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4-Functionally Substituted 3-Heterylpyrazoles: VII.* 3-Aryl(heteryl)-1-phenyl-4-pyrazolecarbonyl Isothiocyanates

V. A. Chornous, N. V. Mel'nichenko, M. K. Bratenko, and M. V. Vovk

Bukovina State Medical Academy, Teatral'naya pl. 2, Chernovtsy, 58000 Ukraine

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kiev, Ukraine

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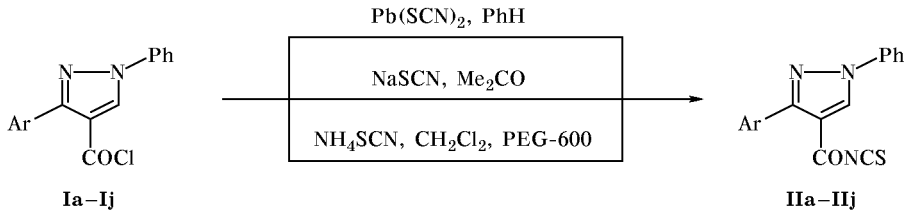
Abstract—3-Aryl(heteryl)-1-phenyl-4-pyrazolecarbonyl isothiocyanates were synthesized by treatment of 3-aryl(heteryl)-1-phenyl-4-pyrazolecarbonyl chlorides with lead, sodium, or ammonium thiocyanate. Their reactions with amines, hydrazines, and acylhydrazines gave the corresponding thioureas and thiosemicarbazides.

Acyl isothiocyanates have found wide application in the synthesis of various acyclic and heterocyclic compounds, including those possessing biological activity [2]. Alkanoyl and aroyl isothiocyanates have been studied most thoroughly. However, the available data on heterocyclic acyl isocyanates are much poorer. Among these, furoyl isothiocyanates [3–5], nicotinoyl isothiocyanates [6], and 5-pyrazolecarbonyl isothiocyanates [7] have been reported. The goal of the present study was to synthesize previously unknown 4-pyrazolecarbonyl isothiocyanates and examine their reactions with nitrogen-containig nucleophiles.

The target compounds were prepared by exchange reaction of 4-pyrazolecarbonyl chlorides **Ia**–**Ij** with salts of thiocyanic acid. By heating chlorides **Ia**, **Ib**, **Id**, **Ig**, **Ih**, and **Ij** with lead(II) thiocyanate for 6 h in boiling benzene we obtained 4-pyrazolecarbonyl isothiocyanates **IIa**, **IIb**, **IId**, **IIg**, **IIh**, and **IIj** in 55–64% yield (method *a*; Scheme 1). When the reaction was performed with sodium thiocyanate in acetone at room temperature, the yield of isothiocyanates **IIa**–**IIj** was raised to 68–82% (method *b*).

According to the recent data [8, 9], the yield of aroyl isothiocyanates approaches almost quantitative in reactions of aroyl chlorides with ammonium thiocyanate, carried out in the presence of phase-transfer catalysts. However, the resulting isothiocyanates as a rule were not isolated from the mixture but were converted into the corresponding derivatives. Using acyl chlorides **Ia**, **Ig**, and **Ij** as examples, we have found that their reaction with ammonium thiocyanate in methylene chloride in the presence of poly(ethylene glycol) PEG-600 as catalyst leads to formation of isothiocyanates **IIa**, **IIg**, and **IIj** in 80–86% yield

Scheme 1.



Ia–Ij **IIa–IIj**

I, **II**, Ar = Ph (**a**), 4-FC_6H_4 (**b**), 4-ClC_6H_4 (**c**), 3-BrC_6H_4 (**d**), 4-BrC_6H_4 (**e**), 4-MeC_6H_4 (**f**), 4-$MeOC_6H_4$ (**g**), 3,4-$(MeO)_2C_6H_3$ (**h**), 2-thienyl (**i**), 3-pyridyl (**j**).

* For communication VI, see [1].

