

# Synthesis and spectral properties of 4-(*O,O*-dialkyl(diaryl)-thiophosphorylhydrazono)-2,3-dichloro(2-chloro-3-ethylthio)-2-butenoic acid alkyl esters

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*Dedicated to Professor Ing. J. Kováč, DrSc., in honour of his 60th birthday*

The synthesis of nine novel 4-(*O,O*-dialkyl(diaryl)thiophosphorylhydrazono)-2,3-dichloro(2-chloro-3-ethylthio)-2-butenoic acid esters by the esterification of appropriate acids with alcohols and by the reaction of diazomethane or by the reaction of 3-formyl-2,3-dichloropropenoic acid methyl ester with *O,O*-dialkylthiophosphorylhydrazine is described. It was found that by the esterification cyclic products 2-(*O,O*-dialkyl(diaryl)-thiophosphoryl)-4,5-dichloro-3-oxo-2*H*-pyridazines were also formed. Infrared, ultraviolet, and <sup>1</sup>H NMR spectra of the prepared compounds are interpreted.

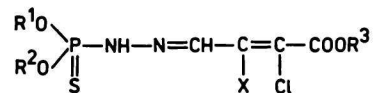
Описано получение девяти новых эфиров 4-(*O,O*-диалкил(диарил)-тиофосфорилгидразоно)-2,3-дихлор(2-хлор-3-этилтио)-2-бутеновой кислоты посредством этерификации соответствующих кислот спиртами, реакцией с диазометаном, или реакцией метилового эфира 3-формил-2,3-дихлорпропеновой кислоты с *O,O*-диалкилтиофосфорилгидразином. Обнаружено, что при этерификации также образовались циклические продукты 2-(*O,O*-диалкил(диарил)тиофосфорил)-4,5-дихлор-3-оксо-2*H*-пиридазины. Интерпретируются ИК-, УФ- и <sup>1</sup>H ЯМР спектры полученных соединений.

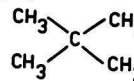
The synthesis of phosphoryl(thiophosphoryl)hydrazonoacetylacetic acid esters by the reaction of phosphoryl(thiophosphoryl)hydrazines with acetylacetic acid esters was reported in [1]. These esters were found to cyclize in the presence of sodium ethylate in benzene to phosphoryl(thiophosphoryl)-3-methyl-5-hydroxypyrazole.

In the present paper a synthesis and spectral properties of 4-(*O,O*-dialkyl(diaryl)thiophosphorylhydrazono)-2,3-dichloro(2-chloro-3-ethylthio)-2-butenoic acid alkyl esters are described. The aim of this work was to find novel pes-

Table 1

Characterization of the synthesized compounds



Compound	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	X	Formula <i>M<sub>r</sub></i>	<i>w<sub>i</sub></i> (calc.)/%				Yield/%	M.p./°C <i>n</i> (D, 20 °C)
						<i>w<sub>i</sub></i> (found)/%					
						N	S	P	Cl		
<i>I</i>	C <sub>2</sub> H <sub>5</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	Cl	C <sub>11</sub> H <sub>19</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> PS 377.19	7.42 7.72	8.27 8.88	8.01 8.13	18.00 19.07	41.8	1.5175
<i>II</i>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	Cl	C <sub>17</sub> H <sub>15</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> PS 445.25	6.29 6.57	7.20 7.36	6.96 6.95	15.92 15.72	74.2	119—120
<i>III</i>			CH <sub>3</sub>	Cl	C <sub>10</sub> H <sub>15</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> PS 361.19	7.76 7.81	8.88 8.98	8.58 8.79	19.63 19.58	80.4	179—180
<i>IV</i>	C <sub>2</sub> H <sub>5</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub>	C <sub>2</sub> H <sub>5</sub>	Cl	C <sub>12</sub> H <sub>21</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> PS 391.25	7.16 7.31	8.19 8.42	7.92 7.82	18.12 18.42	41.2	1.5092
<i>V</i>	C <sub>2</sub> H <sub>5</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub>	C <sub>3</sub> H <sub>7</sub>	Cl	C <sub>13</sub> H <sub>23</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> PS 405.28	6.91 7.12	7.91 8.05	7.64 7.58	17.50 17.59	39.1	1.5085
<i>VI</i>	C <sub>2</sub> H <sub>5</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub>	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	Cl	C <sub>13</sub> H <sub>23</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> PS 405.28	6.91 7.17	7.91 8.21	7.64 7.92	17.50 17.74	38.0	1.5275
<i>VII<sup>a</sup></i>	C <sub>2</sub> H <sub>5</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub>	Cl	C <sub>14</sub> H <sub>25</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> PS 419.27	6.68 6.83	7.65 7.81	7.39 7.36	16.91 16.83	40.3	1.5060
<i>VIII</i>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	SC <sub>2</sub> H <sub>5</sub>	C <sub>11</sub> H <sub>20</sub> ClN <sub>2</sub> O <sub>4</sub> PS 374.81	7.47 7.33	17.11 17.16	8.26 8.05	9.46 9.81	84.1	80—82
<i>IX<sup>b</sup></i>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	Cl	C <sub>9</sub> H <sub>15</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> PS 349.2	8.02 7.91	9.18 9.05	8.87 9.02	20.31 20.11	64.1	57—59

