

SYNTHESIS, SPECTRAL PROPERTIES AND PESTICIDAL ACTIVITY OF SOME O-(2,4,5-TRICHLORO-6-BROMO/IODO, NITRO/PHENYL) ESTERS OF CARBAMIC AND THIOCARBAMIC ACIDS

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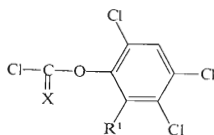
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2,4,5-Trichloro-6-bromo/iodo, nitro/phenyl carbamates have been prepared by reaction of 2,4,5-trichloro-6-bromo/iodo, nitro/phenyl chlorocarbonates with amines or by reaction of carbamoyl chloride with sodium 2,4,5-trichloro-6-bromo/iodo, nitro/phenolate, and the thiocarbamate esters have been prepared by reaction of O-(2,4,5-trichloro-6-bromo/iodo, nitro/phenyl) ester of chlorothiocarbamic acid with amines. IR and UV spectra of the synthesized compounds have been interpreted. The compounds have been tested for contact and systemic insecticidal, acaricidal, ovicidal, fungicidal and herbicidal activity. The highest fungicidal activity has been observed against powdery mildew disease.

2,4,5-Trichloro-6-nitrophenyl carbamates are mentioned in literature¹ as herbicides, 2,4,5-trichloro-6-nitrophenyl N-alkylcarbamates being known mostly as fungicides and nematocides². Also 2,4,5-trichloro-6-iodophenyl³ and 2,4,5,6-tetrachlorophenyl N-alkylcarbamates⁴ are described. The starting 2,4,5-trichloro-6-nitrophenol is known as a herbicide⁵. The present communication gives the preparation of O-(2,4,5-trichloro-6-bromo/iodo, nitro/phenyl) esters of carbamic and thiocarbamic acids, their UV and IR spectral data and pesticidal activity.

The starting 2,4,5-trichloro-6-bromo/nitro/phenols were prepared by known procedures^{6,7}; 2,4,5-trichloro-6-iodophenol was prepared by the procedure described for preparation of 2,4-dichloro-6-iodophenol⁸ with the yields 60 to 70 per cent. The 2,4,5-trichloro-6-bromo/iodo, nitro/phenyl chlorocarbonates were prepared according to a modified procedure for preparation of 2,4,5-trichloro-6-nitrophenyl chlorocarbonate¹, the yields being about 90 per cent. The O-(2,4,5-trichloro-6-bromo/iodo, nitro/phenyl) esters of chlorothiocarbamic acid were prepared by two procedures: *i*) by simultaneous action of triethylamine and thiophosgene on the respective phenol, or *ii*) by action of thiophosgene on the respective sodium phenolate. In the both cases the yields were only 10 to 20 per cent when using non-polar solvents (benzene, toluene). In protic solvents or their mixtures with non-polar ones the yields increased to 85 to 90 per cent (Table I).



- I*, R = Br, X = O *IV*, R = Br, X = S
II, R = I, X = O *V*, R = I, X = S
III, R = NO₂, X = O *VI*, R = NO₂, X = S

Reaction of 2,4,5-trichloro-6-bromo/iodo, nitro/phenyl chlorocarbonates with amines or reaction of carbamoyl chloride with sodium 2,4,5-trichloro-6-bromo/iodo, nitro/phenolates was used for preparation of the corresponding carbamates (Table II).

TABLE I

O-2,4,5-Trichloro-6-bromo/iodo,nitro/phenyl Chlorocarbonates and Chlorothiocarbonates

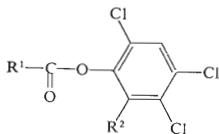
Compound yield, %	Formula (m.w.)	Calculated/Found		
		% Cl	% N	% X
<i>I</i> (88·0)	C ₇ HBrCl ₄ O ₂ (338·8)	41·85	—	23·60 Br
		41·71		23·51 Br
<i>II</i> (91·0)	C ₇ HCl ₄ IO ₂ (385·8)	36·80	—	32·90 I
		36·75		32·89 I
<i>III</i> (90·5)	C ₇ HCl ₄ NO ₄ (304·87)	46·50	4·58	—
		46·71	4·33	
<i>IV</i> ^a (88·2)	C ₇ HBrCl ₄ OS (354·8)	40·00	—	22·54 Br
		39·95		22·23 Br
<i>V</i> ^b (91·2)	C ₇ HCl ₄ IOS (401·8)	35·33	—	31·58 I
		35·45		30·91 I
<i>VI</i> ^c (84·9)	C ₇ HCl ₄ NO ₃ S (320·9)	44·30	4·37	—
		43·91	4·72	

