

# Synthesis and pesticidal activity of new esters of carbamic acid

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Synthesis and pesticidal activity of new carbamates are described. From 64 compounds tested, 2-methoxymethyl-4-nitrophenyl dimethylcarbamate was found to have the best insecticidal activity.

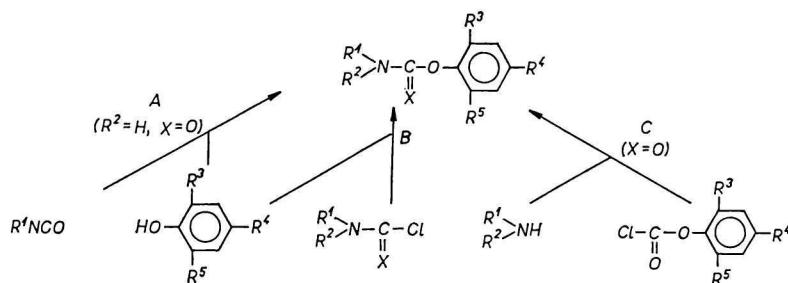
Описывается синтез и пестицидное действие новых эфиров карбамидовой кислоты. Среди 64 веществ найдено очень хорошее инсектицидное действие для *N,N*-диметил-*O*-(2-метоксиметил-4-нитрофенил)карбамида.

Various derivatives of 2-alkoxymethyl-4,6-dinitrophenol are described as pesticides in the literature [1]. So far, 2-ethoxymethyl-4,6-dinitrophenol (Etinofen) [2] and 2-alkoxymethyl-6-halo-4-nitrophenols or their acetates [3] are used in practice as herbicides.

We prepared 64 carbamates (Tables 1–4) according to the Scheme 1 and tested these compounds for pesticidal activity.

In the i.r. spectra of the prepared compounds strong absorption bands were observed in the region of 1720–1770 cm<sup>-1</sup> which belonged to the stretching vibrations of C=O bonds. The characteristic absorption bands  $\nu_s(\text{NO}_2)$  and  $\nu_{as}(\text{NO}_2)$  were observed in the region of 1348–1352 cm<sup>-1</sup> and 1532–1555 cm<sup>-1</sup>, respectively. The absorption bands  $\nu(\text{C}-\text{N})$  appeared in the spectra of all compounds in the region of 1230–1250 cm<sup>-1</sup>. The spectra of the compounds 1–20, 34–47, and 53–60 revealed the absorption bands  $\nu(\tilde{\text{N}}-\text{H})$  at 3430–3470 cm<sup>-1</sup> (Table 5).

The synthesized compounds were less active than the used standards in insecticidal (on *Musca domestica* L., *Calandra granaria* L.), acaricidal (on *Tetranychus urticae*