*a*) Prepared according to Procedure B; *b*) prepared according to Procedure C.

tidically active compounds of the group of organophosphoric compounds. The esters formed according to all three procedures were contaminated and therefore it was necessary to purify them by column chromatography. The procedure (C) starting from 2,3-dichloro-3-formylpropenoic acid methyl ester appeared to be the most convenient. The yields of prepared esters (Table 1) were in a wide range (39.1—80.4 %).

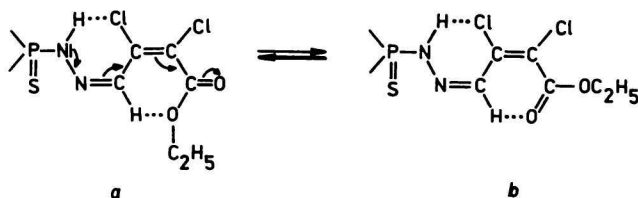
In the infrared spectra of compounds prepared (Table 2) the  $\nu(\text{N—H})$  medium intense bands in the region of  $\tilde{\nu} = 3226\text{—}3266\text{ cm}^{-1}$  are observed. The wavenumber as well as the intensity of these bands was practically unchanged even if a strong dilution of compounds measured was made. The low wavenumbers of these bands can be, therefore, explained by conjugation effects and by the presence of the  $\text{N—H} \cdots \text{Cl}$  intramolecular hydrogen bonds [2] (Scheme 1).

Table 2

Infrared, ultraviolet, and  $^1\text{H}$  NMR spectral data of the synthesized compounds

Compound	$\tilde{\nu}/\text{cm}^{-1}$			$\lambda/\text{nm}$	$\log(\epsilon/(\text{m}^2\text{ mol}^{-1}))$	$\delta/\text{ppm}$	
	$\nu(\text{N—H})$	$\nu(\text{C=O})$	$\nu(\text{P=S})$			=CH	NH
<i>I</i>	3265	1749	660	220	2.04	5.40 <sup>a</sup>	6.06 <sup>a</sup>
<i>II</i>	3226	1751	656	217	3.25	5.61	9.04
<i>III</i>	3246	1748	653	218	3.11	5.58	8.75
<i>IV</i>	3256	1751	663	220	2.01	5.63	9.01
<i>V</i>	3260	1751	656	224	3.03	5.72	9.12
<i>VI</i>	3257	1750	657	225	3.05	5.77	8.99
<i>VII</i>	3263	1748	661	225	3.04	5.69	9.06
<i>VIII</i>	3266	1711	676	308	3.44	5.30	8.82
<i>IX</i>	3266	1749	657	219	2.01	5.63	9.07

a) Measured in  $\text{CCl}_4$ .