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Table 1. Yields, melting points, spectral parameters, and elemental analyses of 3-aryl(heteryl)-1-phenyl-4-pyrazolecarbonyl isothiocyanates **IIa**–**IIj**

Comp. no.	Yield, %		mp,[a] °C	IR spectrum, ν, cm^{-1}		^1H NMR spectrum (C_6D_6), δ, ppm
	a	*b*		N=C=S	C=O	
IIa	59	68	105–107	2000	1700	7.18–7.39 m (10H, H_{arom}), 7.71 s (1H, CH=)
IIb	60	71	132–133	1945	1700	6.91–7.23 m (7H, H_{arom}), 7.61 s (1H, CH=), 7.82–7.97 m (2H, H_{arom})
IIc	–	82	106–107	2000	1700	6.90–7.18 m (5H, H_{arom}), 7.36 d (2H, H_{arom}), 7.70 s (1H, CH=), 7.81 d (2H, H_{arom})
IId	64	80	132–133	1990	1690	7.37–7.56 m (5H, H_{arom}), 7.66 s (1H, CH=), 7.86–8.05 m (4H, H_{arom})
IIe	–	80	128–129	1990	1695	7.32–7.59 m (5H, H_{arom}), 7.69–8.03 m (4H, H_{arom}), 7.70 s (1H, CH=)
IIf	–	71	85–86	1995	1690	2.26 s (3H, CH_3), 7.07–7.63 m (9H, H_{arom}), 7.68 s (1H, CH=)
IIg	61	79	102–103	2000	1690	3.80 s (3H, CH_3O), 7.70 s (1H, CH=), 7.21–7.82 m (9H, H_{arom})
IIh	56	69	71–72	1990	1690	3.38 s (3H, CH_3O), 3.61 s (3H, CH_3O), 6.69 d (1H, H_{arom}), 6.93–7.02 m (4H, H_{arom}), 7.31–7.34 m (2H, H_{arom}), 7.72 s (1H, CH=), 7.83 d (1H, H_{arom})
IIi	–	75	90–91	1990	1700	6.82–7.10 m (5H, H_{arom}), 7.19 d (1H, thiophene), 7.22 d (1H, thiophene), 8.50 s (1H, CH=), 8.59 d.d (1H, thiophene)
IIj	55	77	109–111	1995	1700	7.14–7.43 m (5H, H_{arom}), 7.40 t (1H, pyridine), 7.65 s (1H, CH=), 8.24 d.t (1H, pyridine), 8.57 d.d (1H, pyridine), 9.03 d (1H, pyridine)

Comp. no.	Found, %			Formula	Calculated, %		
	C	H	N		C	H	N
IIa	66.54	3.85	13.60	$C_{17}H_{11}N_3OS$	66.87	3.63	13.76
IIb	63.57	2.88	13.21	$C_{17}H_{10}FN_3OS$	63.31	3.12	13.00
IIc	59.88	3.14	12.52	$C_{17}H_{10}ClN_3OS$	60.09	2.97	12.37
IId	53.47	2.83	11.04	$C_{17}H_{10}BrN_3OS$	53.14	2.62	10.94
IIe	53.33	2.46	10.77	$C_{17}H_{10}BrN_3OS$	53.14	2.62	10.94
IIf	67.92	3.93	13.34	$C_{18}H_{13}N_3OS$	67.69	4.10	13.16
IIg	64.27	4.06	12.44	$C_{18}H_{13}N_3O_2S$	64.46	3.91	12.53
IIh	62.54	4.30	11.27	$C_{19}H_{15}N_3O_3S$	62.45	4.14	11.50
IIi	58.03	3.14	13.69	$C_{15}H_9N_3OS_2$	57.86	2.91	13.49
IIj	62.95	3.34	18.17	$C_{16}H_{10}N_4OS$	62.73	3.29	18.29

[a] The compounds were recrystalized from benzene–hexane mixtures: 1:1 (**IIb**), 2:1 (**IIh**), 3:1 (**IIc**, **IIi**, **IIj**), 4:1 (**IIa**, **IId**, **IIf**, **IIg**), and 5:1 (**IIe**).

