

THE SYNTHESIS, SPECTRAL PROPERTIES AND PESTICIDAL ACTIVITY OF O-(1-BENZYL, CYCLOHEXYL, METHYL-5-ETHOXY, METHOXY, METHYLTHIO-6-OXO-1H-PYRIDAZIN-4-YL) ESTERS OF PHOSPHORIC, THIOPHOSPHORIC AND THIOPHOSPHONIC ACIDS

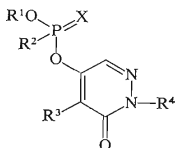
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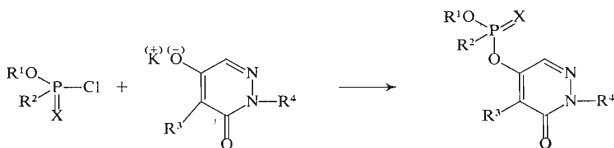
The synthesis of O-(5-ethoxy-1-methyl-6-oxo-1H-pyridazin-4-yl), O-(5-methoxy-1-benzyl-6-oxo-1H-pyridazin-4-yl), O-(5-methylthio-1-methyl-6-oxo-1H-pyridazin-4-yl) and O-(5-methoxy-1-cyclohexyl-6-oxo-1H-pyridazin-4-yl) esters of phosphoric, thiophosphoric and thiophosphonic acids is described. The IR and UV spectra of the synthesized compounds were measured and interpreted and their contact and systemic insecticidal, acaricidal and ovicidal activity was determined. Several of the compounds tested displayed high activity.

In continuation of our studies concerning the synthesis and pesticidal activity of pyridazin-4-yl-esters of organophosphoric acids we concentrated on the synthesis, studies of the spectral data, and the determination of contact and systemic insecticidal, acaricidal and ovicidal activity of pyridazin-4-yl esters of phosphoric, thiophosphoric and thiophosphonic acids of formula I:



For this study such groups of substituents on phosphorus were selected which proved most effective in earlier studies concerning pesticidal activity: diethylphosphoryl-, O,O-dimethylthiophosphoryl-, O-methyl-O-ethylthiophosphoryl-, O,O-diethylthiophosphoryl-, O-ethyl-O-isopropylthiophosphoryl-, O-methyl-N-isopropylamidothiophosphoryl- and O-ethyl-ethylthiophosphonyl. On the other hand such substituents were selected for the pyridazine ring which were expected to be very interesting from the point of view of pesticidal activity.

The synthesis of compounds was carried out using the reaction of the chlorophosphoric, chlorothiophosphoric, or chlorothiophosphonic acid esters with the potassium salt of 1,5-disubstituted 6-oxo-1*H*-pyridazin-4-ol in acetonitrile:



SCHEME 1

The esters of chlorophosphoric acid reacted more rapidly, but the products *II*, *IX*, *XVI* and *XXIII* thus obtained were less stable at room temperature than the corresponding thiophosphates. The stability of thiophosphates was dependent on the substituents R^1 and R^2 and it increased directly with the size of the alkyl. The purity