Scheme 1

The observation of only one  $\nu(\text{C=O})$  band in the region of  $\tilde{\nu} = 1711\text{—}1751\text{ cm}^{-1}$  points to the presence of only one conformer (*a*), while in the case of appropriate acids two  $\nu(\text{C=O})$  bands are observed [3]. While in the IR spectra of acids [3] besides the  $\nu(\text{P=S})$  bands the  $\nu(\text{S—H})$  bands were observed, in the

IR spectra of esters investigated only the  $\nu(\text{P}=\text{S})$  bands in the region of  $\tilde{\nu} = 653$ — $676\text{ cm}^{-1}$  were observed [4]. In the IR spectra of cyclic compounds isolated after esterification of starting compounds (compounds *X* and *XI*) the  $\nu(\text{C}=\text{O})$  at  $\tilde{\nu} = 1684\text{ cm}^{-1}$  and  $\tilde{\nu} = 1697\text{ cm}^{-1}$  and the  $\nu(\text{P}=\text{S})$  at  $\tilde{\nu} = 666\text{ cm}^{-1}$  and  $\tilde{\nu} = 656\text{ cm}^{-1}$  bands are observed.

In the ultraviolet spectra of the compounds studied, excepting the compound *VIII* absorbing at  $\lambda = 308\text{ nm}$ , one band at  $\lambda = 220\text{ nm}$  is observed. It is interesting that the starting compounds absorb at longer wavelengths ( $\lambda \approx 285\text{ nm}$ ,  $\log(\epsilon/(\text{m}^2\text{ mol}^{-1})) \approx 3.30$ ) than the prepared esters.

In the  $^1\text{H NMR}$  spectra of the studied compounds measured in  $\text{DMSO-d}_6$  the signals of the  $\text{N-H}$  protons in the region of  $\delta = 8.75$ — $9.12\text{ ppm}$  are observed. The high  $\delta$  values evidently are connected with the intermolecular hydrogen bond of the  $\text{N-H}$  group with dimethyl sulfoxide.

## Experimental

### Procedure A

To the *O,O*-dialkyl(diaryl)thiophosphorylhydrazono-2,3-dichloro-2-butenic acid (0.03 mol) in corresponding alcohol ( $190\text{ cm}^3$ ) sulfuric acid (98 %,  $2.5\text{ cm}^3$ ) was added with stirring. The reaction mixture was heated to reflux. The completion of the reaction was followed by thin-layer chromatography. After completion of the reaction the reaction mixture was cooled and alcohol was distilled off under reduced pressure. The distilled residue was dissolved in chloroform ( $100\text{ cm}^3$ ) and washed three times with water ( $100\text{ cm}^3$ ). The chloroform layer was dried with sodium sulfate and chloroform was distilled off under reduced pressure. The crude product was purified by column chromatography.

### Procedure B

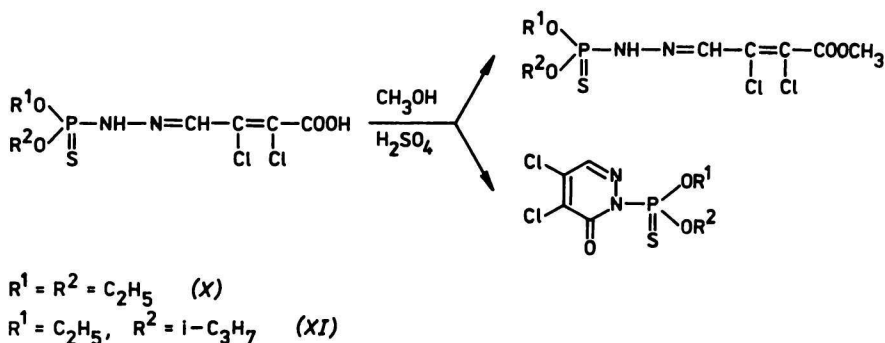
To the *O,O*-dialkyl(diaryl)thiophosphorylhydrazono-2,3-dichloro(2-chloro-3-ethylthio)-2-butenic acid (0.05 mol) in ether ( $80\text{ cm}^3$ ) an ethereal solution of diazomethane ( $100\text{ cm}^3$ ) was added with stirring at  $20^\circ\text{C}$ . The desired amount of diazomethane was followed by thin-layer chromatography. After completion of the reaction the reaction mixture was stirred for 1 h. The ether was distilled off under reduced pressure and the residue was purified by column chromatography.