(the yield was calculated from the yield of thioureas **IVb**, **IVg**, and **IVj**–**IVl** derived therefrom; see Scheme 2).

Isothiocyanates **IIa**–**IIj** (Table 1) are colorless crystalline substances. Their structure is confirmed by the data of elemental analysis and ^1H NMR and IR spectroscopy. The IR spectra of **IIa**–**IIj** contain strong absorption bands from stretching vibrations of the isothiocyanate (1900–2000 cm^{-1}) and carbonyl groups (1690–1700 cm^{-1}). In the ^1H NMR spectra of these compounds (dissolved in C_6D_6) we observed signals from aromatic and heteroaromatic substituents in

positions *1* and *3* of the pyrazole ring and a singlet from the pyrazole 5-H proton at δ 7.50–7.72 ppm.

According to published data, *N*-acylthioureas are derivatives of acyl isothiocyanates, which have found the most wide application. They are used as herbicides [10], insecticides [11], and plant growth regulators [12]. With the above in mind and taking into account the known data on high physiological activity of 4-substituted pyrazoles [13–15], we examined reactions of 4-pyrazolecarbonyl isothiocyanates **IIa**, **IIb**, **IId**, **IIe**, **IIg**, and **IIj** with amines **IIIa**–**IIIh**. The process was complete in 2 h in boiling benzene or in 3–4 h in methylene chloride at room temperature in the presence of PEG-600. As a result, the corresponding *N*-(4-pyrazolecarbonyl)thioureas **IVa**–**IVl** were obtained (Scheme 2, Table 2).

Isothiocyanates **IIa**, **IIe**, and **IIg** were brought into reaction with hydrazines **Va**–**Vc**, hydrazide **Vd**, and thiosemicarbazide **Ve**. The reactions were carried our by heating the initial compounds for 3 h in boiling

Table 2. Yields, melting points, spectral parameters, and elemental analyses of *N*-[3-aryl(heteryl)-1-phenyl-4-pyrazolecarbonyl]thioureas **IVa**–**IVl**