No	R^1	R^2	X	R^3	R^4
<i>I</i>	CH ₃	CH ₃ O	S	C ₂ H ₅ O	CH ₃
<i>II</i>	C ₂ H ₅	C ₂ H ₅ O	O	C ₂ H ₅ O	CH ₃
<i>III</i>	CH ₃	C ₂ H ₅ O	S	C ₂ H ₅ O	CH ₃
<i>IV</i>	C ₂ H ₅	C ₂ H ₅ O	S	C ₂ H ₅ O	CH ₃
<i>V</i>	C ₂ H ₅	(CH ₃) ₂ CHO	S	C ₂ H ₅ O	CH ₃
<i>VI</i>	C ₂ H ₅	C ₂ H ₅	S	C ₂ H ₅ O	CH ₃
<i>VII</i>	CH ₃	(CH ₃) ₂ CHNH	S	C ₂ H ₅ O	CH ₃
<i>VIII</i>	CH ₃	CH ₃ O	S	CH ₃ S	CH ₃
<i>IX</i>	C ₂ H ₅	C ₂ H ₅ O	O	CH ₃ S	CH ₃
<i>X</i>	C ₂ H ₅	C ₂ H ₅ O	S	CH ₃ S	CH ₃
<i>XI</i>	CH ₃	C ₂ H ₅ O	S	CH ₃ S	CH ₃
<i>XII</i>	C ₂ H ₅	(CH ₃) ₂ CHO	S	CH ₃ S	CH ₃
<i>XIII</i>	C ₂ H ₅	C ₂ H ₅	S	CH ₃ S	CH ₃
<i>XIV</i>	CH ₃	(CH ₃) ₂ CHNH	S	CH ₃ O	CH ₃
<i>XV</i>	CH ₃	CH ₃ O	S	CH ₃ O	C ₆ H ₁₁
<i>XVI</i>	C ₂ H ₅	C ₂ H ₅ O	O	CH ₃ O	C ₆ H ₁₁
<i>XVII</i>	CH ₃	C ₂ H ₅ O	S	CH ₃ O	C ₆ H ₁₁
<i>XVIII</i>	C ₂ H ₅	C ₂ H ₅ O	S	CH ₃ O	C ₆ H ₁₁
<i>XIX</i>	C ₂ H ₅	(CH ₃) ₂ CHO	S	CH ₃ O	C ₆ H ₁₁
<i>XX</i>	C ₂ H ₅	C ₂ H ₅	S	CH ₃ O	C ₆ H ₁₁
<i>XXI</i>	CH ₃	(CH ₃) ₂ CHNH	S	CH ₃ O	C ₆ H ₁₁
<i>XXII</i>	CH ₃	CH ₃ O	S	CH ₃ O	CH ₂ C ₆ H ₅
<i>XXIII</i>	C ₂ H ₅	C ₂ H ₅ O	O	CH ₃ O	CH ₂ C ₆ H ₅
<i>XXIV</i>	C ₂ H ₅	C ₂ H ₅ O	S	CH ₃ O	CH ₂ C ₆ H ₅
<i>XXV</i>	CH ₃	C ₂ H ₅ O	S	CH ₃ O	CH ₂ C ₆ H ₅
<i>XXVI</i>	C ₂ H ₅	(CH ₃) ₂ CHO	S	CH ₃ O	CH ₂ C ₆ H ₅
<i>XXVII</i>	C ₂ H ₅	C ₂ H ₅	S	CH ₃ O	CH ₂ C ₆ H ₅
<i>XXVIII</i>	CH ₃	(CH ₃) ₂ CHNH	S	CH ₃ O	CH ₂ C ₆ H ₅