Scheme 1

Table 1

Characterization of the synthesized compounds

 $R^2 = H$ ,  $R^3 = CH_2R^6$ ,  $R^4 = NO_2$ ,  $R^5 = H$ ,  $X = O$ ,  $E = S, P, Cl$ 

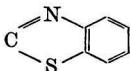
No.	R <sup>1</sup>	R <sup>6</sup>	Formula	M	Calculated/found		Yield %	M.p. (°C) Solvent $n_D^{20}$
					% N	% E		
1	CH <sub>3</sub>	OCH <sub>3</sub>	C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O <sub>5</sub>	240.2	11.67 11.81		84.5	96–98 Heptane
2	CH <sub>3</sub>	SC <sub>2</sub> H <sub>5</sub>	C <sub>11</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub> S	270.3	10.35 10.49	11.72 S 11.50	74.1	107–109 Benzene
3	CH <sub>3</sub>	SCHC <sub>2</sub> H <sub>5</sub>   CH <sub>3</sub>	C <sub>13</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> S	298.3	9.37 8.98	10.71 S 10.40	74.6	78–80 Benzene
4	CH <sub>3</sub>	SCN	C <sub>10</sub> H <sub>9</sub> N <sub>3</sub> O <sub>4</sub> S	267.3	15.35 15.70	11.95 S 11.64	58.4	182–183 Acetonitrile
5	CH <sub>3</sub>	SCOCH <sub>3</sub>    S	C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> O <sub>5</sub> S <sub>2</sub>	316.4	8.86 8.50	20.40 S 20.71	68.3	144–146 Benzene
6	CH <sub>3</sub>	SCN(CH <sub>3</sub> ) <sub>2</sub>    S	C <sub>12</sub> H <sub>15</sub> N <sub>3</sub> O <sub>4</sub> S <sub>2</sub>	329.4	12.75 12.65	19.48 S 19.70	55.0	126.5–128 Benzene
7	CH <sub>3</sub>	SP(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>    O	C <sub>13</sub> H <sub>19</sub> N <sub>2</sub> O <sub>7</sub> PS	378.4	7.40 7.11	8.19 P 8.54	38.5	94.5–96 Benzene
8	CH <sub>3</sub>	SP(OCH <sub>3</sub> ) <sub>2</sub>    S	C <sub>11</sub> H <sub>15</sub> N <sub>2</sub> O <sub>6</sub> PS <sub>2</sub>	366.4	7.64 7.71	8.45 P 8.49	32.1	71–73 Cyclohexane
9	CH <sub>3</sub>		C <sub>10</sub> H <sub>13</sub> N <sub>3</sub> O <sub>4</sub> S <sub>2</sub>	375.4	11.20 10.92	17.05 S 16.99	95.3	151–153 Ethanol

Table 1 (Continued)

No.	R <sup>1</sup>	R <sup>6</sup>	Formula	<i>M</i>	Calculated/found		Yield %	M.p. (°C) Solvent <i>n</i> <sub>D</sub> <sup>20</sup>
					% N	% E		
10	C <sub>4</sub> H <sub>9</sub>	SCN(CH <sub>3</sub> ) <sub>2</sub>    S	C <sub>15</sub> H <sub>21</sub> N <sub>3</sub> O <sub>4</sub> S <sub>2</sub>	371.4	11.32 11.02	17.23 S 16.98	59.2	120–122 Benzene
11	Ph	OC <sub>2</sub> H <sub>5</sub>	C <sub>16</sub> H <sub>16</sub> N <sub>2</sub> O <sub>5</sub>	316.3	8.85 8.48		91.8	82–84 Cyclohexane
12	Ph	SCN	C <sub>15</sub> H <sub>11</sub> N <sub>3</sub> O <sub>4</sub> S	329.1	12.79 12.56	9.73 S 9.77	75.2	187–190 Benzene
13	Ph	SCN(CH <sub>3</sub> ) <sub>2</sub>    S	C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> O <sub>4</sub> S <sub>2</sub>	391.3	10.75 10.96	16.40 S 16.89	79.8	131–132 Benzene
14	3-CH <sub>3</sub> -Ph	SCN	C <sub>16</sub> H <sub>13</sub> N <sub>3</sub> O <sub>4</sub> S	343.1	12.22 12.00	9.34 S 9.12	70.1	109–112 Methanol
15	3-Cl-Ph	SCN(CH <sub>3</sub> ) <sub>2</sub>    S	C <sub>18</sub> H <sub>19</sub> N <sub>3</sub> O <sub>4</sub> S <sub>2</sub>	405.5	10.36 10.42	15.81 S 15.30	90.2	Liquid 1.5483
16	3-Cl-Ph	SCN	C <sub>15</sub> H <sub>10</sub> ClN <sub>3</sub> O <sub>4</sub> S	367.0	11.45 11.81	8.71 S 8.41	70.5	136–139 Benzene
17	4-Cl-Ph	OC <sub>2</sub> H <sub>5</sub>	C <sub>16</sub> H <sub>15</sub> ClN <sub>2</sub> O <sub>5</sub>	315.8	7.99 8.36	10.12 Cl 10.50	83.1	139–140 Benzene
18	4-Cl-Ph	SCOCH <sub>3</sub>    S	C <sub>16</sub> H <sub>13</sub> ClN <sub>2</sub> O <sub>5</sub> S <sub>2</sub>	412.9	6.78 7.09	8.60 S 8.99	72.9	212–215 Chloroform
19	4-Cl-Ph	SCN(CH <sub>3</sub> ) <sub>2</sub>    S	C <sub>17</sub> H <sub>16</sub> ClN <sub>3</sub> O <sub>4</sub> S <sub>2</sub>	425.9	9.86 10.03	15.05 S 14.70	82.4	164–165 Benzene
20	4-Cl-3-CF <sub>3</sub> -Ph	OCH <sub>3</sub>	C <sub>16</sub> H <sub>12</sub> ClF <sub>3</sub> N <sub>2</sub> O <sub>5</sub>	404.7	6.89 7.18	8.77 Cl 8.40	93.8	132–134 Benzene