^a Calculated: 9·05% S; found: 9·03% S. ^b Calculated: 7·96% S; found: 8·16% S. ^c Calculated: 10·00% S; found: 10·02% S.

TABLE II
2,4,5-Trichloro-6-bromo/iodo,nitro/phenyl Carbamates

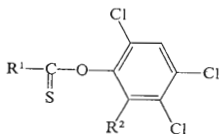
Compound	Formula (m.w.)	Calculated/Found			Yield, % M.p., °C
		% Cl	% N	% X	
VII	C ₉ H ₇ BrCl ₃ NO ₂ (347.1)	30.62	4.04	23.01 Br	67.9
		30.53	3.84	22.99 Br	133—135
VIII	C ₉ H ₇ Cl ₃ INO ₂ (394.3)	26.95	3.55	32.18 I	94.3
		27.10	3.57	32.32 I	143—145
IX	C ₉ H ₇ Cl ₃ N ₂ O ₄ (313.5)	33.92	8.96	—	63.6
		34.12	9.10	—	113—115
X	C ₁₁ H ₁₁ BrCl ₃ NO ₂ (375.4)	28.31	3.74	21.30 Br	81.8
		28.33	3.54	21.51 Br	56—58
XI	C ₁₁ H ₁₁ Cl ₃ INO ₂ (422.4)	25.20	3.32	30.00 I	86.1
		25.40	3.51	30.31 I	72—74
XII	C ₁₁ H ₁₁ Cl ₃ N ₂ O ₄ (341.6)	31.18	8.20	—	39.7
		31.61	8.40	—	84—85
XIII	C ₁₃ H ₁₁ BrCl ₃ NO ₂ (399.5)	26.48	3.55	20.00 Br	48.8
		26.93	3.85	20.23 Br	148/13.3 ^a
XIV	C ₁₃ H ₁₁ Cl ₃ INO ₂ (446.5)	23.80	3.13	28.40 I	94.6
		24.08	3.01	28.60 I	31—33
XV	C ₁₃ H ₁₁ Cl ₃ N ₂ O ₄ (365.4)	29.10	7.67	—	39.1
		28.95	7.65	—	148/13.3 ^a
XVI	C ₁₃ H ₁₅ BrCl ₃ NO ₂ (403.5)	26.40	3.12	19.75 Br	25.8
		26.46	3.35	20.28 Br	105—107
XVII	C ₁₃ H ₁₅ Cl ₃ INO ₂ (450.5)	23.60	3.12	28.17 I	25.6
		24.09	3.35	28.34	109—112
XVIII	C ₁₃ H ₁₅ Cl ₃ N ₂ O ₄ (369.6)	28.78	7.58	—	42.0
		28.93	8.01	—	125—128
XIX	C ₁₁ H ₉ BrCl ₃ NO ₃ (388.4)	27.40	3.60	20.55 Br	44.3
		27.61	3.75	20.75 Br	112—114
XX	C ₁₁ H ₉ Cl ₃ INO ₃ (436.4)	24.38	3.21	29.10 I	37.6
		24.67	3.44	29.43 I	141—142
XXI	C ₁₁ H ₉ Cl ₃ N ₂ O ₅ (355.5)	29.96	7.88	—	46.4
		30.23	8.12	—	133—135
XXII	C ₁₄ H ₉ Cl ₃ N ₂ O ₄ (375.6)	28.30	7.47	—	88.0
		28.76	7.60	—	160 ^b
XXIII	C ₁₃ H ₆ Cl ₃ N ₃ O ₆ (406.6)	26.10	10.31	—	63.5
		26.43	10.60	—	200 ^b
XXIV	C ₁₃ H ₄ Cl ₆ N ₂ O ₄ (464.1)	45.80	6.05	—	97.8
		46.08	6.18	—	82—84

^a B.p., °C/Pa; ^b decomposition.