TABLE I
Compounds Prepared

Compound	Composition (M.w.)	Calculated/Found		n_D^{20} (yield, %)
		% P	% S	
<i>I</i>	C ₉ H ₁₅ N ₂ O ₅ PS (294.3)	10.53 10.50	10.90 11.16	1.5311 (68)
<i>II</i>	C ₁₁ H ₁₉ N ₂ O ₆ P (306.2)	10.11 9.82	—	1.4869 (91)
<i>III</i>	C ₁₀ H ₁₇ N ₂ O ₅ PS (308.3)	10.05 10.03	10.40 10.62	1.5249 (84)
<i>IV</i>	C ₁₁ H ₁₉ N ₂ O ₅ PS (322.3)	9.61 9.98	9.95 10.15	1.5183 (87)
<i>V</i>	C ₁₂ H ₂₁ N ₂ O ₅ PS (336.4)	9.21 9.13	9.53 9.71	1.5120 (91)
<i>VI</i>	C ₁₁ H ₁₉ N ₂ O ₄ PS (306.3)	10.11 10.22	10.47 10.60	1.5411 (79)
<i>VII</i>	C ₁₁ H ₂₀ N ₃ O ₄ PS (321.3)	9.69 9.84	9.98 10.05	1.5371 (78)
<i>VIII</i>	C ₈ H ₁₃ N ₂ O ₄ PS ₂ (296.3)	10.45 10.38	21.64 21.82	1.5592 (67)
<i>IX</i>	C ₁₀ H ₁₇ N ₂ O ₅ PS (308.4)	10.05 9.72	10.40 10.22	1.5170 (72)
<i>X</i>	C ₁₀ H ₁₇ N ₂ O ₄ PS ₂ (324.3)	9.55 9.36	19.77 19.55	1.5540 (84)
<i>XI</i>	C ₉ H ₁₅ N ₂ O ₄ PS ₂ (310.3)	9.98 10.11	20.66 20.88	1.5634 (88)
<i>XII</i>	C ₁₁ H ₁₉ N ₂ O ₄ PS ₂ (338.4)	9.15 8.93	18.95 18.61	1.5498 (77)
<i>XIII</i>	C ₁₀ H ₁₇ N ₂ O ₃ PS ₂ (308.3)	10.05 9.91	20.80 20.28	1.5815 (89)
<i>XIV</i>	C ₁₀ H ₁₈ N ₃ O ₃ PS ₂ (323.3)	9.58 9.32	19.83 20.04	1.5866 (80)
<i>XV</i>	C ₁₃ H ₂₁ N ₂ O ₅ PS (348.3)	8.89 9.67	9.20 9.45	1.5399 (86)
<i>XVI</i>	C ₁₅ H ₂₅ N ₂ O ₆ P (360.3)	8.59 8.51	—	1.5055 (78)
<i>XVII</i>	C ₁₄ H ₂₃ N ₂ O ₅ PS (362.4)	8.55 8.44	8.85 9.02	1.5342 (85)

TABLE I
 (Continued)

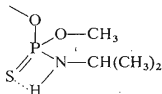
Compound	Composition (M.w.)	Calculated/Found		n_D^{20} (yield, %)
		%P	%S	
XVIII	C ₁₅ H ₂₅ N ₂ O ₅ PS (376.4)	8.23	8.52	1.5280
		8.18	8.47	(96)
XIX	C ₁₆ H ₂₇ N ₂ O ₅ PS (390.5)	7.93	8.21	1.5227
		7.94	8.40	(91)
XX	C ₁₅ H ₂₅ N ₂ O ₄ PS (360.4)	8.59	8.90	1.5490
		8.49	8.63	(69)
XXI	C ₁₅ H ₂₆ N ₃ O ₄ PS (375.4)	8.25	8.54	^a
		8.34	8.70	(64)
XXII	C ₁₄ H ₁₇ N ₂ O ₅ PS (356.3)	8.69	9.00	1.5709
		8.66	8.78	(58)
XXIII	C ₁₆ H ₂₁ N ₂ O ₆ P (368.3)	8.41	—	1.5325
		8.50		(64)
XXIV	C ₁₆ H ₂₁ N ₂ O ₅ PS (384.4)	8.06	8.34	1.5516
		8.12	8.52	(72)
XXV	C ₁₅ H ₁₉ N ₂ O ₅ PS (370.3)	8.36	8.66	1.5672
		8.40	8.88	(73)
XXVI	C ₁₇ H ₂₃ N ₂ O ₅ PS (398.4)	7.77	8.05	1.5484
		7.91	8.19	(84)
XXVII	C ₁₆ H ₂₁ N ₂ O ₄ PS (368.4)	8.41	8.70	1.5728
		8.35	8.90	(71)
XXVIII	C ₁₆ H ₂₂ N ₃ O ₄ PS (383.4)	8.08	8.36	1.5836
		7.92	8.48	(89)

^a M.p. 72–73°C.

of the phosphates prepared was very high; however, some thiophosphates had to be purified by column chromatography. The purity of the substances was followed by thin-layer chromatography (Table I).

