Synthesis, spectral properties, and pesticidal activity of thiophosphorylsemicarbazides

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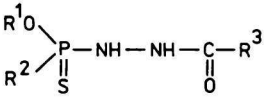
A synthesis of novel thiophosphorylsemicarbazides prepared by the reaction of thiophosphorylhydrazine with isocyanates is described. Infrared spectra of all compounds prepared were measured and evaluated. All compounds were tested on contact and systemic insecticidal, acaricidal, ovicidal, fungicidal, and herbicidal activity. None of the prepared compounds showed in tests required pesticidal activity so as to be included into advanced stage of testing.

Описан синтез новых тиофосфорилсемикарбазидов путем реакции тиофосфорилгидразина с изоцианатами. Измерены и изучены ИК-спектры всех полученных соединений. У всех соединений были исследованы их контактная и системная инсектицидная, акарицидная, овицидная, фунгицидная и гербицидная активности. Ни одно из полученных веществ не проявило в тестах пестицидную активность, необходимую для того, чтобы это соединение было подвергнуто дальнейшему тщательному тестированию.

With the aim to find novel pesticidally active compounds of the group of organophosphoric compounds, we prepared compounds of the general formula



by the reaction of the thiophosphorylhydrazine with appropriate isocyanate and dimethylcarbamoyl chloride, respectively. Thiophosphorylhydrazines were prepared after [1] by the reaction of thiophosphoryl chloride with hydrazine hydrate. The prepared thiophosphorylsemicarbazides are summarized in Table 1. In the

Table 1

Characterization of the compounds prepared

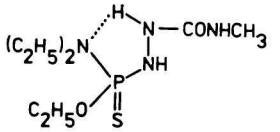
Compound	R^1	R^2	R^3	Formula	M_r	w_i(calc.)/% / w_i(found)/%					Yield	M.p.
						C	H	N	P	S	%	°C
I	CH_3	C_2H_5O	NH—C_4H_9	$C_8H_{20}N_3O_3PS$	269.11	35.69	8.92	15.60	11.50	11.90	52.0	40—41
						35.76	8.99	15.87	11.28	11.59		
II	C_2H_5	$(C_2H_5)_2N$	NH—CH_3	$C_8H_{21}N_4O_2PS$	268.13	35.83	7.83	20.89	11.55	11.20	79.5	35—37
						35.95	7.90	21.05	11.82	11.41		
III	CH_3	C_2H_5O	NH—CH_3	$C_5H_{14}N_3O_3PS$	227.10	26.44	6.18	18.49	13.64	14.11	86.3	112—113
						26.50	6.48	18.08	13.85	14.15		
IV	C_2H_5	C_3H_7O	NH—CH_3	$C_7H_{18}N_3O_3PS$	255.12	32.95	7.05	16.46	12.13	12.56	83.7	67—70
						32.22	7.22	16.73	12.26	12.35		
V	C_2H_5	˙-C_3H_7O	NH—CH_3	$C_7H_{18}N_3O_3PS$	255.12	32.95	7.05	16.46	12.13	12.56	95.6	77—78
						32.71	7.29	16.82	12.35	12.48		
VI	C_2H_5	i-C_3H_7NH	NH—CH_3	$C_7H_{19}N_4O_2PS$	254.12	33.08	7.48	22.04	12.18	12.62	93.6	118—119
						33.51	7.90	22.48	11.91	12.99		
VII	C_2H_5	˙-C_3H_7O	$N(CH_3)_2$	$C_8H_{20}N_3O_3PS$	269.12	35.70	7.43	15.60	11.50	11.91	66.5	79—80
						35.64	7.22	15.97	11.27	11.95		
VIII	CH_2O—C	$(CH_3)_2$—CH_2O	NH—CH_3	$C_7H_{16}N_3O_3PS$	253.12	33.21	6.32	16.59	12.23	12.66	97.0	163—165
						33.34	6.77	16.77	11.88	12.56		
IX	CH_3	C_2H_5O	NH—C_6H_5	$C_{10}H_{16}N_3O_3PS$	289.14	41.53	5.54	14.52	10.70	11.08	90.0	85—86
						41.50	6.02	14.98	10.43	10.94		
X	CH_3	C_2H_5O	NH—4-F—C_6H_4	$C_{10}H_{15}FN_3O_3PS$	307.14	39.10	4.88	13.67	10.08	10.43	81.4	112—114
						39.28	4.51	13.43	9.87	9.95		

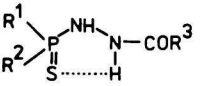
Table 1 (Continued)