Table 2

Characterization of the synthesized compounds

 $R^3 = CH_2R^6$ ,  $R^4 = NO_2$ ,  $R^5 = H$ ,  $X = O$ ,  $E = Cl, Br, I, S$ 

No.	R <sup>1</sup>	R <sup>2</sup>	R <sup>6</sup>	Formula	M	Calculated/found		Yield %	M.p. (°C) Solvent $n_D^{20}$
						% N	% E		
21	CH <sub>3</sub>	CH <sub>3</sub>	OCH <sub>3</sub>	C <sub>11</sub> H <sub>14</sub> N <sub>2</sub> O <sub>5</sub>	254.2	10.98	11.24	97.2	79—80 Cyclohexane
22	CH <sub>3</sub>	CH <sub>3</sub>	OC <sub>2</sub> H <sub>5</sub>	C <sub>12</sub> H <sub>16</sub> N <sub>2</sub> O <sub>5</sub>	268.3	10.43	10.50	90.3	
23	CH <sub>3</sub>	CH <sub>3</sub>	OCH <sub>2</sub> CH=CH <sub>2</sub>	C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> O <sub>5</sub>	280.3	9.99	9.65	92.1	Liquid 1.5524 Liquid 1.5431
24	CH <sub>3</sub>	CH <sub>3</sub>	OCH <sub>2</sub> CHC <sub>4</sub> H <sub>9</sub>   C <sub>2</sub> H <sub>5</sub>	C <sub>18</sub> H <sub>28</sub> N <sub>2</sub> O <sub>5</sub>	352.4	7.95	7.60	91.5	
25	CH <sub>3</sub>	CH <sub>3</sub>	OCH <sub>2</sub> CH <sub>2</sub> Cl	C <sub>12</sub> H <sub>15</sub> ClN <sub>2</sub> O <sub>5</sub>	302.7	9.25	9.15	11.72 Cl	90.0
26	CH <sub>3</sub>	CH <sub>3</sub>	SCHC <sub>2</sub> H <sub>5</sub>   CH <sub>3</sub>	C <sub>14</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> S	312.4	8.96	8.69	10.24 S	94.1
27	CH <sub>3</sub>	CH <sub>3</sub>	SCN	C <sub>11</sub> H <sub>11</sub> N <sub>3</sub> O <sub>4</sub> S	281.3	14.95	15.07	11.4 S	81.8
28	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	OCH <sub>3</sub>	C <sub>13</sub> H <sub>18</sub> N <sub>2</sub> O <sub>5</sub>	282.3	9.29	9.50	89.2	205—208 Methanol
29	CH <sub>3</sub>	CH <sub>2</sub> =CHCH <sub>2</sub>	OC <sub>2</sub> H <sub>5</sub>	C <sub>14</sub> H <sub>18</sub> N <sub>2</sub> O <sub>5</sub>	294.3	9.52	9.40	87.0	
30	CH <sub>2</sub> =CHCH <sub>2</sub>	CH <sub>2</sub> =CHCH <sub>2</sub>	OCH <sub>3</sub>	C <sub>15</sub> H <sub>18</sub> N <sub>2</sub> O <sub>5</sub>	306.3	9.13	8.89	83.5	Liquid 1.5436 Liquid 1.5445
31	i-C <sub>3</sub> H <sub>7</sub>	·C <sub>3</sub> H <sub>7</sub>	OCH <sub>3</sub>	C <sub>15</sub> H <sub>22</sub> N <sub>2</sub> O <sub>5</sub>	310.3	9.03	8.90	98.5	
32	$\begin{array}{c} CH_2-CH_2 \\ \diagdown \quad \diagup \\ CH_2-CH_2 \\   \quad   \\ CH_2-CH_2 \end{array}$		OCH <sub>3</sub>	C <sub>14</sub> H <sub>18</sub> N <sub>2</sub> O <sub>5</sub>	294.3	9.52	9.38	91.8	Liquid 1.5514
33	$\begin{array}{c} CH_2-CH_2 \\ \diagdown \quad \diagup \\ O \\   \quad   \\ CH_2-CH_2 \end{array}$		OC <sub>2</sub> H <sub>5</sub>	C <sub>14</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub>	310.3	9.06	8.92	86.6	73—75 Cyclohexane