In the IR spectra of the synthesized compounds a very intensive band of the $\nu(\text{C}=\text{O})$ stretching vibration is observed at 1648–1658 cm^{-1} , then a medium strong band $\nu(\text{C}=\text{N})$ in compounds I–VII, XV–XXVIII at 1618–1620 cm^{-1} , while in compounds VIII–XIV it was at 1578–1582 cm^{-1} , further a weak band of $\nu(\text{C}=\text{C})$ in compounds I–VII, XV–XVIII at 1531–1540 cm^{-1} or in compounds VIII–XIV at 1602–1609 cm^{-1} . The moderately intensive band at 1370–1388 is

due to the bending vibration $\delta(=\text{CH}-)$. The stretching vibration $\nu(\text{C}-\text{N})$ at 1260 to 1279 is of medium intensity. In compounds containing the $\text{P}=\text{S}$ bond the first stretching vibration band $\nu(\text{P}=\text{S})$ is at 668–675 cm^{-1} for compounds VIII–XIV while for other compounds it is at 660–667 cm^{-1} . The second band of compounds I–XXI is at 685–720 cm^{-1} , while it is absent in the case of compounds XXII to XXVII. For compounds VIII–XIV the stretching vibration band of medium intensity $\nu(\text{CH}_3-\text{S}-\text{C})$, at 643–650 cm^{-1} is characteristic. In compounds II, IX, XVI and XXIII the intensive band of the $\nu(\text{P}=\text{O})$ stretching vibration is at 1280–1300 cm^{-1} . For compounds VII, XIV, XXI and XXVIII the stretching vibration band $\nu(\text{N}-\text{H})$ occurring at 3408–3412 cm^{-1} is characteristic, while the second band at 3262 to 3280 cm^{-1} can be assigned to the bond formed by the amide group hydrogen and the sulphur atom bound to phosphorus (Table II).



In the ultraviolet spectra of the synthesized compounds two to three maxima are present. The first maximum is in all cases at 211–215 nm, in the case of compounds VIII–XIV the second maximum is at 237–238 nm and the third at 320–321 nm. In other compounds only the second maximum is present, at 285.5–290 nm. The bands at the shortest wave-lengths belong to $\pi \rightarrow \pi^*$ transitions, while the bands at the longest wave-lengths belong to $n \rightarrow \pi^*$ transitions (Table II).

During the testing of the insecticidal activity none of the substances was so active in the first screening as to warrant a further more accurate testing. In the test for contact insecticidal activity on *Musca domestica* the substances studied were very well active, with a few exceptions (V, IX–XII, XV, XXII and XXV). More than a half were more active than the standard malathion used, while substances I, VI and IX were about as active as phenitrothion; in the test on *Calandra granaria* generally less substances were active. Thus, in comparison with malathion only compound IX was more active, while in the test on *Aphis fabae* the highest activity could be measured. All the substances were submitted to more accurate tests. More active than both standards used (malathion and phenitrothion) were compounds III, V, VI, VII and XII, while substances IV, XI, XIV and XXII were about equally active. For the test with *M. domestica* carried out with respect to time 12 substances were selected for more accurate tests. All but two of them were more active than malathion.

TABLE II
Spectral Data of the Synthesized Compounds

Com- pound	IR Spectra, cm^{-1}					
	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	$\delta(=\text{CH}-)$	$\nu(\text{C}-\text{N})$	$\nu(\text{P}=\text{S})$
<i>I</i>	1 651	1 619	1 534	1 380	1 261	662 686
<i>II</i>	1 653	1 620	1 533	1 380	1 263	—
<i>III</i>	1 655	1 618	1 535	1 380	1260	663 687
<i>IV</i>	1 654	1 619	1 535	1 389	1 261	661 686
<i>V</i>	1 656	1 619	1 536	1 385	1 260	662 686
<i>VI</i>	1 655	1 620	1 534	1 381	1 260	662 685
<i>VII</i>	1 646	1 615	1 531	1 380	1 262	661 684
<i>VIII</i>	1 651	1 582	1 605	1 375	1 267	674 705
<i>IX</i>	1 652	1 581	1 606	1 374	1 268	—
<i>X</i>	1 650	1 581	1 605	1 373	1 267	675 704
<i>XI</i>	1 650	1 581	1 606	1 373	1 265	673 706
<i>XII</i>	1 651	1 582	1 609	1 374	1 374	672 701
<i>XIII</i>	1 652	1 578	1 606	1 378	1 265	670 703
<i>XIV</i>	1 648	1 578	1 602	1 376	1 263	668 702
<i>XV</i>	1 650	1 620	1 540	1 373	1 278	665 710
<i>XVI</i>	1 648	1 620	1 537	1 370	1 279	—
<i>XVII</i>	1 650	1 620	1 540	1 371	1 273	663 706
<i>XVIII</i>	1 650	1 619	1 538	1 370	1 276	663 708
<i>XIX</i>	1 648	1 620	1 540	1 374	1 278	662 707

