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## Preparation and Pesticide Properties of Some 1-Substituted (1*H*)-1,2,4-Triazoles

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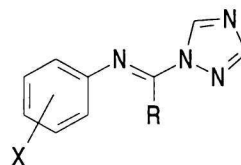
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The preparation, infrared and <sup>1</sup>H NMR spectra of five types of substituted 1-imidoyl-(1*H*)-1,2,4-triazoles are described. Herbicidal, fungicidal, and growth-regulating properties, tested on selected plants, are given.

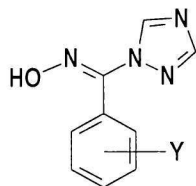
So far, numerous pesticidally active compounds possessing the 1-substituted (1*H*)-1,2,4-triazole ring system have been prepared, and commercialized [1]. Triazoles with an imidoyl moiety have recently been added to this family of compounds (Formulas 1 and 2). Some diarylformamidinoyltriazoles [2] have been found to possess good fungicidal and nematocidal activity (type II, Formula 1), structures containing sulfonamide group were good herbicides [3], S-benzoylthiourea-substituted derivatives (type V, Formula 2) displayed bactericidal and fungicidal properties [4].

In our effort to enlarge the family of 1-substituted (1*H*)-1,2,4-triazoles we described the synthesis and biological properties of some azolylquinazolines [5], in which the imidoyl moiety was built in the pyrimidine ring. Now we describe another five types of imidoyltriazoles, namely four *N*-phenylbenzimidoyltriazoles Ia—Id, nine *N*-phenylformamidinoyltriazoles IIa—III, and four bis-triazolyl derivatives, formally guanidines IIIa—IIIId. Compounds IVa, IVb are derivatives of *O*-methylthiourea, Va, Vb can be classified as *N*-phenylhydroxamoyltriazoles.



	R	Z	X
Ia	C <sub>6</sub> H <sub>4</sub> -Z	H	H
Ib	C <sub>6</sub> H <sub>4</sub> -Z	H	4-Cl
Ic	C <sub>6</sub> H <sub>4</sub> -Z	3,4-di-Cl	4-Cl
Id	C <sub>6</sub> H <sub>4</sub> -Z	H	2-CH <sub>3</sub>
IIa	morpholinyl		H
IIb	morpholinyl		4-Cl
IIc	piperidinyl		4-Cl
IId	diethylamino		4-Cl
IIe	piperidinyl		2,4-di-Cl
IIf	morpholinyl		2,3,4,5,6-penta-Cl
IIg	morpholinyl		4-Br
IIh	piperidinyl		4-Br
III	diethylamino		4-Br
IIIa	1,2,4-triazol-1-yl		4-Cl
IIIb	1,2,4-triazol-1-yl		2,4-di-Cl
IIIc	1,2,4-triazol-1-yl		2,3,4,5,6-penta-Cl
IIId	1,2,4-triazol-1-yl		4-Br
IVa	OCH <sub>3</sub>		4-Cl
IVb	OCH <sub>3</sub>		4-Br

Formula 1



Formula 2

	Y
Va	4-Cl
Vb	3,4-di-Cl

absorption band at  $\lambda = 1630\text{--}1690\text{ cm}^{-1}$ , which can be assigned to the vibrations of the imido bond (C=N). Similar vibrations of the triazole skeleton are overlapped by bands belonging to  $\nu(\text{C}=\text{C})$  vibrations and cannot be unequivocally assigned. In a number of compounds, especially in those of the type *II*, anomalously shifted  $\nu(\text{CH})_{\text{arom}}$  can be observed. By comparing such spectra with those of the compound *III*f, which lacks phenyl hydrogens, the shifted absorption bands could be assigned to  $\nu(\text{N}=\text{C}-\text{H})$  of the triazole. The hydroxamoyl derivatives *Va*, *Vb* show in their IR spectra two maxima in the  $\nu(\text{CH})$  region, one broad at  $\tilde{\nu} = 2800\text{ cm}^{-1}$  ( $\nu(\text{OH})$ ) and a sharp one at  $\tilde{\nu} = 3130\text{ cm}^{-1}$ , the latter belong-

