Phosphorylated isothioureas. IV. Preparation and properties of *N*-phosphorylated and *N*-thiophosphorylated *N'*,*S*-substituted isothioureas

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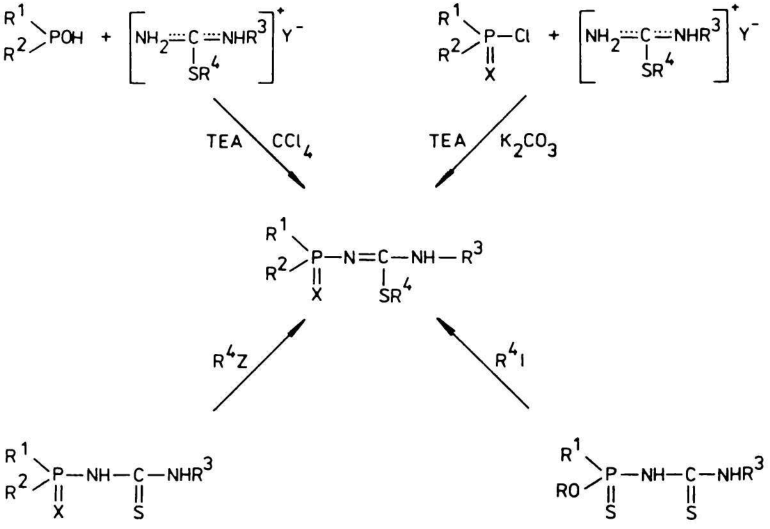
The synthesis and properties of *N*-[(R^1,R^2)-phosphoryl- and -thiophosphoryl]-*N'*-(R^3)-*S*-(R^4)-isothioureas are described. They were prepared by the reaction of *O*,*O*-dialkyl phosphorochloridates, *O*,*O*-dialkyl phosphorochloridothioates, and *O*,*S*-dialkyl phosphorochloridothioates with thiouronium salts in the presence of different agents binding hydrogen chloride as well as by the reaction of the appropriate dialkyl phosphites with thiouronium salts in the presence of triethylamine in carbon tetrachloride or by alkylation of *N*-(*O*,*O*-dialkylthiophosphoryl)-*N'*-(R^3)-thioureas with dimethyl sulfate, diazomethane, methyl iodide, and benzyl bromide. The i.r., u.v., and ^{1}H-n.m.r. spectra of the prepared compounds are interpreted. The results obtained with the prepared compounds at tests for pesticidal activity are discussed.

Описывается синтез и свойства *N*-[диалкил(тио)фосфорил]-*N'*-алкил(арил)-*S*-алкил(аралкил)изотиомочевин, полученных по реакции *O*,*O*-диалкилхлорфосфатов, *O*,*O*-диалкилхлортиофосфатов и *O*,*S*-диалкилхлортиофосфатов с солями тиоурония в присутствии различных реагентов, связывающих хлористый водород, и по реакции соответственных диалкилфосфитов с солями тиоурония в присутствии триэтиламина в четыреххлористом углероде или алкилированием *N*-(*O*,*O*-диалкилтиофосфорил-*N'*-алкил(арил)тиомочевин с диметилсульфатом, диазометаном, иодистым метилом и бензилбромидом. Расшифрованы ИК, УФ и ^{1}H-ЯМР спектры полученных соединений. Обсуждается испытание соединений на их пестицидное действие.

In previous works the synthesis, structures, and properties of *N*-(*O*,*O*-dialkylthiophosphoryl)-*S*-(R^4)-isothioureas [1], *N*-(*O*,*O*-dialkyl- and -diphenylphosphoryl)-*S*-(R^4)-isothioureas [2], and *N*-(*O*-alkyl-*N'*-alkylamidothiophosphoryl)-, *N*-(*O*-methyl-*N'*,*N'*-dimethylamidothiophosphoryl)-, *N*-(*O*-alkyl-*S*-alkylthiophosphoryl)-, and *N*-(*O*-alkyl-*P*-alkylthiophosphonyl)-*S*-alkyl substituted isothioureas [3] were described. *Bödeker* [4] prepared *N*-(diphenyl-



Scheme 1

thiophosphinyl)-*N'*-(*p*-methoxyphenyl)-*S*-methylisothiourea by the reaction of *N*-(diphenylthiophosphinyl)-*N'*-(*p*-methoxyphenyl)thiourea with diazomethane and on the basis of the ν(C=N) band attributed to this compound a structure with the −NH group on phosphorus.