Table 3  
Characterization of the synthesized compounds  
 $R^3 = CH_2R^6$ ,  $R^4 = NO_2$ ,  $X = O$ ,  $E = Cl, Br, I, S$

No.	$R^1$	$R^2$	$R^5$	$R^6$	Formula	$M$	Calculated/found		Yield %	M.p. (°C) Solvent $n_D^{20}$
							% N	% E		
34	CH <sub>3</sub>	H	Cl	OCH <sub>3</sub>	C <sub>10</sub> H <sub>11</sub> ClN <sub>2</sub> O <sub>5</sub>	274.6	10.21 10.10	12.80 Cl 12.48	91.4	131–132 Benzene
35	CH <sub>3</sub>	H	Br	OCH <sub>3</sub>	C <sub>10</sub> H <sub>11</sub> BrN <sub>2</sub> O <sub>5</sub>	319.1	8.77 8.57	25.1 Br 25.4	71.2	103–104.5 Benzene
36	CH <sub>3</sub>	H	I	OCH <sub>3</sub>	C <sub>10</sub> H <sub>11</sub> IN <sub>2</sub> O <sub>5</sub>	366.1	7.65 7.40	34.7 I 35.1	89.8	138–140 Benzene
37	CH <sub>3</sub>	H	Cl	OC <sub>2</sub> H <sub>5</sub>	C <sub>11</sub> H <sub>13</sub> ClN <sub>2</sub> O <sub>5</sub>	288.7	9.73 9.58	12.3 Cl 12.4	71.2	137–139 Benzene
38	CH <sub>3</sub>	H	Br	OC <sub>2</sub> H <sub>5</sub>	C <sub>11</sub> H <sub>13</sub> BrN <sub>2</sub> O <sub>5</sub>	333.2	8.42 8.12	24.05 Br 24.5	92.4	78–79 Benzene
39	Ph	H	Cl	OCH <sub>3</sub>	C <sub>15</sub> H <sub>13</sub> ClN <sub>2</sub> O <sub>5</sub>	336.7	8.33 8.50	10.54 Cl 10.61	96.4	79–82 Benzene
40	Ph	H	Br	OC <sub>2</sub> H <sub>5</sub>	C <sub>16</sub> H <sub>15</sub> BrN <sub>2</sub> O <sub>5</sub>	395.2	7.09 7.15	20.25 Br 19.96	92.0	115.5–118 Cyclohexane
41	Ph	H	I	OC <sub>2</sub> H <sub>5</sub>	C <sub>16</sub> H <sub>15</sub> IN <sub>2</sub> O <sub>5</sub>	442.2	6.34 6.25	28.7 I 28.4	94.5	115–118 Cyclohexane
42	3-Cl-Ph	H	Cl	OC <sub>2</sub> H <sub>5</sub>	C <sub>16</sub> H <sub>14</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>5</sub>	385.2	7.27 7.35	18.42 Cl 18.78	95.3	71–73 Heptane