- VII*, $R^1 = (\text{CH}_3)_2\text{N}$, $R^2 = \text{Br}$
VIII, $R^1 = (\text{CH}_3)_2\text{N}$, $R^2 = \text{I}$
IX, $R^1 = (\text{CH}_3)_2\text{N}$, $R^2 = \text{NO}_2$
X, $R^1 = (\text{C}_2\text{H}_5)_2\text{N}$, $R^2 = \text{Br}$
XI, $R^1 = (\text{C}_2\text{H}_5)_2\text{N}$, $R^2 = \text{I}$
XII, $R^1 = (\text{C}_2\text{H}_5)_2\text{N}$, $R^2 = \text{NO}_2$
XIII, $R^1 = (\text{CH}_2=\text{CHCH}_2)_2\text{N}$, $R^2 = \text{Br}$
XIV, $R^1 = (\text{CH}_2=\text{CHCH}_2)_2\text{N}$, $R^2 = \text{I}$
XV, $R^1 = (\text{CH}_2=\text{CHCH}_2)_2\text{N}$, $R^2 = \text{NO}_2$
XVI, $R^1 = ((\text{CH}_3)_2\text{CH})_2\text{N}$, $R^2 = \text{Br}$
XVII, $R^1 = ((\text{CH}_3)_2\text{CH})_2\text{N}$, $R^2 = \text{I}$
XVIII, $R^1 = ((\text{CH}_3)_2\text{CH})_2\text{N}$, $R^2 = \text{NO}_2$
XIX, $R^1 = \text{O} \begin{array}{l} \diagup \text{CH}_2-\text{CH}_2 \\ \diagdown \text{CH}_2-\text{CH}_2 \end{array} \text{N}$, $R^2 = \text{Br}$
XX, $R^1 = \text{O} \begin{array}{l} \diagup \text{CH}_2-\text{CH}_2 \\ \diagdown \text{CH}_2-\text{CH}_2 \end{array} \text{N}$, $R^2 = \text{I}$
XXI, $R^1 = \text{O} \begin{array}{l} \diagup \text{CH}_2-\text{CH}_2 \\ \diagdown \text{CH}_2-\text{CH}_2 \end{array} \text{N}$, $R^2 = \text{NO}_2$
XXII, $R^1 = 4\text{-CH}_3\text{-C}_6\text{H}_4\text{NH}$, $R^2 = \text{NO}_2$
XXIII, $R^1 = 4\text{-NO}_2\text{-C}_6\text{H}_4\text{NH}$, $R^2 = \text{NO}_2$
XXIV, $R^1 = 2,4,5\text{-Cl}_3\text{-C}_6\text{H}_2\text{NH}$, $R^2 = \text{NO}_2$

Preparation of the carbamates by reaction of carbamoyl chloride with the respective sodium phenolate gave substantially lower yields (25 to 45%) than that by reaction of amine with 2,4,5-trichloro-6-bromo/iodo, nitro/phenyl chlorocarbonate (yields above 60%). Out of the prepared carbamates the compounds *XVIII* and *IX* are described in ref.¹, for the latter substance, however, m.p. 170°C being given, whereas our product melted at 113–114°C. The thiocarbamates were prepared by reaction of N,N-dimethylthiocarbamoyl chloride with the respective sodium phenolate or by reaction of O-(2,4,5-trichloro-6-bromo/iodo, nitro/phenyl) esters of chloro-carbonic acid with amines, the both procedures giving good yields (Table III).



