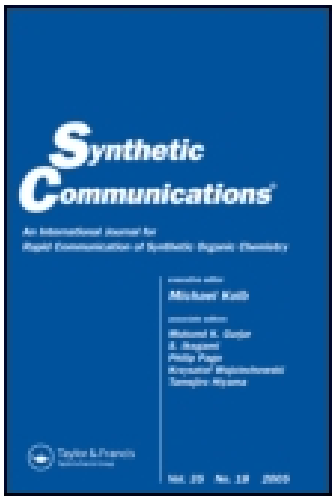

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A Convenient Synthesis of Novel 4-(1,2,4-Triazol-1-yl)-2-pyrazolines and Their Derivatives

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A Convenient Synthesis of Novel 4-(1,2,4-Triazol-1-yl)-2-pyrazolines and Their Derivatives

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ABSTRACT

Upon the study of powerful insecticidal and fungicidal properties of 1-phenylcarbamoyl-2-pyrazolines and 1,2,4-triazoles compounds, a variety of novel 4-(1,2,4-triazol-1-yl)-pyrazolines and their derivatives were prepared in good yields. The structures of these compounds were confirmed with ^{1}H NMR, MS, IR and elemental analyses.

The laboratories of Philips–Duphar (Mulder et al.) discovered 3-(4-chlorophenyl)-1-(4-chlorophenylcarbamoyl)-2-pyrazoline (PH60-41)

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was a novel, highly active insecticide in 1975.[1] Subsequently in a large number of literatures[2–6] this kind compound was reported and found a lot of good insecticides with broad spectrum, such as PH60-42,[7] RH3421[8] (Fig. 1). Results of the relationship of the structure and activity indicated the substitution in 3,4,5 positions of the pyrazline provided variety for activities, hence subsequent researches focused on this point.

In 1997, Rainer et al. reviewed the development of 2-pyrazolines.[6] They studied the relationship of the structure and the activity, and introduced heterocycles into 4-position especially, bonded via nitrogen to C-4 atom and prepared a series of azole-substituted pyrazoline. At the same time, 1,2,4-triazole is an active group in fungicides. Therefore, in a search for new insecticides and fungicides, in this article we bonded via nitrogen atom 1,2,4-triazole to C-4 atom of 2-pyrazolines and *t*-butyl to C-3 atom, and synthesized a variety of novel 4-(1,2,4-triazol-1-yl)-pyrazolines and their derivatives.

When 3,3-dimethyl-1-(1,2,4-triazol-1-yl)-2-butanone (**I_1**) was reacted with aqueous formaldehyde in piperidine and methanol, many by-products was formed and could not be separated easily.[9] We found that 4,4-dimethyl-2-(1,2,4-triazol-1-yl)-1-penten-3-one (**I_1**) was prepared by addition of formaldehyde and elimination of water as shown in Sch. 1.

α,β- unsaturated ketones (**$I_{1–3}$**) were treated with hydrazine hydrate to yield pyrazolines (**$II_{1–3}$**). We found that compound **II-1** is not stable in atmosphere, it must be stored in inert gases and in low temperature. Further condensation with isocyanate or isothiocyanate provided a variety of novel 4-(1,2,4-triazol-1-yl)-pyrazolines **$III_{1–22}$** in good yields as shown in Sch. 2. The reaction activity of isothiocyanate was much lower than isocyanate. When the compounds **II** were treated with isocyanate, the reaction could smoothly provide precipitate product, whereas the compounds **II** were treated with isothiocyanate, several drops triethylamine must be added and the reaction need above 10 h.

When 4-(1,2,4-triazol-1-yl)-pyrazoline **III_7** were reacted with methyl iodide, compound **IV** was obtained in 70% yield as shown in Sch. 2.