Table 3 (Continued)

No.	R <sup>1</sup>	R <sup>2</sup>	R <sup>5</sup>	R <sup>6</sup>	Formula	<i>M</i>	Calculated/found		Yield %	M.p. (°C) Solvent <i>n</i> <sub>D</sub> <sup>20</sup>
							% N	% E		
43	3-Cl-Ph	H	Br	OC <sub>2</sub> H <sub>5</sub>	C <sub>16</sub> H <sub>14</sub> BrClN <sub>2</sub> O <sub>5</sub>	429.7	6.54 6.70	18.65 Br 18.98	91.7	101–102 Cyclohexane
44	3-Cl-Ph	H	I	OC <sub>2</sub> H <sub>5</sub>	C <sub>16</sub> H <sub>14</sub> ClIN <sub>2</sub> O <sub>5</sub>	468.7	5.97 5.71	7.58 Cl 7.39	92.3	102–104 Cyclohexane
45	a	H	Cl	OC <sub>2</sub> H <sub>5</sub>	C <sub>17</sub> H <sub>13</sub> Cl <sub>2</sub> F <sub>3</sub> N <sub>2</sub> O <sub>5</sub>	439.1	6.38 6.01	16.60 Cl 16.35	90.1	143–145 Benzene
46	a	H	Br	OC <sub>2</sub> H <sub>5</sub>	C <sub>17</sub> H <sub>13</sub> BrClF <sub>3</sub> N <sub>2</sub> O <sub>5</sub>	497.5	5.63 5.31	7.12 Cl 6.80	95.4	128–130 Cyclohexane
47	a	H	I	OC <sub>2</sub> H <sub>5</sub>	C <sub>17</sub> H <sub>13</sub> ClF <sub>3</sub> IN <sub>2</sub> O <sub>5</sub>	544.6	5.15 5.48	6.52 Cl 6.31	95.1	Liquid 1.5502
48	CH <sub>3</sub>	CH <sub>3</sub>	Cl	OC <sub>2</sub> H <sub>5</sub>	C <sub>12</sub> H <sub>15</sub> ClN <sub>2</sub> O <sub>5</sub>	302.7	9.25 8.98	11.62 Cl 12.03	68.0	Liquid 1.5328
49	CH <sub>3</sub>	CH <sub>3</sub>	Br	OC <sub>2</sub> H <sub>5</sub>	C <sub>12</sub> H <sub>15</sub> BrN <sub>2</sub> O <sub>5</sub>	347.3	8.08 8.00	23.05 Br 23.38	91.4	73.5–76 Heptane
50	CH <sub>3</sub>	CH <sub>3</sub>	I	OC <sub>2</sub> H <sub>5</sub>	C <sub>12</sub> H <sub>15</sub> IN <sub>2</sub> O <sub>5</sub>	394.2	7.11 6.91	32.1 I 32.6	91.1	95–97 Heptane
51	CH <sub>3</sub>	CH <sub>3</sub>	NO <sub>2</sub>	OC <sub>2</sub> H <sub>5</sub>	C <sub>12</sub> H <sub>15</sub> N <sub>3</sub> O <sub>7</sub>	313.3	13.41 13.32		91.3	Liquid 1.5427
52	CH <sub>3</sub>	CH <sub>3</sub>	Br	SCN	C <sub>10</sub> H <sub>10</sub> BrN <sub>3</sub> O <sub>4</sub> S	360.2	11.69 11.34	8.90 S 8.61	83.3	Liquid 1.5481

a) 4-Cl-3-CF<sub>3</sub>-Ph.