The aim of the present work was to find out suitable methods for the preparation of the studied compounds, determine their physicochemical properties and, mainly, enlighten their structures with regard to the position of the C=N bond as well as examine their pesticidal properties.

The compounds were synthesized according to different pathways indicated in Scheme 1.

Experimental

O,*O*-Dimethyl phosphorochloridothioate [5], *O*,*O*-diethyl phosphorochloridothioate [5], and *O*-ethyl *O*-isopropyl phosphorochloridothioate [6] were prepared by known procedures from thiophosphoryl chloride and the appropriate alcohol. *O*-Isopropyl *S*-ethyl phosphorochloridothioate [7, 8] was prepared by the reaction of phosphorus trichloride with isopropyl alcohol which resulted in diisopropyl chlorophosphite and this was treated with ethylsulfenyl chloride. Diethyl phosphite [9], dipropyl phosphite [10], and dibutyl phosphite [11] were prepared by the reaction of phosphorus trichloride and the appropriate alcohol. Dialkyl phosphorochloridates were prepared by treatment of the appropriate dialkyl phosphites in carbon tetrachloride with freshly distilled sulfuryl chloride at 20—30°C

Table 1

Characterization of the synthesized compounds

Compound	R^1	R^2	R^3	R^4	X	Formula	*M*	Calculated/found			Yield, % Method of preparation	Reaction time, h *T*, °C	n_D^{20} M.p., °C Solvent	T.l.c. R_f
								% N	% P	% S				
I	CH_3O	CH_3O	$CH_2=CHCH_2$	$PhCH_2$	S	$C_{13}H_{19}N_2O_2PS_2$	330.38	8.48 8.27	9.38 9.59	19.41 19.80	84.4 *B*	7 81	1.5886	0.33^b 0.49^d 0.49^e
II	CH_3O	CH_3O	Ph	$PhCH_2$	S	$C_{16}H_{19}N_2O_2PS_2$	378.40	7.40 7.83	8.18 7.81	16.95 17.5	82.1 *A*	20 20	1.6362	0.42^b 0.50^d 0.62^e
III	CH_3S	iC_3H_7O	Ph	CH_3	O	$C_{12}H_{19}N_2O_2PS_2$	318.41	8.80 8.56	9.73 10.04	20.01 19.53	49 *F*	20 42	1.5958	0.66^a 0^b 0.26^c
IV	C_2H_5O	C_2H_5O	Ph	C_4H_9	O	$C_{15}H_{25}N_2O_3PS$	344.42	8.13 8.40	8.99 9.25	9.31 9.80	90.7 *A*	2 19	1.5480	0.85^a 0.04^b 0.88^c
V	C_2H_5O	C_2H_5O	$CH_2=CHCH_2$	$PhCH_2$	S	$C_{15}H_{23}N_2O_2PS_2$	358.47	7.83 7.49	8.64 8.43	17.9 17.4	82.1 *B*	10 81	1.5740	0.32^b 0.28^d 0.69^e
VI	C_2H_5O	C_2H_5O	iC_3H_7	CH_3	S	$C_9H_{21}N_2O_2PS_2$	284.42	9.84 9.8	10.90 10.84	22.47 22.30	80.4 *D* 89.1 *C*	14 56	1.5261	0.32^b 0.70^d 0.52^e
VII	C_2H_5O	C_2H_5O	Ph	$C_2H_5SCH_2CH_2$	O	$C_{15}H_{25}N_2O_3PS_2$	376.49	7.44 7.8	8.23 7.98	17.03 17.7	69.7 *A* 76.8 *G*	2.5 19	1.5345	0.61^a 0.03^b 0.46^c
VIII	C_2H_5O	C_2H_5O	$CH_2=CHCH_2$	$CH_2=CHCH_2$	O	$C_{11}H_{21}N_2O_3PS$	292.35	9.58 9.81	10.60 10.72	10.96 10.6	77.4 *G*	3 19	1.5060	0.73^a 0.01^b 0.91^c