Comp. no.	Yield,[a] %	mp, °C (solvent)	IR spectrum, ν, cm^{-1}		^1H NMR spectrum (C_6D_6), δ, ppm
			C=O	N–H	
IVa	69	113–114 (ethanol)	1685	3260	1.76 t (2H, CH_2), 2.32–2.38 m (6H, CH_2), 3.55–3.68 m (6H, CH_2), 7.43–7.90 m (10H, H_{arom}), 9.37 s (1H, CH=), 10.85 br.s (1H, NH), 11.07 br.s (1H, NH)
IVb	75 (83)	132–133 (ethanol)	1680	3290	7.23–7.94 m (14H, H_{arom}), 9.49 s (1H, CH=), 10.44 s (1H, NH), 11.43 s (1H, NH)
IVc	76	189–190 (dioxane)	1675	3250	7.29–7.87 m (13H, H_{arom}), 9.30 s (1H, CH=), 10.32 s (1H, NH), 10.95 s (1H, NH)
IVd	69	133–135 (ethanol)	1660	3300	1.89–2.03 m (6H, CH_2), 2.76–2.82 m (4H, CH_2N), 7.47–7.64 m (10H, H_{arom}), 9.42 s (1H, CH=), 11.24 s (1H, NH)
IVe	58	232 (dioxane–water, 1:5)	1670	3260	1.88 m (4H, CH_2), 2.84 m (4H, CH_2), 3.57 m (8H, CH_2), 6.91–7.91 m (12H, H_{arom}), 9.50 s (1H, CH=), 11.54 s (1H, NH), 12.02 s (1H, NH)
IVf	62	183–185 (ethanol–water, 10:1)	1685	3300	7.32–8.11 m (17H, H_{arom}), 8.68 br.s (1H, NH), 9.25 s (1H, CH=), 10.57 s (1H, NH), 11.22 s (1H, NH)
IVg	78 (80)	180–181 (dioxane–water, 1:2)	1690	3270	7.13–7.69 m (12H, H_{arom}), 9.27 s (1H, CH=), 10.18 s (1H, NH), 10.85 s (1H, NH)
IVh	67	157–158 (ethanol–water, 5:1)	1670	3240	1.96 m (6H, CH_2), 2.77 m (4H, CH_2N), 7.34–7.72 m (9H, H_{arom}), 9.34 s (1H, CH=), 10.85 s (1H, NH)
IVi	66	184–186 (ethanol)	1680	3250	2.28–2.30 m (4H, CH_2), 3.48–3.54 m (4H, CH_2), 7.29–7.68 m (9H, H_{arom}), 9.45 s (1H, CH=), 10.14 s (1H, NH), 11.10 s (1H, NH)
IVj	75 (86)	125–126 (benzene–hexane, 5:1)	1675	3290	1.34–1.95 m (10H, CH_2), 3.81 s (3H, CH_3O), 4.18 m (1H, CH), 7.03–7.88 m (9H, H_{arom}), 9.32 s (1H, CH=), 10.75 d (1H, NH), 11.02 s (1H, NH)
IVk	65 (87)	186–187 (dioxane–water, 1:2)	1670	3260	3.75 s (1H, CH_3O), 7.12–7.74 m (12H, H_{arom}), 9.40 s (1H, CH=), 10.54 s (1H, NH), 11.08 s (1H, NH)
IVl	61 (80)	157–158 (ethanol)	1660	3230	2.80–2.84 m (4H, CH_2N), 3.52–3.57 m (4H, CH_2O), 7.21–7.48 m (6H, pyridine, H_{arom}), 8.30 d.t (1H, pyridine), 8.60 d.d (1H, pyridine), 8.89 d (1H, pyridine), 9.27 s (1H, CH=), 11.27 s (1H, NH)

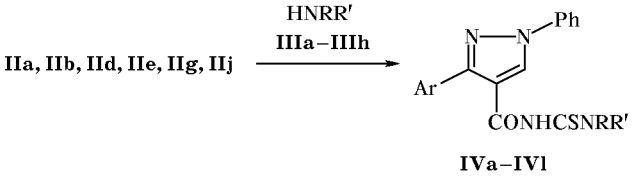
Table 2. (Contd.)

Comp. no.	Found, %			Formula	Calculated, %		
	C	H	N		C	H	N
IVa	63.83	6.26	15.42	$C_{24}H_{27}N_5O_2S$	64.12	6.05	15.58
IVb	66.50	3.85	13.17	$C_{23}H_{17}FN_4OS$	66.33	4.11	13.45
IVc	58.90	3.61	12.20	$C_{23}H_{16}Cl_2N_4OS$	59.11	3.45	11.99
IVd	67.32	5.80	14.06	$C_{22}H_{22}N_4OS$	67.67	5.67	14.35
IVe	58.99	5.03	12.16	$C_{31}H_{31}FN_6O_4S_2$	58.66	4.92	12.10
IVf	60.94	3.44	14.14	$C_{30}H_{21}BrN_6OS$	60.71	3.57	14.16
IVg	50.24	3.00	10.53	$C_{23}H_{15}BrCl_2N_4OS$	50.57	2.77	10.26
IVh	56.11	4.70	11.83	$C_{22}H_{21}BrN_4OS$	56.29	4.57	11.94
IVi	53.79	4.22	11.61	$C_{21}H_{19}BrN_4O_2S$	53.51	4.06	11.89
IVj	66.57	6.07	13.04	$C_{24}H_{26}N_4O_2S$	66.33	6.03	12.89
IVk	58.34	3.79	11.01	$C_{24}H_{18}Cl_2N_4OS$	57.95	3.65	11.26
IVl	64.62	5.29	17.84	$C_{21}H_{21}N_5OS$	64.43	5.41	17.89

[a] Method *a*; the yields obtained according to method *b* are given in parentheses.

acetonitrile. As a result, the corresponding thiosemicarbazides **VIa**–**VIj** were isolated (Scheme 3, Table 3).