Table 4  
Characterization of the synthesized compounds  
E = S, Cl, Br

No.	R <sup>1</sup>	R <sup>2</sup>	X	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	Formula	M	Calculated/found		Yield %	M.p. (°C) Solvent <i>n</i> <sub>D</sub> <sup>20</sup>
									% N	% E		
53	CH <sub>3</sub>	H	O	CH <sub>2</sub> OCH <sub>3</sub>	NHCNHC <sub>3</sub>    O	H	C <sub>11</sub> H <sub>17</sub> N <sub>3</sub> O <sub>4</sub>	267.2	15.74 15.38		86.2	170–172 Acetone
54	CH <sub>3</sub>	H	O	CH <sub>2</sub> OCH <sub>3</sub>	NHCCH <sub>3</sub>    O	H	C <sub>12</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>	252.2	10.08 10.81		65.0	132–134 Acetonitrile
55	CH <sub>3</sub>	H	O	CH <sub>2</sub> OCH <sub>3</sub>	NHCOC <sub>3</sub>    O	H	C <sub>12</sub> H <sub>16</sub> N <sub>2</sub> O <sub>5</sub>	268.3	10.48 10.19		78.2	140–142 Benzene
56	CH <sub>3</sub>	H	O	CH <sub>2</sub> SC <sub>2</sub> H <sub>5</sub>	NHCOC <sub>3</sub>    O	H	C <sub>13</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> S	300.3	9.35 9.18	10.64 S 10.41	58.2	122–124 Benzene
57	CH <sub>3</sub>	H	O	CH <sub>2</sub> OCH <sub>3</sub>	NHCNHC <sub>3</sub>    S	H	C <sub>12</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> S	271.3	15.55 15.72	11.72 S 11.79	94.6	113–116 Acetonitrile
58	CH <sub>3</sub>	H	O	CH <sub>2</sub> OCH <sub>3</sub>	N=C(SCH <sub>3</sub> )   NHCH <sub>3</sub>	H	C <sub>13</sub> H <sub>19</sub> N <sub>3</sub> O <sub>3</sub> S	297.4	14.11 14.12	10.74 S 10.93	46.2	144–146 Acetonitrile
59	CH <sub>3</sub>	H	O	CH <sub>2</sub> SCN	Cl	NO <sub>2</sub>	C <sub>10</sub> H <sub>8</sub> ClN <sub>3</sub> O <sub>4</sub> S	301.7	13.95 13.87	10.62 S 10.28	98.4	Liquid 1.5432
60	3-Cl-Ph	H	O	NO <sub>2</sub>	CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	H	C <sub>16</sub> H <sub>15</sub> ClN <sub>2</sub> O <sub>5</sub>	350.7	7.95 8.21	10.10 Cl 10.32	91.6	Liquid 1.5481
61	CH <sub>3</sub>	CH <sub>3</sub>	O	NO <sub>2</sub>	CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	H	C <sub>12</sub> H <sub>16</sub> N <sub>2</sub> O <sub>5</sub>	268.3	10.45 10.21		90.7	Liquid 1.5392
62	CH <sub>3</sub>	CH <sub>3</sub>	O	NO <sub>2</sub>	CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	Br	C <sub>12</sub> H <sub>15</sub> BrN <sub>2</sub> O <sub>5</sub>	347.3	8.08 8.15	23.05 Br 23.49	93.1	Liquid 1.5421
63	CH <sub>3</sub>	CH <sub>3</sub>	S	CH <sub>2</sub> OCH <sub>3</sub>	NO <sub>2</sub>	H	C <sub>11</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub> S	270.3	10.36 10.27	11.83 S 11.51	70.6	93–95 Benzene
64	CH <sub>3</sub>	CH <sub>3</sub>	S	CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	NO <sub>2</sub>	NO <sub>2</sub>	C <sub>12</sub> H <sub>16</sub> N <sub>3</sub> O <sub>6</sub> S	330.3	8.47 8.79	9.68 S 9.96	66.7	120–122 Ethanol