### Procedure C

To 2,3-dichloro-3-formyl-2-propenoic acid (0.04 mol) in ether ( $80\text{ cm}^3$ ) an ethereal solution of diazomethane ( $80\text{ cm}^3$ ) was added with stirring at  $20^\circ\text{C}$ . The desired amount of diazomethane was followed by thin-layer chromatography. After completion of the reaction the reaction mixture was stirred for another hour, the ether was then distilled off under reduced pressure and the residue was dissolved in ethanol ( $100\text{ cm}^3$ ) and

*O,O*-dialkylthiophosphorylhydrazine (0.04 mol) was added with stirring. After addition the reaction mixture was stirred for 2 h at room temperature. The course of the reaction was followed by thin-layer chromatography. After completion of the reaction ethanol was distilled off under reduced pressure and the distilled residue was purified by column chromatography.

After esterification of *O,O*-diethyl(*O*-ethyl, *O*-isopropyl)thiophosphorylhydrazono-2,3-dichloro-2-butenoic acid with methanol in the presence of sulfuric acid cyclic products (Scheme 2) (in  $\approx 20\%$  yields) were besides esters isolated by a column chromatography. The structure of these compounds was proved by spectral methods.



Scheme 2

For C<sub>8</sub>H<sub>11</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>3</sub>PS (X) ( $M_r = 317.10$ )  $w_i$ (calc.): 8.83% N, 10.11% S, 9.76% P, 22.36% Cl;  $w_i$ (found): 8.72% N, 10.24% S, 9.64% P, 22.24% Cl. M.p. = 67–68°C. IR spectrum,  $\tilde{\nu}/\text{cm}^{-1}$ : 1684, 666. UV spectrum,  $\lambda/\text{nm}$  ( $\log(\epsilon/(\text{m}^2 \text{mol}^{-1}))$ ): 217 (2.17), 257 (1.56), 302 (1.64). <sup>1</sup>H NMR spectrum,  $\delta/\text{ppm}$ : 1.33 (m, 9H, CH<sub>3</sub>CH<sub>2</sub>), 4.40 (q, 4H, CH<sub>3</sub>CH<sub>2</sub>), 7.75 (s, 1H, =CH). Mass spectrum:  $M_r^{+ \cdot} = 316$ .

For C<sub>9</sub>H<sub>13</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>3</sub>PS (XI) ( $M_r = 331.12$ )  $w_i$ (calc.): 8.47% N, 9.68% S, 9.36% P, 21.42% Cl;  $w_i$ (found): 8.29% N, 9.88% S, 9.46% P, 21.85% Cl. M.p. = 64–66°C. IR spectrum,  $\tilde{\nu}/\text{cm}^{-1}$ : 1697, 656. UV spectrum,  $\lambda/\text{nm}$  ( $\log(\epsilon/(\text{m}^2 \text{mol}^{-1}))$ ): 212 (2.11), 302 (1.69). <sup>1</sup>H NMR spectrum,  $\delta/\text{ppm}$ : 1.35 (m, 9H), 4.72 (m, 3H), 7.73 (s, 1H, =CH). Mass spectrum:  $M_r^{+ \cdot} = 330$ .

Thin-layer chromatography was carried out on the Silufol R foils (Lachema, Brno) in the system benzene—acetone (volume ratio = 9 : 1). The detection was carried out with 0.5% petroleum ether solution of 2,6-dibromo-4-chloroimidoquinone at 120°C. Column chromatography was carried out on Silica gel 90—150  $\mu\text{m}$  (Lachema, Brno) activated at 140°C using benzene with an addition of acetone from 0 to 2%. The course of the separation was followed by thin-layer chromatography.

Infrared spectra of the prepared compounds were recorded with a Specord IR 71 (Zeiss, Jena) instrument in chloroform, tetrachloromethane, and acetonitrile ( $c \approx 0.002$ — $0.02 \text{ mol dm}^{-3}$ ). The wavenumber calibration was carried out on the spectrum of the polystyrene foil. Ultraviolet spectra were recorded with a Unicam SP 8000 in methanol

( $c = 2 \times 10^{-5}$ — $5 \times 10^{-5}$  mol dm $^{-3}$ ).  $^1\text{H}$  NMR spectra were recorded with a Tesla BS 487 C (80 MHz) in  $\text{C}^2\text{HCl}_3$  and  $(\text{C}^2\text{H}_5)_2\text{SO}$ .

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