Table 1. Characterization of Prepared Compounds

Compound	Formula $M_r$	$w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$			Yield/%	M.p./°C
		C	H	N		
<i>Ia</i>	$\text{C}_{13}\text{H}_{12}\text{N}_4$	69.62	5.39	24.99	86	106—107
	224.3	69.58	5.35	24.71		
<i>Ib</i>	$\text{C}_{13}\text{H}_{11}\text{N}_4\text{Cl}$	60.35	4.28	21.65	82	87—89
	258.7	60.12	4.13	21.49		
<i>Ic</i>	$\text{C}_{13}\text{H}_9\text{N}_4\text{Cl}_3$	47.69	2.77	17.11	80	163—166
	327.4	47.55	2.75	16.89		
<i>Id</i>	$\text{C}_{14}\text{H}_{14}\text{N}_4$	70.56	5.92	23.51	78	73—74
	238.3	70.44	5.83	23.37		
<i>IIa</i>	$\text{C}_{13}\text{H}_{15}\text{N}_5\text{O}$	60.68	5.87	27.22	75	129—131
	257.3	60.57	5.80	27.18		
<i>IIb</i>	$\text{C}_{13}\text{H}_{14}\text{N}_5\text{OCl}$	53.52	4.83	24.00	73	125—128
	291.7	53.41	4.80	23.96		
<i>IIc</i>	$\text{C}_{14}\text{H}_{16}\text{N}_5\text{Cl}$	58.04	5.56	24.17	81	132—134
	289.7	57.92	5.50	24.03		
<i>IId</i>	$\text{C}_{13}\text{H}_{16}\text{N}_5\text{Cl}$	56.22	5.80	25.21	78	112—114
	277.7	56.15	5.73	25.09		
<i>IIe</i>	$\text{C}_{14}\text{H}_{15}\text{N}_5\text{Cl}_2$	51.89	4.66	21.61	81	103—106
	324.0	51.78	4.61	21.56		
<i>IIIf</i>	$\text{C}_{13}\text{H}_{16}\text{N}_5\text{OCl}_5$	36.35	2.34	16.30	67	210—213
	429.5	36.22	2.31	16.24		
<i>IIg</i>	$\text{C}_{13}\text{H}_{14}\text{N}_5\text{OBr}$	46.44	4.19	20.83	80	117—120
	336.5	46.42	4.12	20.76		
<i>IIh</i>	$\text{C}_{14}\text{H}_{16}\text{N}_5\text{Br}$	50.31	4.82	20.95	78	91—93
	334.2	50.26	4.78	20.87		
<i>IIIi</i>	$\text{C}_{13}\text{H}_{16}\text{N}_5\text{Br}$	48.46	5.00	20.77	82	112—114
	322.2	48.37	4.95	20.71		
<i>IIIa</i>	$\text{C}_{11}\text{H}_8\text{N}_7\text{Cl}$	48.29	2.94	35.83	79	108—110
	273.6	48.13	2.90	35.71		
<i>IIIb</i>	$\text{C}_{11}\text{H}_7\text{N}_7\text{Cl}_2$	42.89	2.29	31.83	77	98—102
	308.0	42.83	2.22	31.70		
<i>IIIc</i>	$\text{C}_{11}\text{H}_4\text{N}_7\text{Cl}_5$	32.53	0.98	23.84	68	209—214
	411.2	32.47	0.95	23.72		
<i>IIId</i>	$\text{C}_{11}\text{H}_8\text{N}_7\text{Br}$	41.53	2.53	30.82	81	117—119
	318.1	41.48	2.51	30.76		
<i>IVa</i>	$\text{C}_{10}\text{H}_9\text{N}_4\text{OCl}$	47.34	3.83	23.68	66	139—141
	236.6	47.29	3.80	23.59		
<i>IVb</i>	$\text{C}_{10}\text{H}_9\text{N}_4\text{OBr}$	42.72	3.22	19.93	70	124—125
	281.1	42.68	3.19	19.80		
<i>Va</i>	$\text{C}_9\text{H}_7\text{N}_4\text{OCl}$	48.56	3.16	25.16	63	158—160
	222.6	48.49	3.13	25.03		
<i>Vb</i>	$\text{C}_9\text{H}_6\text{N}_4\text{OCl}_2$	41.88	2.34	21.70	67	129—132
	258.1	41.81	2.29	21.63		