Table 1 (Continued)

Compound	R^1	R^2	R^3	R^4	X	Formula	*M*	Calculated/found			Yield, % Method of preparation	Reaction time, h *T*, °C	n_D^{20} M.p., °C Solvent	T.l.c. R_f
								% N	% P	% S				
IX	C_2H_5O	C_2H_5O	Ph	CH_3	S	$C_{12}H_{19}N_2O_2PS_2$	318.41	8.80	9.73	20.01	95.9 *C*	3	1.5830	0.30^b
								8.57	10.04	20.5		25		0.23^d
														0.29^e
X	C_2H_5O	C_2H_5O	Ph	$PhCH_2$	S	$C_{18}H_{23}N_2O_2PS_2$	394.50	7.10	7.84	16.25	87.1 *E*	12	1.6070	0.56^b
								7.23	7.43	16.78	81 *A*	56		0.41^d
														0.77^e
XI	C_2H_5O	iC_3H_7O	$CH_2=CHCH_2$	$CH_2=CHCH_2$	S	$C_{12}H_{23}N_2O_2PS_2$	322.40	8.69	9.61	19.89	70.1 *A*	10	1.5320	0.32^b
								8.60	9.92	20.5		50		0.51^d
														0.42^e
XII	C_2H_5S	iC_3H_7O	$CH_2=CHCH_2$	$PhCH_2$	O	$C_{16}H_{25}N_2O_2PS_2$	372.50	7.52	8.30	17.27	73.1 *A*	10	1.5618	0.62^a
								7.49	8.54	17.40		21		0.03^b
														0.54^c
XIII	C_3H_7O	C_3H_7O	$CH_2=CHCH_2$	$CH_2=CHCH_2$	O	$C_{13}H_{25}N_2O_3PS$	320.40	8.74	9.67	10.01	78.7 *A*	2	1.5001	0.52^a
								8.97	9.54	10.33		50		0.01^b
														0.62^c
XIV	C_3H_7O	C_3H_7O	$CH_2=CHCH_2$	$PhCH_2$	O	$C_{17}H_{27}N_2O_3PS$	358.45	7.82	8.64	8.92	89.8 *A*	3	1.5393	0.72^a
								7.55	8.81	9.23		18		0.02^b
														0.92^c
XV	C_4H_9O	C_4H_9O	$CH_2=CHCH_2$	$PhCH_2$	O	$C_{19}H_{31}N_2O_3PS$	398.51	7.03	7.77	8.08	93.2 *A*	5	1.5320	0.65^a
								6.91	7.50	8.40		19		0.01^b
														0.39^c
XVI	C_4H_9O	C_4H_9O	Ph	$PhCH_2$	O	$C_{22}H_{31}N_2O_3PS$	434.54	6.45	7.12	7.38	94.9 *A*	7	67—68	0.66^a
								6.71	7.39	7.12		21	Heptane	0^b
														0.32^c

Mobile phase: *a*) $CHCl_3 : C_2H_5OH$ (95 : 5); *b*) benzene; *c*) petroleum ether : acetone (7 : 3); *d*) petroleum ether : acetone (9 : 1); *e*) chloroform.

Compounds *I* and *V* prepared in acetonitrile; *II* in toluene : water (2 : 1); *III* in methyl iodide; *IV*, *VII*, *IX*, *XI*, and *XIII* in acetonitrile : water (1 : 1); *VI* and *X* in acetone; *VIII* in carbon tetrachloride; *XII*, *XIV*, *XV*, and *XVI* in benzene : water (2 : 1).