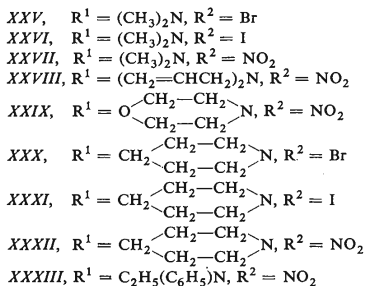


TABLE III
O-2,4,5-Trichloro-6-bromo/iodo,nitro/phenyl Thiocarbamates

Compound	Formula (m.w.)	Calculated/Found				Yield, % m.p., °C
		% Cl	% N	% S	% X	
XXV	C ₉ H ₇ BrCl ₃ NOS (363.5)	29.30	3.85	8.82	22.00 Br	90.8
		29.41	3.97	8.80	22.10 Br	164—167
XXVI	C ₉ H ₇ Cl ₃ INOS (410.5)	25.93	3.42	7.82	30.90 I	88.0
		26.13	3.50	7.89	31.20 I	142—144
XXVII	C ₉ H ₇ Cl ₃ N ₂ O ₃ S (329.6)	32.30	8.50	9.83	—	85.6
		32.56	7.91	9.58	—	123—125
XXVIII	C ₁₁ H ₉ Cl ₃ N ₂ O ₃ S (355.6)	29.85	7.88	9.00	—	72.0
		30.02	8.02	8.91	—	68—70
XXIX	C ₁₁ H ₉ Cl ₃ N ₂ O ₄ S (371.6)	28.60	7.85	8.62	—	71.3
		29.31	7.80	8.83	—	146—148
XXX	C ₁₂ H ₁₁ BrCl ₃ NOS (403.5)	26.36	6.94	7.93	19.80 Br	78.8
		26.16	7.12	8.23	19.65 Br	161—163
XXXI	C ₁₂ H ₁₁ Cl ₃ INOS (450.5)	23.38	6.23	7.02	27.94 I	80.2
		23.47	6.31	7.24	28.01 I	150—153
XXXII	C ₁₂ H ₁₁ Cl ₃ N ₂ O ₃ S (369.8)	28.80	7.58	8.66	—	84.2
		28.78	7.98	9.04	—	122—124
XXXIII	C ₁₅ H ₁₁ Cl ₃ N ₂ O ₃ S (405.6)	26.14	6.90	7.88	—	91.0
		26.10	7.11	7.71	—	143—145

IR spectra of the compounds VII to XX show intensive band of valence vibration of carbonyl group in the region 1758 to 1729 cm^{-1} . Position of the band is affected by the substituent at 6 position of the benzene ring and also by substituents at nitrogen of the carbamate group. The highest wavenumber is encountered with the compounds IX, XII, XV, XVIII and XXI having nitro group at 6 position of the benzene ring. The increase in the wavenumber of carbonyl group is due to mutual interactions of NO_2 and $\text{C}=\text{O}$ groups. The compounds having bromine or iodine at 6 position, *i.e.* VII, VIII, X, XI, XIII, XIV, XVI, XVII, XIX and XX show practically no changes in the wavenumber $\nu(\text{C}=\text{O})$. If there is bromine or iodine at the 6 position, then increasing size of the substituents at the carbamate nitrogen causes the wavenumber of $\text{C}=\text{O}$ group to increase in the following order:



In the case of NO_2 group at 6 position the wavenumber of $\text{C}=\text{O}$ group does not change until isopropyl groups are bound to the nitrogen; then it is lower by 9 to 14 cm^{-1} . Valence vibrations of NO_2 group do not change in the studied compound series, the wavenumbers being at 1560–1557 cm^{-1} and 1360–1356 cm^{-1} for asymmetrical and symmetrical vibrations, respectively. Value of the deformation $=\text{CH}-$ vibration is observed at 1448–1388 cm^{-1} , and it cannot be stated unambiguously what effects influence the given range of vibrations. Bands of the $\text{C}-\text{N}$ valence vibrations are found in the region 1256–1232 cm^{-1} and have medium intensity, whereas those of $\nu(\text{C}-\text{O}-\text{Ar})$ have strong intensity and are observed at 1162 to 1142 cm^{-1} ; for the morpholine derivatives $\nu(\text{C}-\text{O}-\text{Ar})$ and $\nu(\text{C}-\text{O}-\text{C})$ are found at 1123–1120 cm^{-1} and at 1094–1049 cm^{-1} , respectively. The thiocarbamate esters have their $\nu(\text{C}-\text{O}-\text{Ar})$ and $\nu(\text{C}=\text{S})$ at 1137–1093 cm^{-1} and at 1290 to 1288 cm^{-1} , respectively. All the studied compounds show broad band of medium intensity within 532 to 520 cm^{-1} due to valence vibration of $=\text{C}-\text{halogen}$ (Table IV).