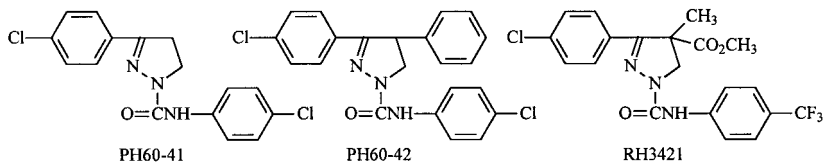
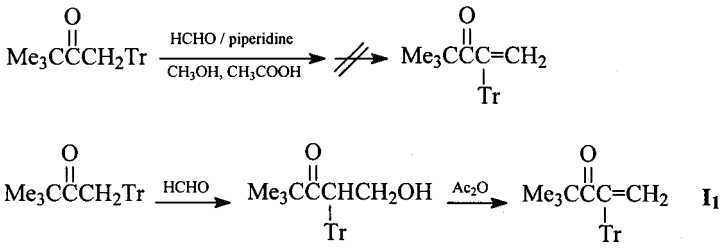
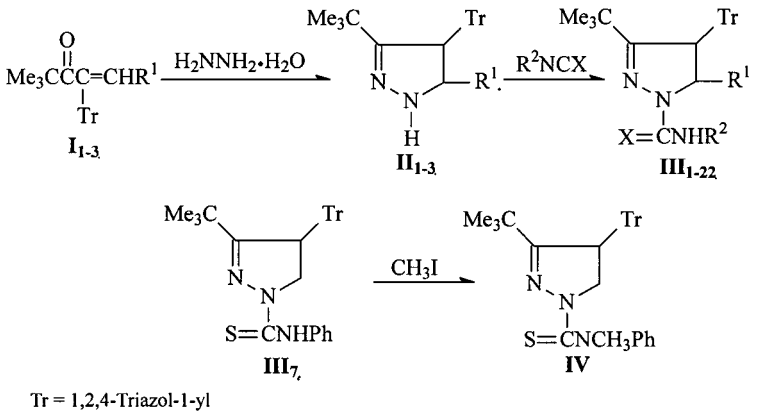


Figure 1.



Scheme 1.



Scheme 2.

All the products were white powders, and their structures were confirmed by ^{1}H NMR, MS, IR spectroscopy, and by elemental analysis. The data were listed in Table 1.

The IR spectra (KBr) of **III$_{20}$** had a strong absorption at 1672 cm^{-1}, characteristic of a carbonyl group. 3379 cm^{-1} (s) corresponds to N–H stretching absorption, 3089 and 2954 cm^{-1} were C–H stretching absorption bands.

The ^{1}H NMR data of all the products were listed in Table 2. We can see from the data, proton of the *t*-butyl, which should be at the range of 1.0–1.2. The proton of 1,2,4-triazole, which should be at the range of δ 7.5–9.5 (two single peaks). But for the *X*, it aroused the difference between the solubility in solvent. When *X* is O, we found that the title compounds could be dissolved in $CDCl_3$, whereas when *X* is S, the title

Table 1. Physical data of compounds **II–IV**.

No.	R^1	R^2	X	M.p. (°C)	Yield (%)	Elementary analysis (calcd.) (%)		
						C	H	N
II-1[a]	H	—	—	80	98.0			
II-2	4-Cl-C_6H_4	—	—	152–154	78.6	58.97 (59.29)	5.82 (5.98)	22.94 (23.05)
II-3	2,4-$Cl_2C_6H_3$	—	—	132–134	80.3	53.24 (53.26)	5.06 (5.08)	20.49 (20.71)
III-1	H	Ph	O	172–174	76.3	61.03 (61.51)	6.18 (6.47)	26.68 (26.91)
III-2	H	3-Cl-C_6H_4	O	180–182	98.0	55.04 (55.40)	5.28 (5.53)	23.90 (24.24)
III-3	H	4-Cl-C_6H_4	O	192–194	70.6	55.39 (55.40)	5.43 (5.53)	23.96 (24.24)
III-4	H	4-CH_3-C_6H_4	O	166–168	90.1	62.46 (62.54)	6.70 (6.81)	25.52 (25.75)
III-5	H	2,4-Cl_2-C_6H_3	O	210–212	92.6	50.22 (50.40)	4.66 (4.77)	21.82 (22.05)
III-6	H	3,4-Cl_2-C_6H_3	O	178–180	66.4	50.30 (50.40)	4.71 (4.77)	21.95 (22.05)
III-7	H	Ph	S	210–212	91.7	58.55 (58.51)	5.96 (6.15)	25.59 (25.59)
III-8	H	CH_2-C_6H_4	S	146–148	87.5	59.45 (59.62)	6.29 (6.49)	24.49 (24.54)
III-9	H	2-F-C_6H_4	S	186–188	98.0	55.46 (55.46)	5.45 (5.54)	23.87 (24.26)
III-10	H	4-OCH_3-C_6H_4	S	168–170	77.2	56.78 (56.95)	6.16 (6.20)	23.44 (23.45)
III-11	H	Naphthyl	S	216–218	85.9	63.45 (63.45)	5.80 (5.87)	21.95 (22.21)
III-12	H	2,4-Cl_2-C_6H_3	S	224–226	80.6	48.26 (48.36)	4.52 (4.58)	21.20 (21.15)
III-13	4-Cl-C_6H_4	4-Cl-C_6H_4	O	232–234	66.3	57.87 (57.76)	4.58 (4.86)	18.40 (18.38)
III-14	4-Cl-C_6H_4	4-CH_3-C_6H_4	O	250–252	74.5	63.25 (63.21)	5.63 (5.78)	19.04 (19.24)
III-15	4-Cl-C_6H_4	2,4-Cl_2-C_6H_3	O	176–178	69.0	53.42 (53.72)	4.29 (4.31)	16.95 (17.09)
III-16	4-Cl-C_6H_4	3,4-Cl_2-C_6H_3	O	221–223	61.3	53.39 (53.72)	3.96 (4.31)	17.03 (17.09)
III-17	2,4-Cl_2-C_6H_3	3-Cl-C_6H_4	O	280–282	75.8	53.43 (53.72)	4.29 (4.31)	17.17 (17.09)
III-18	2,4-Cl_2-C_6H_3	4-Cl-C_6H_4	O	194–196	83.2	53.48 (53.72)	4.00 (4.31)	16.86 (17.09)
III-19	2,4-Cl_2-C_6H_3	2,4-Cl_2-C_6H_3	O	226–228	85.4	50.10 (50.21)	3.76 (3.84)	16.13 (15.97)
III-20	2,4-Cl_2-C_6H_3	3,4-Cl_2-C_6H_3	O	216–218	88.5	49.98 (50.21)	4.05 (3.84)	16.00 (15.97)
III-21	2,4-Cl_2-C_6H_3	2,4-Cl_2-C_6H_3	S	202–204	75.6	48.61 (48.72)	3.62 (3.72)	15.35 (15.50)
III-22	2,4-Cl_2-C_6H_3	Naphthyl	S	230–232	46.3	59.52 (59.65)	4.87 (4.63)	16.10 (16.06)
IV	H	Ph	S	104–106	70.0	55.57 (55.31)	6.14 (6.10)	19.91 (20.16)