[10, 12]. Thiouronium salts were prepared by alkylation of *N*-phenylthiourea and *N*-allylthiourea, respectively, with the appropriate alkyl halides under reflux in ethanol [13, 14]. *N*-(*O*,*O*-Diethylthiophosphoryl)-*N*′-phenylthiourea [15, 16] and *N*-(*O*,*O*-diethylthiophosphoryl)-*N*′-isopropylthiourea [14] were prepared from *O*,*O*-diethylthiophosphoryl isothiocyanate [17, 18] with equimolar amount of aniline and isopropylamine, respectively. *N*-(*O*,*O*-Diethylthiophosphoryl)thiourea was prepared from *O*,*O*-diethylthiophosphoryl isothiocyanate [17, 18] and gaseous ammonia [16]. *N*,*N*-Dimethyl-*N*′-(*O*,*O*-dimethylthiophosphoryl)formamidine [19] was prepared by the reaction of *O*,*O*-dimethylamidothiophosphate with dimethylformamide dimethyl acetal in methanol. The preparation of *N*-[*N*-(*O*,*O*-diethylthiophosphoryl)thiocarbamoyl]-*N*′,*N*′-dimethylformamidine by the reaction of *N*-(*O*,*O*-diethylthiophosphoryl)thiourea with dimethylformamide dimethyl acetal is described in [1] as well as the preparation of *N*-diisobutylphosphoryl-*N*,*N*′,*S*-trimethylisothiourea by the reaction of diisobutyl phosphorochloridate with *N*,*N*′,*S*-trimethylthiouronium iodide [2], where also the preparation of *N*-(*O*,*O*-diethylthiophosphoryl)-*S*-methylisothiourea is described.

Data of elemental analysis, yields, reaction conditions, R_f, n_D^{20}, and melting points are presented in Table 1.

Infrared spectra of the compounds investigated were measured on UR-20 and IR-71 Zeiss instruments in CCl_4 and $CHCl_3$. The instruments were calibrated by polystyrene foil. The reading accuracy was $\pm cm^{-1}$ (Table 2).

Ultraviolet spectra were measured on a Unicam SP 8000 ($d = 1$ cm, $c = 10^{-4}$—10^{-5} M in methanol) spectrophotometer.

^{1}H-N.m.r. spectra were measured on a Tesla BS 487 C apparatus at 80 MHz in $CDCl_3$ (99.5% D-isotope) at 25°C using TMS as internal standard.

The purity of compounds and the reaction course was checked by t.l.c. using Silufol R UV 254 (Kavalier) plates with luminescence indicator and Silufol R (Kavalier) without an indicator. The used eluents are presented in Table 1. The compounds were detected by u.v. light ($\lambda = 254$ nm) and by spraying the plates with 0.5% petroleum ether solution of DQC (2,6-dibromoquinone-4-chloroimide) and subsequent heating for 2—5 min at 120°C.

The crude liquid compounds were purified by column chromatography on Silica gel L (100/160 mesh, Lachema, Brno). Mixtures of benzene—acetone or chloroform—acetone were used as eluents so that the amount of acetone increased from 0 to 20%.

Some liquid compounds were purified by t.l.c. on silica gel layers (Merck H for t.l.c.) using the eluents presented in Table 1. Part of the thin layer was detected with DQC and the residual silica gel was scraped down from the plate at the corresponding R_f and the product was eluted with acetone.

Pesticidal activity was followed at the conditions presented in the previous work [1] applying the methods described earlier [20, 21].

N-(R^1,R^2)-Phosphoryl- and -thiophosphoryl-N′-(R^3)-S-(R^4)-isothioureas (I—XVI)

The compounds (Table 1) were prepared after some of the presented common procedures; some compounds were actually prepared after two procedures.