Table 2. IR and <sup>1</sup>H NMR Characteristics of Compounds I—V

Compound	IR, $\tilde{\nu}/\text{cm}^{-1}$			<sup>1</sup> H NMR, $\delta$		
	$\nu(\text{C}=\text{N})$	$\nu(\text{CH}_{\text{arom}})$	$\nu(\text{CH}_{\text{aliph}})$	$\text{H}_{\text{triazole}}$	$\text{H}_{\text{arom}}$	Others
Ia	1660	3144		8.06 s, 9.00 s	6.77—7.34 m	
Ib	1648	3130		8.07 s, 8.97 s	6.71—7.46 m	
Ic	1656	3288		7.94 s, 7.96 s	7.32—7.70 m	
Id	1670	3130		8.07 s, 9.08 s	6.47—7.32 m	2.25 s (CH <sub>3</sub> )
IIa	1640	3096	2930, 2860	7.81 s, 8.01 s	6.58—7.16 m	3.41 m, 3.84 m
IIb	1630	3080	2980, 2860	7.83 s, 8.02 s	6.48—7.10 m	3.39 m, 3.82 m
IIc	1630	3304	2936, 2840	8.15 s, 7.31 s	6.85—7.27 m	1.63 m, 3.45 m
IId	1630	3110	2980, 2930	7.83 s, 7.97 s	6.45—7.06 m	1.24 t, 3.33 q
IIE	1635	3190	2950, 2850	8.15 s, 8.18 s	7.19—7.34 m	1.66 m, 3.48 m
IIf	1656	3112	2928, 2864	8.65 s, 8.90 s	—	2.47 m, 3.75 m
IIg	1630	3300	2980, 2860	8.31 s, 8.68 s	7.26—7.51 m	3.40 m, 3.61 m
IIh	1632	3112	2930, 2856	8.14 s, 8.56 s	6.47—7.15 m	1.59 m, 3.23 m
III	1636	3328	2984	7.44 s, 8.27 s	7.36—7.49 m	1.07 t, 3.31 q
IIIa	1680	3328, 3232		8.87 s, 9.51 s	—	
IIIb	1696	3220, 3130		8.20 s, 8.23 s	6.86—7.39 m	
IIIc	1660	3416, 3392		7.91 s, 8.13 s	—	
IIId	1636	3296, 3120		8.22 s, 8.32 s	6.67—7.43 m	
IVa	1632	3192, 3112		8.06 s, 8.97 s	7.37—7.58 m	2.17 s (CH <sub>3</sub> )
IVb	1680	3130, 3104		8.30 s, 9.05 s	7.45—7.67 m	1.66 s (CH <sub>3</sub> )
Va	1636	3136	2864 $\nu(\text{OH})$	8.13 s, 9.02 s	7.36—7.53 m	
Vb	1624	3128	2768 $\nu(\text{OH})$	8.15 s, 9.01 s	7.55—7.71 m	

ing by analogy to the CH bonds of triazole. In the <sup>1</sup>H NMR spectra (Table 2) there are two signals of triazole protons well separated from signals of aromatic hydrogens.

Herbicidal, fungicidal, and growth-regulating properties were tested (Tables 3 and 4). None of the compounds affected growth characteristics of tested plants. Potential *in vitro* fungicidal activity was observed in groups III and IV, where all but the penta-

substituted IIIc were active. About the same activity was observed in group II, but not in group I and V. In the *in vivo* tests noticeable fungicidal activity was observed only in compounds IIb, IId, and IIh. Compounds of the type I, III, IV, and V displayed none herbicidal activity. In the cases of the formamidinoyl derivatives only two, namely diethylamino derivatives IId and III, showed various degrees of herbicidal activity on all tested plants.

Table 3. Herbicidal Activity of Prepared Compounds<sup>a</sup>

Compound	<i>Avena sativa</i>		<i>Panicum miliaceum</i>		<i>Fagopyrum esculentum</i>		<i>Lepidium sativum</i>		<i>Sinapis alba</i>	
	pre <sup>c</sup>	post <sup>d</sup>	pre <sup>c</sup>	post <sup>d</sup>	pre <sup>c</sup>	post <sup>d</sup>	pre <sup>c</sup>	post <sup>d</sup>	pre <sup>c</sup>	post <sup>d</sup>
Ia	— <sup>b</sup>	—	—	—	—	—	—	—	—	—
Ib	—	—	—	—	—	—	—	—	—	—
Ic	—	—	—	—	—	—	—	—	—	—
Id	—	—	—	—	—	—	—	—	—	1
IIa	—	—	—	—	1	—	—	—	1	1
IIb	1	—	—	—	1.5	—	—	—	2	—
IIc	—	1	—	—	—	—	—	—	2.5	2
IId	2.5	1	—	1	4.5	1.5	2	2	4	2
IIE	—	—	—	—	—	1	—	—	—	1
IIf	—	—	—	—	—	—	—	—	—	—
IIg	—	—	—	—	1	—	—	—	1	2
IIh	—	—	—	—	—	—	—	—	—	1
III	1	1	—	—	4.5	1	1	—	4	2
IIIa	—	—	—	—	—	—	—	—	—	—
IIIb	—	—	—	—	—	—	—	—	—	—
IIIc	—	—	—	—	—	—	—	—	—	—
IIId	—	—	—	—	—	—	—	—	—	—
IVa	—	—	—	—	—	—	—	—	—	—
IVb	—	—	—	—	—	—	—	—	—	—
Va	—	—	—	—	—	—	—	—	—	—
Vb	—	—	—	—	—	—	—	—	—	1