Table 5

Infrared spectral data of some substances investigated

Compound	$\nu$ , cm <sup>-1</sup>				
	$\nu(C=O)$	$\nu_s(NO_2)$	$\nu_{as}(NO_2)$	$\nu(C-N)$	$\nu(N-H)$
9	1730	1350	1545	1245	
11	1760	1350	1535	1230	3432
16	1758	1355	1540	1217	
	1724				
21	1730	1352	1532	1238	
24	1730	1350	1532	1240	
27	1720	1352	1555	1235	
30	1725	1350	1535	1235	
33	1725	1350	1532	1240	
36	1760	1348	1535	1235	3462
43	1770	1350	1538	1230	3430
44	1770	1350	1538	1230	3430
45	1720	1352	1555	1235	
55	1740	—	—	1235	3440 3470
61	1735	1350	1545	1250	

Table 6

Herbicidal activity of some compounds (postemergence application)

Test-objects	11		34		40		41		44		50		PCA	DNBP-TEA
	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y
<i>Avena sativa</i> L.	2	1	1	0	1	0	2	0	2	0	2	0	4	2
<i>Echinochloa crus-galli</i> (L.)	2	1	0	0	2	0	4	1	3	2	0	0	2	0
<i>Beta vulgaris</i> L.	1	0	0	0	5	3	5	5	5	5	5	0	0	5
<i>Persicaria vulgaris</i> WEBB. et MOQU.	5	5	3	2	5	5	5	5	5	5	5	5	5	5
<i>Chenopodium album</i> L.	5	5	5	1	5	5	5	5	5	5	5	5	5	5
<i>Brassica napus</i> L.	5	1	4	0	5	3	5	3	5	4	5	4	5	5
<i>Pisum sativum</i> L.	0	0	2	0	1	0	2	0	3	1	3	0	1	0
<i>Avena fatua</i> L.	2	1	0	0	0	0	2	0	1	0	1	0	4	2
<i>Hordeum sativum</i> L.	1	0	2	0	1	0	2	0	2	0	1	0	4	1
<i>Vicia sativa</i> L.	0	0	1	0	1	0	2	0	3	0	5	0	5	1
<i>Fagopyrum sagittatum</i> L.	5	2	5	3	5	5	5	5	5	5	5	5	5	5
<i>Sinapis alba</i> L.	5	2	3	0	4	2	5	2	5	3	5	3	5	4
<i>Amaranthus retroflexus</i> L.	5	0	1	0	4	0	5	0	5	0	5	0	5	5
<i>Linum usitatissimum</i> L.	3	1	5	1	4	1	5	2	5	3	5	3	5	0
<i>Zea mays</i> L.	1	0	2	1	1	0	2	0	2	0	2	0	0	0
<i>Triticum sativum</i> L.	0	0	0	0	1	0	2	0	2	0	1	0	4	0

X = dose 3.16 kg/ha; Y = dose 1.0 kg/ha.

PCA and DNBP-TEA: the used standards.

KOCH), and ovicidal (on the eggs of *Tetranychus urticae* KOCH) tests. In tests for a contact insecticidal activity on the lice of *Aphis fabae* SCOP, 2-methoxymethyl-4-nitrophenyl dimethylcarbamate (21) was more active ( $LC_{50} = 8.1$  p.p.m.) than the used standards Malation ( $LC_{50} = 11.0$  p.p.m.) and Baygon ( $LC_{50} = 8.5$  p.p.m.). The systemic insecticidal activity of the compound 55 on *Macrosyphoniella sanborni* THEOB. was one third of that of the standard Intration. The compound 37 ( $ED_{50} = 6.3$  g/q) was on the same level with the standard Metylenrodanid ( $ED_{50} = 2.7$  g/q) in fungicidal tests on corns of rye (*Fusarium nivale*). Several compounds were taken into the second screening as herbicides; the compounds 11, 34, 40, 41, 44, and 50 showed the highest activity (Table 6).

The pesticidal properties of the investigated carbamates and thiocarbamates indicated that only the compound 21 was more active than the used standards. Therefore, the insecticidal as well as physicochemical properties of this compound were studied in detail. The results will be published in a subsequent work.

### Experimental

Physical constants and data obtained at the elemental analysis of the synthesized compounds are presented in Tables 1—4. Infrared spectra were measured in chloroform (region 4000—400  $\text{cm}^{-1}$ ) and in KBr pellets region 2000—700  $\text{cm}^{-1}$  (compounds 9, 16, 27, and 45) using a double-beam UR-20 (Zeiss, Jena) spectrophotometer.