Table 2

Infrared spectral data ($\tilde{\nu}/\mathrm{cm}^{-1}$) of the studied compounds (in CCl_4)

Compound	ν(POC)	ν(P=O)	δ(NH)	ν(C=N)	ν(NH)
II	1031 1055	—	1575	1602	3196
IV	1045 1062	1211	1580	1608	3200
V	1028 1048	—	1590	1590	3205
VI	1032 1051	—	1598	1598	3208
VII	1035 1060	1207	1588	1607	3200
VIII	1026 1050	1220	1587	1599	3209
IX	1026 1050	—	1578	1601	3198
X	1034 1054	—	1588	1607	3200
XI	1002 1048	—	1604	1604	3207
XIII	1014 1068	1236	1582	1600	3200
XIV	996 1071	1232	1591	1591	3210
XV	1029 1068	1234	1599	1599	3208
XVI	1032 1071	1212	1582	1608	3205

Method A

To the reaction mixture containing dialkyl phosphorochloridate or phosphorochloridothioate (0.1 mol), *N*-phenyl- and *N*-allylthiouronium salt (0.1 mol), respectively, potassium carbonate (0.2 mol), and acetonitrile (50 ml), water (50 ml) was added under stirring, while the temperature increased by 2—7°C. Stirring was continued under the conditions presented in Table 1 and the reaction course was checked by t.l.c. At the end the product was extracted with chloroform (2 × 50 ml), dried, and the solvent was distilled off under reduced pressure. The crude products were purified by column chromatography.

Method B

The reaction mixture containing the appropriate phosphorochloridothioate (0.1 mol), *N*-allyl-*S*-benzylthiouronium chloride (0.1 mol), triethylamine (0.2 mol), and ethyl methyl ketone (100 ml) was refluxed until the starting compound disappeared from the reaction mixture. The reaction course was checked by t.l.c. At the end the formed triethylammonium chloride was filtered off and the filtrate was evaporated under reduced pressure. The obtained crude products were purified by column chromatography.

Method C

To *N*-(*O*,*O*-diethylthiophosphoryl)-*N'*-isopropyl- and -phenylthiourea (0.1 mol), respectively, dissolved in ether (100 ml), ethereal solution of diazomethane (0.12 mol) was added at laboratory temperature under stirring. After stirring at laboratory temperature for 3 h and distillation of ether, light-yellow viscous liquids were obtained.

Method D

To *N*-(*O*,*O*-diethylthiophosphoryl)-*N'*-isopropylthiourea (0.1 mol) and potassium carbonate (0.1 mol) in acetone (200 ml), dimethyl sulfate (0.11 mol) was added under stirring and the reaction mixture was refluxed for 14 h. The end of the reaction was indicated by disappearance of the starting thiourea from the reaction mixture (t.l.c.). Then the solid compound was filtered off and the filtrate was evaporated under reduced pressure. To the residue benzene (100 ml) was added and after washing with water and drying, benzene was distilled off under reduced pressure. The obtained viscous liquid was purified by column chromatography. Its R_f, n_D^{20}, and the i.r. spectra were found to be identical with those of the compound *VI* prepared by the method *C*.

Method E

To *N*-(*O*,*O*-diethylthiophosphoryl)-*N'*-phenylthiourea (0.1 mol) and potassium carbonate (0.11 mol) in acetone (100 ml), benzyl bromide (0.11 mol) was added. The reaction mixture was refluxed for 12 h under continuous stirring. After the reaction was over, the solid compound was filtered off and the filtrate was evaporated under reduced pressure. To the residue benzene (100 ml) was added and after washing with water and drying, benzene was distilled off under reduced pressure. After purification by column chromatography a yellow viscous liquid was obtained which had R_f, n_D^{20}, and the i.r. spectra identical with the compound *X* prepared by the method *A*.

Method F

The reaction mixture of *N*-(*O*-ethyl-*O*-isopropylthiophosphoryl)-*N'*-phenylthiourea (0.02 mol) and methyl iodide (40 ml) was refluxed under stirring until the starting compound disappeared as indicated by t.l.c. Then the volatile compounds were distilled off and the product was purified by column chromatography.

