. Reaction time: 3 h. Yield: 78 %. M.p. 134 °C.[7] ^1H NMR ($CDCl_3$): δ 10.8 (br.s, NH), 7.95 (d, 3−CH, *J* 15 Hz), 7.40 (m, Ph_2), 6.93 (d, 2−CH, *J* 15 Hz). ^{13}C NMR ($(CD_3)_2CO$): δ 192.4 (C=S), 141.8, 139.9 (2 quart. C's), 135.4 (3−C), 129.8, 129.5, 129.2, 128.6, 128.0, 126.0 (Ph_2), 123.4 (2−C). MS: *m/e* (% rel. int.): 239 (M^+, 64), 238 (65), 206 (21), 147 (100).

(E)-N,N-*Diethyl-3-phenyl-propenethioamide*, *8* (diethylthiocinnamamide). Reaction temp.: 60 °C. Reaction time: 1.5 h. Yield: 98 %. M.p. 48−50 °C.[7] ^1H NMR ($CDCl_3$): δ 7.90 (d, 3−CH, *J* 16 Hz), 7.35 (m, Ph), 7.10 (d, 2−CH, *J* 16 Hz), 4.06 (q, *syn* CH_2), 3.70 (q, *anti* CH_2), 1.30 (t, *syn* and *anti* CH_3). ^{13}C NMR given in text. MS: *m/e* (% rel.int.): 219 (M^+, 78), 147 (100).

General procedure for the preparation of 2H-1,3,2-thiazaphosphorin-4-ones, 10−12. The 2,3-unsaturated amide (10.0 mmol) and *1* (2.02 g, 5.00 mmol) were stirred at 50−60 °C in HMPA (5 ml) for the times given below. After cooling to room temperature the mixture was placed on a column and elution with ether/ligroin (75:25 v/v) gave the product contaminated with HMPA. Repeated column chromatography yielded the pure product which was recrystallized from diisopropyl ether.

Tetrahydro-2-(4-methoxyphenyl)-2H-1,3,2-thiazaphosphorin-4-one 2-sulfide, 10. Reaction time: 1.5 h. Yield: 70 %. M.p. 124 °C. ^{31}P NMR ($CDCl_3$): δ 60.8. ^1H NMR ($CDCl_3$): 10.3 (br.s, NH), 7.87 (2H, dd, J_{PH} 14 Hz, J_{HH} 9 Hz), 7.15 (2H, dd, J_{PH} 4 Hz, J_{HH} 9 Hz), 3.90 (s, OCH_3), 3.6−2.6 (4H, m, CH_2-CH_2). ^{13}C NMR ($(CD_3)_2SO$): δ [J_{PC}(Hz)], C=O and CH_2 given in Table 1, 162.5 [3.3], [O−Ph(C1)], 132.5 [14.7] [P−Ph(C2, C5)], 127.0 [112.2] [P−Ph(C1)], 114.2[15.9] [O−Ph(C2,C5)], 55.3 (CH_3). IR ($CHCl_3$), cm^{-1}: 1695 (C=O), 1105 (POC). MS: *m/e* (% rel.int.): 273 (M^+, 21), 202 (20), 187 (47), 181 (36), 180 (22), 170 (16), 155 (37), 140 (47), 139 (58), 139 (58), 137 (47), 108 (100). Anal. $C_{10}H_{12}NO_2PS_2$: C, H, N, P.

Tetrahydro-2-(4-methoxyphenyl)-6-methyl-2H-1,3,2-thiazaphosphorin-4-one 2-sulfide, 11. Reaction time: 22 h. Yield (total): 51 %.

11t. Yield: 21 %. M.p. 171 °C. ^{31}P NMR ($(CD_3)_2SO$): 60.3. ^1H NMR: 4-methoxyphenyl as above, others given in Table 3. ^{13}C NMR: 4-methoxyphenyl as above $\delta\pm1.3$ [$J_{PC}\pm0.5$ Hz], others given in Table 3. IR (KBr), cm^{-1}: 1675 (C=O). MS: *m/e* (% rel.int.): 287 (M^+, 68), 254 (30), 202 (16), 187 (41), 135 (100), 102 (80).

11c. Yield: 30 %. M.p. 167−69 °C. ^{31}P NMR ($(CD_3)_2SO$): δ 57.6. ^1H NMR: see Table 3 and *10*. ^{13}C NMR: see Table 3 and *10*, $\delta\pm0.8$ [$J_{PC}\pm1.1$ Hz]. IR (KBr), cm^{-1}: 1680 (C=O). MS: *m/e* (% rel.int.): 287 (M^+, 100), 254 (28), 207 (33), 202 (28), 187 (93), 155 (13), 140 (18), 139(35), 108 (25).

Tetrahedro-2-(4-methoxyphenyl)-6,6-dimethyl-2H-1,3,2-thiazaphosphorin-4-one 2-sulfide, 12. Reaction time: 18 h. Yield: 15 %. M.p. 78−83 °C. ^{31}P NMR ($CDCl_3$): δ 59.2. ^1H NMR ($CDCl_3$): 8.3 (br.s, NH), 7.9 (dd), 7.0 (dd), 3.9 (s) OMe, 2.80 (2H, m, CH_2), 2.25 (3H, br.s, CH_3), 1.69 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$): δ [J_{PC} (Hz)]: 171.2 [3.7] (C=O), 50.8 [4.4], 49.1 [2.1], 32.1 [5.3]. Others as for *10* $\delta\pm1.9$ [$J_{PC}\pm0.4$ Hz]. IR (KBr), cm^{-1}: 1665 (C=O). MS: *m/e* (% rel.int.): 301 (M^+, 12), 268 (8) 202 (10), 187 (25), 149 (53), 139 (16), 116 (100).

Tetrahydro-2-(4-methoxyphenyl)-2H-1,3,2-thiazaphosphorine-4-thione 2-sulfide, 13. Prepared from *10* and *1* as earlier described for imides.[4] Yield: 91 %. M.p. 123−25 °C. ^{31}P NMR ($CDCl_3$): δ 59.0. ^1H NMR ($CDCl_3$): 9.1 (br.s, NH), 7.85 (dd), 7.0 (dd), 3.9 (s) OMe, 3.7−2.6 (4H, m, CH_2-CH_2). ^{13}C NMR ($CDCl_3$): δ [J_{PC}]: 162.5 [3.5], 137.2 [14.7], 125.0 [112.1], 114.5 [16.5], 55.6 assignment see *10*, others see Table 1. MS: *m/e* (% rel. int.): 289 (M^+, 55), 256 (42), 202 (83), 171 (23), 139 (100).

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