TABLE II
 (Continued)

Various		UV Spectra	λ_{max} nm	(log ϵ)
		212.5 (4.31)	285.5 (3.72)	
$\nu(\text{P}=\text{O})$	1 280	212.0 (4.31) 212.0 (4.28)	286.0 (3.73) 287.0 (3.70)	
		212.5 (4.28)	286.0 (3.70)	
		211.5 (4.35)	287.0 (3.73)	
		213.0 (4.32)	288.0 (3.68)	
$\nu(\text{NH})$	3 412 3 268	212.5 (4.43)	287.5 (3.66)	
$\nu(\text{CH}_3-\text{S}-\text{C})$	648	211.0 (4.22)	237.5 (3.70)	320.0 (3.86)
$\nu(\text{CH}_3-\text{S}-\text{C})$	647	212.0 (4.18)	238.0 (3.66)	321.0 (3.81)
$\nu(\text{P}=\text{O})$	1 289			
$\nu(\text{CH}_3-\text{S}-\text{C})$	647	211.5 (4.20)	238.0 (3.72)	320.0 (3.82)
$\nu(\text{CH}_3-\text{S}-\text{C})$	650	211.0 (4.13)	237.0 (3.75)	319.0 (3.84)
$\nu(\text{CH}_3-\text{S}-\text{C})$	648	210.0 (4.19)	237.0 (3.76)	320.0 (3.80)
$\nu(\text{CH}_3-\text{S}-\text{C})$	645	212.0 (4.20)	238.0 (3.72)	320.0 (3.79)
$\nu(\text{CH}_3-\text{S}-\text{C})$	643	212.5 (4.19)	237.0 (3.74)	321.0 (3.80)
$\nu(\text{NH})$	3 410 3 270			
		214.0 (4.32)	288.0 (3.74)	
$(\text{P}=\text{O})$	1 292	213.0 (4.32) 214.0 (4.31)	289.0 (3.74) 288.0 (3.73)	
		213.5 (4.27)	288.5 (3.68)	
		215.0 (4.24)	283.0 (3.72)	

TABLE II
(Continued)

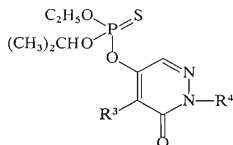
Com- pound	IR Spectra, cm^{-1}					
	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	$\delta(\text{=CH-})$	$\nu(\text{C-N})$	$\nu(\text{P}=\text{S})$
XX	1 650	1 618	1 535	1 372	1 277	660 697
XXI	1 658	1 612	1 536	1 387	1 272	660 700
XXII	1 656	1 620	1 532	1 387	1 278	661
XXIII	1 656	1 620	1 532	1 387	1 278	—
XXIV	1 858	1 618	1 534	1 386	1 272	667
XXV	1 657	1 619	1 532	1 386	1 271	665
XXVI	1 658	1 620	1 534	1 388	1 271	664
XXVII	1 658	1 618	1 533	1 387	1 270	667
XXVIII	1 652	1 612	1 538	1 388	1 272	661 694

Compounds I-IV, VI, XVI-XVIII and XXIII were also highly active which exceeded the activity of malathion 2-3 times. Except for substance VII a very good activity was also found in the test on acaricidal activity tested on the females of *Tetranychus urticae*. Remarkably high activity was also found in compound XXVI, i.e. a double with respect to the standard carbophenothion, while the activity of compounds V, XX and XXIV is also remarkable. In comparison with Acrex as standard 18 compounds were more active, those most active almost by two orders of magnitude. In the test on the eggs of *T. urticae* a remarkable activity was found for compounds XXIV and XXVI, which were about equally active as the standards used.