Method G

Into the reaction mixture composed of diethyl phosphite (0.1 mol), *N*-phenyl-*S*-ethylthioethyl- and *N*,*S*-dialkylthiouronium chloride and bromide (0.1 mol), respectively, and carbon tetrachloride (100 ml), triethylamine (0.2 mol) was added during 10 min under stirring, while the reaction temperature increased by 35°C. After 3 h stirring the reaction was over according to t.l.c. To the reaction mixture water (100 ml) was added and the water layer was extracted with chloroform (2 × 50 ml). The combined organic solutions were dried and the solvents were distilled off under reduced pressure.

N-(O,O-Diethylthiophosphoryl)-N′,N′-dimethyl-S-methylisothiourea

To *N*-(*O*,*O*-diethylthiophosphoryl)-*N*′,*N*′-dimethylthiourea (25.6 g; 0.1 mol) and potassium carbonate (15.2 g; 0.11 mol) in acetone (200 ml), dimethyl sulfate (13.9 g; 0.11 mol) was added dropwise during 10 min while the temperature increased by 5°C. The reaction mixture was refluxed for 6 h and the reaction course was followed by t.l.c. After cooling the solid compound was filtered off and chloroform (100 ml) was added to the residue. The chloroform solution was washed with water (2 × 50 ml), dried and chloroform was distilled off. The product was redistilled under reduced pressure. Light-yellow liquid (22.7 g; 84.1%) of b.p. 146—148°C/26.6 Pa and $n_D^{20} = 1.5508$ was obtained.

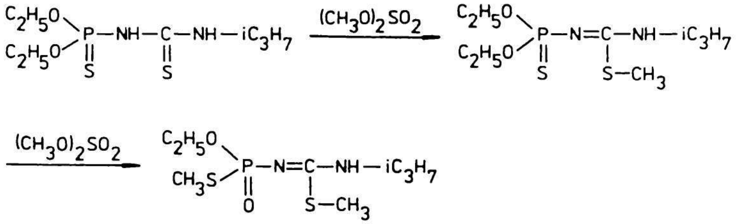
For $C_8H_{19}N_2O_2PS_2$ (270.3) calculated: 10.35% N, 11.34% P, 23.34% S; found: 10.62% N, 10.8% P, 23.85% S.

Results and discussion

O,*O*,*O*-Trialkyl phosphorothioates, accompanying impurities at the preparation of *O*,*O*-dialkyl phosphorochloridothioates by the methods *A* and *B*, were removed from the products by distillation under reduced pressure or column chromatography. Carbonates (Na_2CO_3, $KHCO_3$, K_2CO_3, $NaHCO_3$) and tertiary amines (triethylamine, pyridine) were examined for binding hydrogen halides. Potassium carbonate was found to be most suitable of all these compounds similarly as in the previous work [1]. The reaction can be carried out in heterogeneous phase in the mixture of nonpolar organic solvent—water or in homogeneous phase of polar organic solvent—water. The mixture of acetonitrile and water (1 : 1) was shown to be the most suitable medium. The reaction was slowlier in the mixture of acetone—water, benzene—water or toluene—water and resulted in low yields of less pure products. The reaction rate was significantly dependent on the alkoxy groups on phosphorus. With the increasing number of carbon atoms in the alkoxy groups the reaction rate decreased.

The greatest difference in the reaction rate was observed between dialkyl phosphorochloridates and *O*,*O*-dialkyl phosphorochloridothioates at the same procedure of preparation. For instance, *O*,*O*-dimethyl phosphorochloridothioate at the preparation of *II* reacted within 20 h, diethyl phosphorochloridate at the preparation of *VII* reacted within 2 1/2 h only (Table 1). With the increasing temperature the reaction rate increases at all procedures but so does the amount of impurities.