#### *Procedure A* (1—20, 34—47, 54—60)

To phenol (0.1 mole) dissolved in benzene, toluene, tetrahydrofuran or dioxan (100—150 ml), isocyanate (0.1 mole) in the same solvent (50 ml) and triethylamine (0.5 ml) were added under stirring at 15—20°C. The stirring was continued for 3 hrs and then for 1 hr at boiling. After cooling or evaporating, a solid precipitated (the oily liquid was freed from the solvent by evaporation under reduced pressure).

#### *Procedure B* (21—27, 48—52, 61—64)

To sodium, potassium or triethylammonium phenoxide (0.1 mole) in acetone (100 ml), dimethylcarbamoyl chloride (0.1 mole) was added under stirring at 15—20°C. The stirring was continued for 2 hrs and for another 2 hrs at boiling. The reaction mixture was poured into water (800 ml). The precipitated solid was separated and purified by crystallization. (The oily substances were extracted by chloroform and the residue was dried under reduced pressure after evaporation.)

#### *Procedure C* (28—33)

To phosgene (25.0 g) dissolved in toluene (150 ml), sodium 2-methoxymethyl-4-nitrophenoxide (45.6 g) was added stepwise under stirring and cooling by glacial water at 5—15°C during 30 min. Then the reaction mixture was slowly heated to boiling and refluxed for 15 min. After cooling, the precipitated sodium chloride was filtered. Toluene was distilled off from the filtrate at the end at 60°C and 0.1 Torr. A yellowish viscous liquid (44.6 g) containing 14.50% Cl (calculated: 14.45% Cl) was obtained. 2-Ethoxy-methyl-4-nitrophenyl chloroformate was prepared similarly.

To 2-alkoxymethyl-4-nitrophenyl chloroformate (0.05 mole) in acetone (100 ml), amine (0.1 mole) was added under stirring at 0—5°C during 30 min. The solution was stirred

for 3 hrs at 20°C and the reaction mixture was poured into water (400 ml) and worked up similarly as in the procedure *B*.

### *2-Methoxymethyl-4-(N-methylureido)phenyl methylcarbamate (53)*

To 4-amino-2-methoxymethylphenol (0.05 mole) in benzene (100 ml), methyl isocyanate (0.1 mole) in benzene (30 ml) was added under stirring at 15–20°C. The stirring was continued for 4 hrs and then for 1 hr at reflux. The precipitated solid was filtered and purified by crystallization.

### *Pesticidal activity*

Insecticidal activity was tested on *Musca domestica* L., *Calandra granaria* L., systemic insecticidal activity on *Macrosyphoniella sanborni* THEOB., acaricidal activity on *Tetranychus urticae* KOCH, ovicidal activity on the eggs of *Tetranychus urticae* KOCH, and the contact insecticidal activity on *Aphis fabae* SCOP.

Fungicidal activity was determined by the *in vitro* as well as *in vivo* methods. The inherent activity was followed on the spores of fungi *Sclerotinia fructicola* (WINT.), *Aspergillus niger* TIEGH., *Fusarium nivale* (FR.) CES., *Alternaria* sp., and *Stemphylium sarcinaformae* (CAV.) WITHSHIRE by the Sharvell method. The antipowdery mildew activity was tested on the living plants of barley, sort Dunajský trh (*Erysiphe graminis* DC.), on cucumbers, sort Znojemské (*Erysiphe cichoracearum* DC.), and on tomatoes (*Phytophtora infestans* DE BY).

Herbicidal activity was determined by the method of preemergence (into the soil) and postemergence (to the leaf) applications using the following test-objects: *Avena sativa* L., *Polygonum persicaria*, *Fagopyrum sagitatum* L., and *Sinapis alba* L. In the second screening, more test-objects were used.

Methods for the determination of pesticidal activities on the individual test-objects were published earlier [4, 5].

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