UV spectra of the studied compounds have the main maximum in the region 209 to 211.5 nm except for those having iodine at 6 position (*i.e.* VII, XI, XIV, XVII, XX, XXVI and XXXI) which have the maximum in the range 216.5 to 217.5 nm. This shift is due to iodine having smaller electric effect than bromine or nitro group at the same position of the benzene ring. The compounds having 6- NO_2 group show a band of small intensity within 291 to 292 nm. The thiocarbamate esters have their second maxima within 242 to 256 nm. These maxima can be assigned to $\pi \rightarrow \pi^*$ transitions (Table IV).

Preliminary screening for contact and systemic insecticidal, acaricidal, ovicidal and herbicidal activity showed that none of the prepared substances exhibited such activity that more detailed tests could be justified. Testing the fungicidal activity we found some of the substances to be selectively active against powdery mildew disease.

TABLE IV
 Infrared (cm^{-1}) and Ultraviolet Spectral Data (nm) of the Synthesized Compounds

Compound	$\nu(\text{C}=\text{O})$ $\nu(\text{C}=\text{S})$	$\nu_{\text{as}}(\text{NO}_2)$	$\nu_s(\text{NO}_2)$	$\delta(\text{C}-\text{H})$	$\nu(\text{C}-\text{N})$	$\nu(\text{C}-\text{O}-\text{Ar})$ $\nu(\text{C}-\text{O}-\text{C})$	λ_{max} nm (log ϵ)
VII	1 747	—	—	1 392	1 249	1 162	210.0 (4.77), 224 ex.
VIII	1 747	—	—	1 388	1 247	1 160	217.5 (4.50), 240 ex.
LX	1 758	1 558	1 356	1 397	1 256	1 149	209.0 (4.55), 292 (3.42)
X	1 738	—	—	1 413	1 252	1 152	210.0 (4.75), 223 ex.
XI	1 737	—	—	1 408	1 252	1 152	217.5 (4.57), 240 ex.
XII	1 753	1 660	1 359	1 428	1 259	1 147	209.0 (4.45), 227 ex., 292 (3.48)
XIII	1 743	—	—	1 411	1 243	1 148	210.0 (4.77), 223 ex.
XIV	1 743	—	—	1 408	1 243	1 147	217.0 (4.56), 224 ex.
XV	1 753	1 558	1 357	1 418	1 239	1 144	209.5 (4.56), 224 ex., 291 (3.48)
XVI	1 729	—	—	1 421	1 251	1 162	210.5 (4.77), 223 ex.
XVII	1 730	—	—	1 419	1 248	1 161	217.5 (4.55), 240 ex., 295 (3.11)
XVIII	1 744	1 558	1 360	1 439	1 256	1 142	210.5 (4.45), 225 ex., 292 (3.12)
XIX	1 744	—	—	1 418	1 250	1 123	210.0 (4.77), 223 ex.
XX	1 743	—	—	1 410	1 248	1 123	217.5 (4.56), 242 ex.
XXI	1 753	1 558	1 356	1 428	1 244	1 122	209.0 (4.50), 223 ex., 292 (3.12)
XXV	(1 290)	—	—	1 428	1 248	1 049	210.5 1 (4.74), 224 ex., 248 (4.16)
XXVI	(1 288)	—	—	1 418	1 243	1 113	216.5 (4.58), 242 (4.32)
XXVII	(1 290)	1 567	1 358	1 410	1 255	1 093	209.0 (4.56), 248 (4.12)
XXVIII	(1 288)	1 559	1 356	1 414	1 254	1 098	209.0 (4.53), 251 (4.16)
XXIX	(1 288)	1 558	1 355	1 449	1 256	1 120	209.0 (4.515), 256 (4.184)
XXX	(1 270)	—	—	1 438	1 254	1 094	211.5 (4.723), 245 (4.198), 223 ex.
XXXI	(1 290)	—	—	1 448	1 234	1 100	217.0 (4.559), 245 (4.231)
XXXII	(1 290)	1 559	1 358	1 450	1 237	1 129	209.0 (4.599), 255 (4.196)
XXXIII	(1 288)	1 560	1 357	1 448	1 232	1 136	209.5 (4.572), 251 (4.202)