At the method *D* formation of a small amount of *N*-(*O*-ethyl-*S*-methylthiophosphoryl)-*N*′-isopropyl-*S*-methylisothiourea was observed in addition to the expected *N*-(*O*,*O*-diethylthiophosphoryl)-*N*′-isopropyl-*S*-methylisothiourea. Thus, the reaction simultaneously proceeded in a small degree also on the other reaction centre on phosphorus according to Scheme 2.



Scheme 2

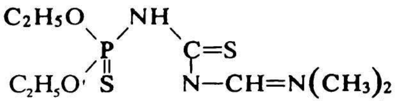
In the i.r. spectra the following changes of the absorption bands were observed

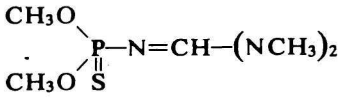
Compound	ν(P=O)	ν(C=N)	ν(N—H)
VI	—	1598	3208
S-Methyl derivative	1194	1583	3220

Also the R_f values changed and the colours of spots on t.l.c. turned from brown to yellow both corresponding to compounds containing a P=O bond.

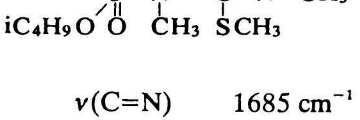
The purest compounds were obtained by the method *A* when dialkyl phosphorochloridates were used for the reaction and by the methods *C* and *G*. The products obtained by these methods were in most cases so pure that it was not necessary to purify them chromatographically; the other procedures resulted in products which had to be purified chromatographically.

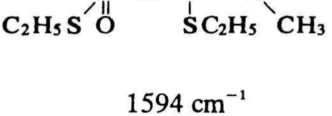
The structures of the prepared compounds were determined by i.r., u.v., and ^{1}H-n.m.r. spectrometry as well as by comparing their spectra with those of the model compounds



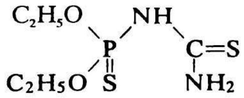


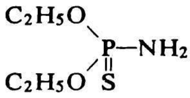
ν(N—H)	3384 cm^{-1}	—
ν(C=N)	1623 cm^{-1}	1629 cm^{-1}
(in CHCl$_3$)		



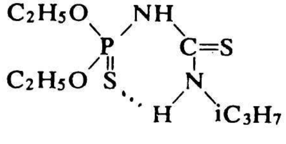


ν(C=N)	1685 cm^{-1}	1594 cm^{-1}



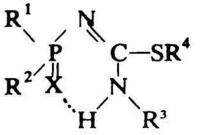


$\nu_s(NH_2)$	3274 cm^{-1}	3390 cm^{-1}
$\nu_{as}(NH_2)$	3476 cm^{-1}	3476 cm^{-1}
$\nu(NH)$	3380 cm^{-1}	

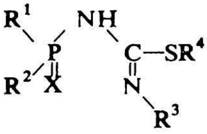


$\nu(NH)$	3252 cm^{-1}	3378 cm^{-1}

It was evident from the obtained spectra that the synthesized compounds appeared only in the tautomeric form *a*



a



b

In the ^1H-n.m.r. spectra of the compounds investigated broad resonance signals were observed at ~7 p.p.m. indicating the presence of –NH group.

In the u.v. spectra very strong bands were observed in the region of 220—240 nm (log ε 3—4) similarly as with the compounds reported in previous works.

The acaricidal and ovicidal activities of the investigated phosphorylated isothioureas were higher than those of the appropriate phosphorylated thioureas, however, none of the synthesized compounds showed so high activity as the used standards Fenitrothion, Malathion, and Karbofenthion. In tests for ovicidal activity on eggs of *Tetranychus urticae* KOCH the compound *IX* was found to be most active while the compounds *V*, *XI*, *XIV*, and *XV* were somewhat less active. In tests for acaricidal activity on *Tetranychus urticae* KOCH the compounds *V* and *XI* showed the highest activity. The compounds studied did not exhibit herbicidal and fungicidal activities.

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