Scheme 2.



IVa–IVl

III, R = H, R′ = 3-morpholinopropyl (**a**), *cyclo*-C_6H_{11} (**b**), 4-FC_6H_4 (**c**), 2,5-$Cl_2C_6H_3$ (**d**), 2-(1-pyrrolidinyl)-5-morpholinosulfonylphenyl (**e**), 2-(2-benzimidazolyl)phenyl (**f**); RR′ = $(CH_2)_5$ (**g**), $(CH_2)_2O(CH_2)_2$ (**h**); **IV**, Ar = Ph, R = H, R′ = 3-morpholinopropyl (**a**), 4-FC_6H_4 (**b**), 2,5-$Cl_2C_6H_3$ (**c**), RR′ = $(CH_2)_5$ (**d**); Ar = 4-FC_6H_4, R = H, R′ = 2-(1-pyrrolidinyl)-5-morpholinosulfonylphenyl (**e**); Ar = 3-BrC_6H_4, R = H, R′ = 2-(2-benzimidazolyl)phenyl (**f**); Ar = 4-BrC_6H_4, R = H, R′ = 2,5-$Cl_2C_6H_3$ (**g**), RR′ = $(CH_2)_5$ (**h**), $(CH_2)_2O(CH_2)_2$ (**i**); Ar = 4-$MeOC_6H_4$, R = H, R′ = *cyclo*-C_6H_{11} (**j**), 2,5-$Cl_2C_6H_3$ (**k**), Ar = 3-pyridyl, RR′ = $(CH_2)_2O(CH_2)_2$ (**l**).

EXPERIMENTAL

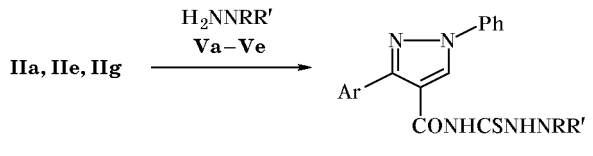
The IR spectra were recorded on a UR-20 instrument in KBr. The ^{1}H NMR spectra were obtained on a Varian Gemini spectrometer (300 MHz) using TMS as internal reference. 4-Pyrazolecarbonyl chlorides **Id** and **If**–**Ih** and the corresponding acids were synthesized by the procedure reported in [16].

3-(3-Bromophenyl)-1-phenylpyrazole-4-carboxylic acid. Yield 73%. mp 173–175°C (from acetic acid). IR spectrum, ν, cm^{-1}: 1710 (C=O), 2600–3000 (OH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.34–7.69 m (9H, H_{arom}), 9.04 s (1H, CH=). Found, %: C 56.39; H 3.06; N 8.42. $C_{16}H_{11}BrN_2O_2$. Calculated, %: C 56.00; H 3.23; N 8.16.

1-Phenyl-3-(*p*-tolyl)pyrazol-4-carboxylic acid. Yield 69%. mp 191–193°C (from acetic acid). IR spectrum, ν, cm^{-1}: 1705 (C=O), 2550–2900 (OH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.19 s (3H, CH_3), 7.21–7.64 m (9H, H_{arom}), 8.93 s (1H, CH=). Found, %: C 73.72; H 5.16; N 10.01. $C_{17}H_{14}N_2O_2$. Calculated, %: C 73.37; H 5.07; N 10.07.

3-(4-Methoxyphenyl)-1-phenylpyrazole-4-carboxylic acid. Yield 78%. mp 239–241°C (from acetic acid). IR spectrum, ν, cm^{-1}: 1700 (C=O), 2600–3050 (OH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.83 s

Scheme 3.