From the total estimation of the insecticidal, acaricidal and ovicidal activity it follows that the best results were obtained in the tests on contact insecticidal and acaricidal activity. It is impossible to decide unambiguously which substituent ($\text{R}^1 - \text{R}^4$) affects the pesticidal activity and how, even though it seems that in contact insecticidal activity on *A. fabae*, acaricidal and ovicidal activity on *T. urticae*, O-ethyl-O-isopropylthiophosphoryl derivatives of the following formula were the most active:

TABLE II
(Continued)

Various		UV Spectra	λ_{\max} nm	(log ϵ)
		215.0 (4.38)	288.5 (3.77)	
$\nu(\text{NH})$	3 411 3 262	213.5 (4.30)	287.5 (3.72)	
$\nu(\text{P}=\text{O})$	1 300	213.0 (4.37) 212.5 (4.40) 212.5 (4.39) 213.0 (4.38) 212.0 (4.34) 214.0 (4.43)	288.0 (3.80) 287.0 (3.74) 287.5 (3.72) 288.0 (3.80) 288.5 (3.67) 288.5 (3.74)	
$\nu(\text{NH})$	3 408 3 280	213.0 (4.48)	287.0 (3.62)	



EXPERIMENTAL

Methods

The IR spectra ($400-2200\text{ cm}^{-1}$) were measured on a Zeiss IR Specord 75 instrument. The wave-number calibration was carried out using the spectrum of a polystyrene foil. The spectra were measured in CCl_4 in a 0.1 mm cell (concentration 10^{-2}). The UV spectra were measured on a Unicam SP 8000 spectrophotometer in methanol. The calibration was carried out with a Holmi filter. The concentration of the solutions measured was $2 \cdot 10^{-5}$ – $5.5 \cdot 10^{-5}\text{ M}$, in 1 cm cells. Thin-layer chromatography was carried out on aluminum foils with a layer of silica gel (Silufol "R" without indicator from Lachema, Brno) in benzene-acetone (9 : 1 → 8 : 2). Detection with 0.5% 2,6-dibromoquinone-4-chloroimide in light petroleum, at 120°C . Column chromatography

graphy was carried out on Silica gel L 100/160 mesh for column chromatography (Lachema, Brno). Before use the silica gel was activated at 140°C for 6 h. Toluene with an addition of acetone (from 0 to 5%, depending on the character of the impurities) was used for elution. The course of the separation was followed by means of TLC.

TABLE III
Insecticidal, Acaricidal and Ovicidal Activity of the Synthesized Compounds

Compound	LC ₅₀ , %					Time effect LT ₅₀ , min <i>M. domestica</i>
	<i>M. domestica</i>	<i>C. granaria</i>	<i>A. fabae</i>	<i>T. urticae</i>		
				females	eggs	
I	0.0050	>0.1	0.0067	0.00012	0.016	6.5
II	0.0091	>0.1	0.0042	0.00027	0.022	7.0
III	0.0098	>0.1	0.00020	0.00020	0.038	7.0
IV	0.0102	0.051	0.0012	0.00017	0.017	5.0
V	0.10	0.0104	0.000123	0.0000817	0.012	—
VI	0.0046	>0.1	0.00078	0.00028	0.042	7.5
VII	0.0102	>0.1	0.00098	>0.1	>0.5	12.0
VIII	0.45	>0.1	0.0031	0.00048	>0.5	—
IX	0.0062	0.0021	0.0032	0.0011	>0.5	—
X	>0.5	>0.1	0.0019	0.00092	0.11	—
XI	>0.5	>0.1	0.0011	0.00019	0.10	—
XII	>0.5	>0.1	0.000958	0.00037	>0.5	—
XIII	0.0081	0.049	0.0030	0.00057	0.48	—
XIV	0.048	0.061	0.0019	0.00108	>0.5	—
XV	>0.5	0.092	0.0030	0.0041	0.10	—
XVI	0.029	0.10	0.010	0.00074	>0.5	6.5
XVII	0.023	0.011	0.011	0.00021	0.014	8.5
XVIII	0.016	0.048	0.0057	0.00017	0.051	7.5
XIX	>0.5	>0.1	0.020	0.000202	0.1	—
XX	0.020	>0.1	0.018	0.000070	>0.5	18.0
XXI	0.0236	>0.1	0.088	0.00140	0.44	20.0
XXII	>0.5	>0.1	0.0020	0.082	0.11	—
XXIII	0.0102	>0.1	0.0076	0.041	0.016	4.0
XXIV	0.35	0.085	0.0042	0.000075	0.0043	—
XXV	>0.5	>0.1	0.0053	0.000103	0.000103	—
XXVI	0.088	0.079	0.070	0.0000175	0.0031	—
XXVII	0.10	>0.1	0.016	0.000103	0.0070	—
XXVIII	0.12	>0.1	0.0022	0.055	>0.5	—
Malathion	0.036	0.0076	0.0011	0.00241	—	13.0
Phenitrothion	0.0040	0.00069	0.0010	0.015	—	—
Carbophenothion	>0.1	>0.1	0.00064	0.000037	0.0026	—
Acrex	—	—	—	0.0023	0.0043	—