Some of the substances submitted to more detailed tests with *Erisiphe graminis* (XI, XII, XVIII, XXVI and XXVIII) showed activity comparable with that of the used standard (Dinokap). A noteworthy activity against *E. polyphaga* was observed with the compound XXVII, being almost twice as high as that of the standard (Table V). The compound XXVII is further biologically studied.

EXPERIMENTAL

The IR spectra were measured with a double-beam spectrophotometer UR-20 (Zeiss, Jena) within 400 to 4000 cm^{-1} , the compounds containing carbonyl group being measured with extended scale within 1500 to 1800 cm^{-1} . The spectra were measured in chloroform (0.16 mm NaCl cell). The UV spectra were measured with a Unicam SP 800 in methanol using (1.14 to 2.9) $\cdot 10^{-5}\text{M}$ solutions in 1 cm quartz cells.

2,4,5-Trichloro-6-nitrophenol was prepared according to ref.⁶, 2,4,5-trichloro-6-bromophenol according to ref.⁷, and 2,4,5-trichloro-6-iodophenol was prepared from sodium 2,4,5-trichlorophenolate by action of iodine in aqueous potassium iodide (analogy to preparation of 2,4-dichloro-6-iodophenol⁸).

2,4,5-Trichloro-6-bromo/iodo,nitro/phenyl Chlorocarbonates

0.25 mol sodium 2,4,5-trichloro-6-bromo/iodo,nitro/phenolate was added to 0.5 mol phosgene in 150 ml toluene with stirring at 5 to 12°C within 30 min. The mixture was further stirred at the same temperature 1 h, then it was heated to boiling within 2 h and refluxed 30 min. After cooling the separated sodium chloride was removed by filtration, and the filtrate was distilled to remove toluene under reduced pressure.

TABLE V
Anti-Mildew-Fungicidal Activity (ED₅₀ in ppm)

Compound	Relative lowering of attack	
	<i>E. graminis</i>	<i>E. polyphaga</i>
<i>IX</i>	139.0	820.0
<i>X</i>	980.0	209.0
<i>XI</i>	66.0	81.5
<i>XII</i>	53.0	163.0
<i>XV</i>	159.0	320.0
<i>XVIII</i>	53.8	336.0
<i>XXI</i>	224.0	672.0
<i>XXVI</i>	81.2	85.0
<i>XXVII</i>	46.9	7.1
<i>XXXI</i>	860.6	89.6
<i>XXXII</i>	221.0	38.0
Dinokap	17.8	13.2

O-(2,4,5-Trichloro-6-bromo/iodo,nitro/phenyl) Esters of Chlorothio carbonic Acid

a) 0.1 mol triethylamine and 0.1 mol thiophosgene were added simultaneously to 0.1 mol 2,4,5-trichloro-6-bromo/iodo,nitro/phenol in 80 ml toluene and 70 ml acetonitrile with stirring at 15–20°C. The mixture was stirred at 20–25°C 2 h. The precipitated triethylammonium chloride was filtered off, the filtrate was washed twice with ice water, dried with anhydrous CaCl₂, and toluene was distilled off under reduced pressure.

b) 0.1 mol thiophosgene was added to 0.075 mol sodium 2,4,5-trichloro-6-bromo/iodo,nitro/phenolate in 100 ml butanone with stirring at 10°C. The mixture was stirred at the same temperature 1 h and at 40°C 15 min. After cooling the precipitated sodium chloride was filtered off, and the filtrate was distilled under reduced pressure to remove butanone. The distillation residue was mixed with 100 ml toluene, the solution was washed with ice water, dried with anhydrous CaCl₂, and toluene was distilled off under reduced pressure.