VIa–VIj

V, R = H, R′ = Ph (**a**), 4-hydroxy-6-methylpyrimidin-2-yl (**b**); R = R′ = $(CH_2)_2NMe(CH_2)_2$ (**c**), R = H, R′ = 4-pyridylcarbonyl (**d**), C(S)NH_2 (**e**); **VI**, Ar = Ph, R = H, R′ = Ph (**a**), 4-hydroxy-6-methylpyrimidin-2-yl (**b**), 4-pyridylcarbonyl (**c**), C(S)NH_2 (**d**); Ar = 4-BrC_6H_4, R = H, R′ = Ph (**e**), 4-pyridylcarbonyl (**f**), C(S)NH_2 (**g**); Ar = 4-$MeOC_6H_4$, R = H, R′ = Ph (**h**), RR′ = $(CH_2)_2NMe(CH_2)_2$ (**i**), 4-pyridylcarbonyl (**j**).

Table 3. Yields, melting points, IR spectra, and elemental analyses of *N*-(3-aryl-1-phenyl-4-pyrazolecarbonyl)thiosemicarbazides **VIa**–**VIj**

Comp. no.	Yield, %	mp, °C (solvent)	IR spectrum, ν, cm^{-1}		Found, %			Formula	Calculated, %		
			C=O	N–H	C	H	N		C	H	N
VIa	62	269–270 (ethanol–dioxane, 3:1)	1675	3330	66.42	4.60	17.11	$C_{23}H_{19}N_5OS$	66.81	4.63	16.94
VIb	59	292–293 (DMF)	1670	3300	59.64	4.12	22.17	$C_{22}H_{19}N_7O_2S$	59.31	4.30	22.01
VIc	70	200–201 (ethanol–dioxane, 1:5)	1670	3320	62.10	4.31	19.20	$C_{23}H_{18}N_6O_2S$	62.43	4.10	18.99
VId	73	184–185 (ethanol–DMF, 1:3)	1675	3310	54.33	3.88	21.30	$C_{18}H_{16}N_6OS_2$	54.53	4.07	21.20
VIe	61	260–261 (ethanol–dioxane, 2:1)	1680	3290	55.79	3.56	14.37	$C_{23}H_{18}BrN_5OS$	56.10	3.68	14.22
VIf	74	210–211 (ethanol–dioxane, 1:8)	1675	3315	53.13	3.03	16.31	$C_{23}H_{17}BrN_6O_2S$	52.98	3.29	16.12
VIg	68	230–232 (ethanol–DMF, 1:3)	1680	3315	45.64	3.03	17.89	$C_{18}H_{15}BrN_6OS_2$	45.48	3.18	17.67
VIh	68	252–253 (ethanol–dioxane, 3:1)	1670	3300	65.23	4.88	15.93	$C_{24}H_{21}N_5O_2S$	64.99	4.77	15.79
VIi	51	140–152 (hexane–benzene, 3:1)	1685	3320	61.60	5.96	18.49	$C_{23}H_{26}N_6O_2S$	61.31	5.82	18.65
VIj	64	180–181 (ethanol–dioxane, 1:5)	1680	3290	60.52	3.77	18.62	$C_{23}H_{17}N_6O_3S$	60.38	3.75	18.37

(3H, CH_3O); 7.84 d, 7.37–7.62 m, and 7.16 d (9H, H_{arom}); 8.97 s (1H, CH=). Found, %: C 69.18; H 4.70; N 10.11. $C_{17}H_{14}N_2O_3$. Calculated, %: C 69.38; H 4.79; N 9.52.

3-(3,4-Dimethoxyphenyl)-1-phenylpyrazole-4-carboxylic acid. Yield 71%. mp 173–175°C (from acetic acid). IR spectrum, ν, cm^{-1}: 1705 (C=O), 2650–3000 (OH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.80 s (3H, CH_3O); 3.82 s (3H, CH_3O); 7.05 d, 7.37–7.54 m, and 7.98 d (8H, H_{arom}), 9.04 s (1H, CH=). Found, %: C 66.80; H 5.12; N 8.41. $C_{18}H_{16}N_2O_4$. Calculated, %: C 66.66; H 4.97; N 8.64.