Compound	R^1	R^2	R^3	Formula	M_r	w_i(calc.)/% / w_i(found)/%					Yield	M.p.
						C	H	N	P	S	%	°C
XI	CH_3	C_2H_5O	NH—3-Cl—4-CH_3—C_6H_3—	$C_{11}H_{17}ClN_3O_3PS$	337.64	39.12 39.79	5.03 5.25	12.44 12.67	9.17 9.15	9.49 8.98	82.9	125—126
XII	CH_3	C_2H_5O	NH—4-CF_3—C_6H_4	$C_{11}H_{15}F_3N_3O_3PS$	357.15	36.98 36.90	4.20 4.43	11.76 11.95	8.65 8.74	8.95 8.87	75.6	89—91
XIII	CH_3	C_2H_5O	NH—C_6H_5*	$C_{10}H_{16}N_3O_2PS_2$	305.20	39.35 39.85	5.24 5.31	13.75 13.80	10.15 10.77	21.00 21.26	60.0	60—63
XIV	i-C_4H_9	i-C_4H_9O	NH—CH_3	$C_{10}H_{24}N_3O_3PS$	297.15	40.41 40.79	8.07 7.89	14.13 14.67	10.42 10.32	10.79 10.60	98.9	75—77
XV	i-C_4H_9	i-C_4H_9O	NH—3-Cl—C_6H_4	$C_{15}H_{25}ClN_3O_3PS$	393.65	45.76 46.13	6.35 6.70	10.67 11.10	7.86 7.27	8.14 8.79	94.48	95—96

* Instead of C=O is C=S.

infrared spectra all compounds excepting the compound *VII* showed four absorption bands ν(NH) in the region of 3120—3470 cm^{-1} (Table 2). Compound *VII* showed in the region of 3160—3360 cm^{-1} three absorption bands. The bands at the highest wavenumbers (3410—3470 cm^{-1}) can be assigned to the vibration of the free N—H bonds of the NHR (R^3) groups. This band is absent from the spectrum of compound *VII*. The bands in the region of 3358—3410 cm^{-1}can be assigned to the vibration of NH bonds of the P—NH group. The band at 3320 cm^{-1} in the spectrum of compound *II* can be ascribed to the vibration of the NH bond of the CONH group involved in hydrogen bonding with the nitrogen atom of the $(C_2H_5)_2N$ group. The band at 3330 cm^{-1} in the spectrum of compound *VI* can be assigned to the vibration of the NH bond of the iso-C_3H_7NH group.





II ν(NH...N) at $\tilde{\nu} = 3320$ cm^{-1} ν(NH...SP) at $\tilde{\nu} = 3240$—3295 cm^{-1}

The bands in the region of 3240—3295 cm^{-1} can be assigned to the vibration of the NH bonds of the NHCO group involved in the intramolecular hydrogen bonding with the sulfur atom of the P=S group [2]. In consequence of stronger hydrogen bond of the NH group with the nitrogen atom of the diethylamino group this band is not observed in the spectrum of compound *II*. The bands in the region of 3120—3165 cm^{-1} can be assigned to the vibration of the N—H bonds involved in hydrogen bonding with the C=O group. Very strong absorption bands ν(C=O) of the prepared compounds are observed in the region of 1685—1700 cm^{-1} characteristic of the absorption of carbonyl groups of the amides. The medium intensity bands in the region of 625—695 cm^{-1} can be assigned to the vibration of the P=S bonds the wavenumber of which is dependent on the P=S...H—N hydrogen bond and substituents attached to the phosphorus atom.

All compounds prepared were tested on pesticidal activity:

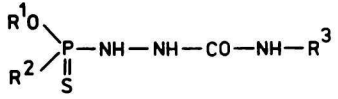
— in contact insecticidal activity against *M. domestica, S. granarius, A. fabae* none of the compounds reached in mass fractions examined (0.1 % and 0.5 %) the activity of the standards Fenitrothion (*O,O*-dimethyl *S*-(3-methyl-4-nitrophenyl)phosphorothioate) and Malathion (diethyl[(dimethoxyphosphinothioyl)-thio]butanedioate),

— in systemic insecticidal activity against *A. fabae* none of the compounds reached in the 0.5 % mass fraction the activity of the standard Thiometon (*O,O*-dimethyl *S*-(2-ethylthiomethyl)phosphorodithioate),

— in acaricidal and ovicidal activity against *T. urticae* none of the compounds reached in mass fractions (0.1 % and 0.5 %) the activity of the standard Car-