2,4,5-Trichloro-6-bromo/iodo,nitro/phenyl Carbamates

a) (XII, XIII, XV–XXI): To 0.1 mol sodium 2,4,5-trichloro-6-bromo/iodo,nitro/phenolate in 100 ml butanone 0.1 mol of the corresponding carbamoyl chloride was added with stirring at 15–20°C. The mixture was stirred and refluxed for 2 h. After cooling the separated salt was filtered off, and the solvent was distilled off from filtrate under reduced pressure. The residue was purified by crystallization or distillation under reduced pressure.

b) (VII–XI, XIV, XXII–XXIV): 0.2 mol of the corresponding amine was introduced under the surface or added at 0 to 5°C to a stirred solution of 0.1 mol 2,4,5-trichloro-6-bromo/iodo,nitro/phenyl chlorocarbonate in 100 ml toluene. After the addition the mixture was stirred at the same temperature 1 h and at 40°C 30 min, washed twice with water, dried, and toluene was distilled off under reduced pressure. The distillation residue was purified by crystallization or distillation under reduced pressure.

O-2,4,5-Trichloro-6-bromo/iodo,nitro/phenyl N,N-Dimethylthiocarbamates (XXV–XXVII)

0.1 mol N,N-dimethylcarbamoyl chloride was added to 0.1 mol of the respective sodium phenolate in 100 ml dimethylformamide with stirring. The mixture was stirred 12 h at 80°C, cooled and poured onto 800 ml ice water; the precipitated solid was separated by filtration, dried and crystallized from cyclohexane.

O-2,4,5-Trichloro-6-bromo/iodo,nitro/phenyl Thiocarbamates (XXVIII–XXXIII)

0.1 mol of the corresponding amine was added to 0.05 mol O-2,4,5-trichloro-6-bromo/iodo,nitro/phenyl chlorothiocarbonate in 100 ml benzene at 0 to 5°C. Stirring was continued 1 h at 20°C, and, after washing with water and drying, benzene was distilled off under reduced pressure.

Pesticidal Activity

Contact insecticidal activity was followed with *Musca domestica* L., *Calandra granaria* L. and *Aphis fabae* Scop. using Malation (O,O-dimethyl-S-1,2-(diethoxycarbonyl)ethyl dithiophosphate) as standard. Systemic insecticidal activity was followed with *Macrosiphoniella sanbornii* L. (the host plant *Chrysanthemum indicum*) using Intration (O,O-dimethyl-S-(2-ethylthioethyl) dithiophosphate) as a standard. Acaricidal activity was followed with female *Tetranychus urticae*

KOCH, ovicidal activity was followed with ova of *T. urticae* using Akarition (O,O-diethyl-S-(4-chlorophenylthiomethyl) dithiophosphate) as standard. The methods used for these activity measurements were described in refs^{9,10}. Fungicidal activity was determined by both *in vivo* and *in vitro* methods. The proper inherent activity was followed by the glass slide method with spores of the fungi *Sclerotinia fructicola* (WINT), *Aspergillus niger* TIEGH, *Fusarium nivale* (FR.) CES, *Alternaria* sp. *Stemphylium sarciniformae* (CAV.), *Cladosporium cucumericum* ELL. et ARTH. by the method of Sharvell using Kaptan (3a,4,7,7a-tetrahydro-N-(trichloromethansulphenyl)-phthalimide) as standard. The anti-powdery-mildew-disease activity was tested on living plants of spring barley the variety Dunajský trh (*Erysiphe graminis* DC and *Erysiphe cichoracearum*), on cucumbers (*Erysiphe polyphaga*) and on tomatoes (*Phytophthora infestans* de BY) using Dinokap (2,4-dinitro-6-octylphenylcrotonate) as standard. The testing methods were described in ref.⁸. Herbicidal activity was determined by pre-emergent application (in soil) and post-emergent application (on leaves) using the testing objects: *Avena sativa*, *Polygonum persicaria*, *Fagopyrum sagittatum* and *Sinapis alba* according to known methods¹¹.

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