3-(3-Bromophenyl)-1-phenyl-4-pyrazolecarbonyl chloride (Id). Yield 87%. mp 100–101°C (from benzene–hexane, 2:1). Found, %: Cl+Br 32.41; N 7.45. $C_{16}H_{10}BrClN_2O$. Calculated, %: Cl+Br 31.90; N 7.75.

1-Phenyl-3-(*p*-tolyl)-4-pyrazolecarbonyl chloride (If). Yield 84%. mp 57–58°C (benzene–hexane, 1:1). Found, %: Cl 11.41; N 9.58. $C_{17}H_{13}ClN_2O$. Calculated, %: Cl 11.95; N 9.44.

3-(4-Methoxyphenyl)-1-phenyl-4-pyrazolecarbonyl chloride (Ig). Yield 90%. mp 79–80°C (benzene–hexane, 1:2). Found, %: Cl 11.69; N 8.52. $C_{17}H_{13}ClN_2O_2$. Calculated, %: Cl 11.34; N 8.96.

3-(3,4-Dimetoxyphenyl)-1-phenyl-4-pyrazolecarbonyl chloride (Ih). Yields 88%. mp 66–67°C (from benzene–hexane, 1:2). Found, %: Cl 10.91; N 8.56. $C_{18}H_{15}ClN_2O_3$. Calculated, %: Cl 10.34; N 8.17.

3-Aryl(heteryl)-1-phenyl-4-pyrazolecarbonyl isothiocyanates IIa–**IIj** (Table 1). *a.* To a solution of 0.01 mol of carbonyl chloride **Ia**, **Ib**, **Id**, **Ig**, **Ih**, or **Ij** in 40 ml of benzene we added 0.005 mol of lead(II)

thiocyanate, and the mixture was stirred for 6 h under reflux. It was then cooled, the precipitate of lead(II) chloride was filtered off, the filtrate was evaporated, and the residue was purified by recrystallization.

b. To a solution of 0.01 mol of chloride **Ia**–**Ij** in 50 ml of anhydrous acetone we added 0.01 mol of sodium thiocyanate, and the mixture was stirred for 4 h at room temperature. The precipitate of sodium chloride was filtered off, the filtrate was evaporated, and the residue was purified by recrystallization.

***N*-[3-Aryl(heteryl)-1-phenyl-4-pyrazolecarbonyl]-thioureas IVa–IVl** (Table 2). *a.* To a solution of 0.005 mol of isothiocyanate **IIa**, **IIb**, **IId**, **IIe**, **IIg**, or **IIj** in 25 ml of benzene we added 0.005 mol of amine **IIIa**–**IIIh**, and the mixture was heated for 2 h under reflux. The solvent was evaporated, and the residue was purified by recrystallization.

b. To a solution of 0.005 mol of chloride **Ia**, **Ig**, or **Ij** in 20 ml of methylene chloride we added 0.005 mol of ammonium thiocyanate and 0.1 g of PEG-600 poly(ethylene glycol), and the mixture was stirred for 3 h at room temperature. Amine **IIIb**–**IIIg** or **IIIh**, 0.005 mol, was then added, and the mixture was stirred for an additional 3 h. The solvent was removed, and the precipitate was washed with 15 ml of water, dried, and recrystallized.

***N*-(3-Aryl-1-phenyl-4-pyrazolecarbonyl)thiosemicarbazides VIa–VIj** (Table 3). To a solution of 0.002 mol of isothiocyanate **IIa**, **IIe**, or **IIg** in 10 ml of acetonitrile we added 0.002 mol of hydrazine **Va**–**Vc**, hydrazide **Vd**, or thiosemicarbazide **Ve**, and the mixture was heated for 3 h under reflux. The solvent was removed, and the precipitate was washed with 15 ml of ethanol and recrystallized.

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