Synthesis of Substances

5-Ethoxy-1-methyl-6-oxo-1*H*-pyridazin-4-ol with m.p. 140–142°C, 5-methylthio-1-methyl-6-oxo-1*H*-pyridazin-4-ol with m.p. 188–190°C, 1-cyclohexyl-5-methoxy-6-oxo-1*H*-pyridazin-4-ol with m.p. 163–165°C, and 1-benzyl-5-methoxy-6-oxo-1*H*-pyridazin-4-ol with m.p. 147–149°C were prepared according to ref.¹.

Compounds II, IX, XVI and XXIII: Diethyl ester of chlorophosphoric acid (0.05 mol) was added to 0.055 mol of the potassium salt of 1,5-disubstituted 6-oxo-1*H*-pyridazin-4-ol in 100 ml acetonitrile at 10°C and under stirring. The stirring was continued at 40°C for 4 h. After cooling the separated salt was filtered off and acetonitrile was evaporated from the filtrate under reduced pressure. The residue was dissolved in 100 ml of toluene, washed with water, 5% sodium carbonate solution, and again with water. After drying the solution toluene was distilled off in a vacuum.

Compounds I, III–VIII, X–XV, XVII–XXII, XXIV–XXVIII: Ester of chlorothiophosphoric acid or chlorothiophosphonic acid (0.055 mol) was added to 0.06 mol of the potassium salt of 1,5-disubstituted 6-oxo-1*H*-pyridazin-4-ol in 100 ml of acetonitrile and the reaction mixture was stirred and refluxed for 2 to 4 h. After cooling 100 ml of toluene were added, the solution was washed with water, 5% sodium carbonate solution and water. After drying over sodium sulfate toluene was distilled off under reduced pressure. The residue was purified by column chromatography as necessary.

Pesticidal Activity

Contact insecticidal activity was tested on domestic fly (*Musca domestica* L.), *Calandra granaria* L., and *Aphis fabae* Scop., using malathion (O,O-dimethyl-S-1,2-(diethoxycarbonyl)ethyl dithiophosphate) and phenitrothion (O,O-dimethyl-O-(3-methyl-4-nitrophenyl) thiophosphate) as standards. Systemic insecticidal activity was tested on *Macrosiphonia sanborni* L. (the host plant was *Chrysanthemum indicum*) using thiometon (O,O-diethyl-S-(2-ethylthioethyl) dithiophosphate) as standard. The acaricidal activity was assayed on spiders (*Tetranychus urticae* Koch), the ovicidal activity on the eggs of spiders (*T. urticae*), using carbophenothion (O,O-diethyl-S-(4-chlorophenylthiomethyl) dithiophosphate) and Acrex (2-sec-butyl-4,6-dinitrophenyl isopropyl carbonate) as standard. The methods for the determination of the insecticidal, acaricidal and ovicidal activity have already been published^{2,3}. The insecticidal effect in time was determined on *M. domestica* using malathion as standard, according to a method already described⁴. The results obtained are summarized in Table III.¹

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