Table 2

Infrared spectral data ($\tilde{\nu}$/cm^{-1}) of the synthesized compounds



Compound	ν(NH—R)	ν(NH—P)	ν(NH...S=P)	ν(NH...O=C)	ν(C=O)	ν(P=S)
I	3455	3395	3250	3125	1690	655
II[a]	3470	3400	3260	3125	1700	665
III	3470	3390	3258	3125	1690	675
IV	3465	3380	3262	3127	1690	660
V	3460	3390	3260	3120	1700	655
VI[b]	3470	3415	3255	3140	1687	663
VII	—	3360	3295	3160	1690	665
VIII	3470	3390	3250	3145	1685	625
IX	3415	3370	3250	3148	1700	645
X	3415	3370	3251	3135	1700	650
XI	3415	3360	3250	3120	1700	660
XII	3415	3365	3240	3135	1700	665
XIII[c]	3410	3358	3245	3165	—	695
XIV	3470	3390	3255	3130	1690	690
XV	3415	3390	3250	3145	1700	690

a) A band at 3320 cm^{-1}, ν(NH) of the CONH...N(C_2H_5) group; *b*) band ν(NH) of the i-C_3H_7NH group at 3390 cm^{-1}; *c*) instead of C=O is C=S.

bophenthion (*O,O*-diethyl *S*-(4-chlorophenylthiomethyl)phosphorodithioate),

— in fungicidal activity using the *in vitro* method against *T. foetida, B. cinerea, F. avenaceum*, and *A. alternata* none of the compounds reached mass fractions (0.04 %) the activity of the standards Dithiocyanatomethan and Captan (3*a*,4,7,7*a*-tetrahydro-2-[(trichloromethyl)thio-1*H*-isoindole]-1,3(2*H*)-dione),

— in antipowdery mildew against *E. graminis* none of the compounds reached in mass fractions (0.04 %) the activity of the standard Trimorfamid (*N*-[2,2,2-trichloro-1-(4-morpholinyl)ethyl]formamide),

— in herbicidal activity none of the compounds in doses 5 kg ha^{-1} and 1 kg ha^{-1}, respectively, reached the activity of the used standards MCPA (dimethylammonium (4-chloro-2-methylphenoxy)acetate) and Pyramin (5-amino-4--chloro-2-phenyl-2*H*-pyridazin-3-one).

Experimental

IR spectra of the compounds prepared were recorded with a UR-20 instrument (Zeiss, Jena) in tetrachloromethane (the spectrum of compound *VI* in trichloromethane) (concentrations 0.01 mol dm^{-3}, cell thickness 1 mm).

Contact insecticidal activity was followed on *Musca domestica, Sitophylus granarius*, and *Aphis fabae* using Malathion and Fenitrothion as standards, systemic insecticidal activity on *Aphis fabae* using *Chrysanthemum indicum* as host plants and Thiometon as standard: acaricidal activity on females of *Tetranychus urticae* KOCH, and ovicidal activity on eggs of *T. urticae* using Carbophenthion as standard according to previously described methods [3, 4].

Herbicidal activity was followed by the preemergent (into the soil) and postemergent (to the leaf) application methods using testing objects: *Avena fatua, Echinochloa cruss-gallii, Panicum miliaceum, Fagopyrum vulgare*, and *Sinapis alba* after previously described methods [5]. Fungicidal activity was followed by the *in vitro* method on fungi: *Tilletia foetida, Botrytis cinerea, Fusarium avenaceum*, and *Alternaria alternata* and by the *in vivo* method on *Erysiphe graminis* (a host plant spring barley, sort Dunajský trh) according to the published methods [6].

1-(O,O-Dialkyl)thiophosphoryl-4-(alkyl or aryl)semicarbazides (I, III, IV, V, VIII—XV)

To 0.025 mol of *O,O*-dialkylthiophosphorylhydrazine in cyclohexane or toluene (80 cm^3) alkyl (or aryl) isocyanate (0.025 mol) was added. The reaction mixture was heated to 60 °C under stirring and stirring was continued for 2 h. After completion of the reaction cyclohexane or toluene was distilled off from the mixture and the residue was purified by crystallization from heptane, toluene or cyclohexane.

1-(O-Alkyl-N-alkylamido)thiophosphoryl-4-alkylsemicarbazides (II and VI)

To 0.045 mol of *O*-alkyl-*N*-alkylamidothiophosphorylhydrazine in heptane (80 cm^3) alkyl isocyanate (0.05 mol) was added. The reaction mixture was heated to 30 °C and stirred for 2 h, then heated to 80 °C for 15 min and cooled. The excluded crystalline compound was separated by filtration and washed with hexane.

1-(O-Isopropyl-O-ethyl)thiophosphoryl-4,4-dimethylsemicarbazide (VII)

To 0.07 mol of *O*-isopropyl-*O*-ethylthiophosphorylhydrazine in toluene (80 cm^3) dimethylcarbamoyl chloride (0.07 mol) and triethylamine (0.07 mol) were added. The reaction mixture was heated to 70 °C and stirred for 2 h. After completion of the reaction the reaction mixture was cooled, washed with water and from filtrate toluene was distilled off. The residue was purified by crystallization from cyclohexane.

References

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