a) 1 — plants attacked to 20 %; 2 — plants attacked to 50 %; 3 — plants attacked to 70 %; 4 — plants damaged up to 90 %; b) — inactive; c) pre — preemergence application into the soil; d) post — postemergence application to the leaf.

Table 4. Fungicidal Activity of Prepared Compounds

Compound	<i>Phytophthora infestans</i> 1st screening <sup>a</sup>	<i>Alternaria species</i> 1st screening <sup>a</sup>	<i>Botrytis cinerea</i> 1st screening <sup>a</sup>	<i>Fusarium nivale</i> 1st screening <sup>a</sup>	<i>Hordeum sativum</i> 1st screening — cont. <sup>b</sup>	<i>Erysiphe graminis</i> 1st screening — cont. <sup>b</sup>	<i>Hordeum sativum</i> 1st screening — syst. <sup>b</sup>	<i>Erysiphe graminis</i> 1st screening — syst. <sup>b</sup>
Ia	—	—	—	—	2	2	2	2
Ib	—	—	—	—	2	2	2	2
Ic	—	—	—	—	3	3	3	3
Id	—	—	—	—	2	2	2	2
IIa	—	—	—	—	—	—	—	—
IIb	—	—	+	—	1.5	1.5	2.5	2.5
IIc	—	—	—	—	2	2	2	2
IId	—	—	+	+	3	3	2	2
IIe	—	—	—	—	2	2	2	2
IIf	—	—	—	—	2	2	2	2
IIg	—	—	—	—	2	2	2	2
IIh	—	—	+	—	3.5	3.5	3.5	3.5
III	—	—	—	+	1.5	1.5	1.5	1.5
IIIa	+	+	+	+	1.5	1.5	1.5	1.5
IIIb	+	+	+	+	2	2	2	2
IIIc	—	—	—	—	2	2	2	2
IIId	+	+	+	+	—	—	—	—
IVa	+	+	+	+	—	—	—	—
IVb	+	+	+	+	—	—	—	—
Va	—	—	—	—	1.5	1.5	1.5	1.5
Vb	—	—	—	—	—	—	—	—

a) *In vitro*: — inactive, + active; b) *in vivo*: 1 — inactive, 2 — weakly active, 3 — active, 4 — active up to 90 %, cont. — contact activity, syst. — systemic activity.

## EXPERIMENTAL

The IR spectra of prepared compounds in KBr pellets and the <sup>1</sup>H NMR spectra of hexadeuterodimethyl sulfoxide solution containing tetramethylsilane as an internal standard were measured with Specord M8 (Zeiss, Jena) and Varian VXR-300 (300 MHz) spectrometers.

The herbicidal activity of studied compounds was assayed by the method of preemergence (into the soil) and postemergence (to the leaf) application on the five plants [6].

The fungicidal activity was determined by both *in vitro* and *in vivo* methods. The inherent activity was tested on the spores of some fungi and antifungal activity on living plants was tested on barley, cucumbers, and tomatoes [7].

The growth-regulating quality was investigated on *Fagopyrum vulgare*. None of the prepared compounds were active.

The starting imidoyl chlorides were prepared by chlorination of the corresponding benzanilides with thionyl chloride and used for preparation of compounds I according to [8].

Formamidinoyl chlorides for syntheses of derivatives II and methylchloroformimidates for preparation of derivatives III were prepared by the reaction of corresponding *N*-phenylcarbimidoyl dichlorides [9] with secondary amine and methanol, respectively.

Hydroxamic acid chlorides, starting material of derivatives V, were obtained by chlorination of substi-

tuted benzaldehyde oximes with nitrosyl chloride [10].

## Preparation of Imidoyl Triazoles I—V

Mixture of corresponding imidoyl chloride (0.01 mol) and sodium salt of 1,2,4-triazole (0.01 mol; 0.9 g) dissolved in 35 cm<sup>3</sup> of absolute acetonitrile was heated on oil bath for 48 h. During the reaction precipitate was formed (NaCl and unreacted sodium salt) which was removed by filtration. The filtrate was concentrated and the crude product crystallized from ether or benzene.

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