[a]It was so unstable that it was not test by elementary analysis.

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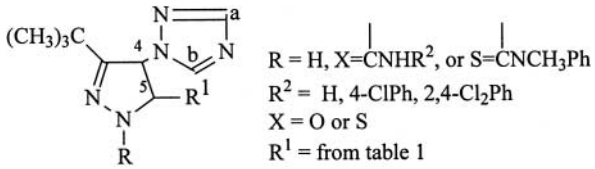
Table 2. ^{1}H NMR data of compounds **II–IV**.



No.	Solvent	Shift (δ ppm)
II-1	$CDCl_3$	1.03 (s, 9H, $(CH_3)_3$), 3.56 (dd, 2H, H_5 and $H_{5'}$), 5.56 (dt, 1H, H_4), 7.88 (s, 1H, H_a or H_b), 8.06 (s, 1H, H_a or H_b)
II-2	$CDCl_3$	1.22 (s, 9H, $(CH_3)_3$), 5.00 (d, 1H, H_5), 5.60 (d, 1H, H_4), 7.35 (s, 4H, PhH), 7.76 (s, 1H, H_a or H_b), 8.03 (s, 1H, H_a or H_b)
II-3	$CDCl_3$	1.02 (s, 9H, $(CH_3)_3$), 5.17 (d, 1H, H_5), 5.37 (d, 1H, H_4), 7.21 (m, 1H, NH), 7.20–7.42 (m, 3H, PhH), 8.04 (s, 1H, H_a or H_b), 8.85 (s, 1H, H_a or H_b)
III-1	$CDCl_3$	1.06 (s, 9H, $(CH_3)_3$), 4.18 (d, 2H, H_5 and $H_{5'}$), 5.94 (t, 1H, H_4), 7.06–7.48 (m, 5H, PhH),7.94 (s, 1H, H_a or H_b), 8.03 (s, 1H, H_a or H_b), 8.56 (s, 1H, NH)
III-2	$CDCl_3$	1.07 (s, 9H, $(CH_3)_3$), 4.18 (d, 2H, H_5 and $H_{5'}$), 5.84 (t, 1H, H_4), 7.03–7.57 (m, 4H, PhH), 7.91 (s, 1H, H_a or H_b), 7.99 (s, 1H, H_a or H_b), 8.25 (s, 1H, NH)
III-3	$CDCl_3$	1.07 (s, 9H, $(CH_3)_3$), 4.20 (d, 2H, H_5 and $H_{5'}$), 5.84 (t, 1H, H_4), 7.25–7.41 (dd, 4H, PhH), 7.88 (s, 1H, H_a or H_b), 7.99 (s, 1H, H_a or H_b), 8.28 (s, 1H, NH)
III-4	$CDCl_3$	1.09 (s, 9H, $(CH_3)_3$), 2.29 (s, 3H, *p*-CH_3), 4.20 (d, 2H, H_5 and $H_{5'}$), 5.68 (d, 1H, H_4), 7.08–7.37 (dd, 4H, PhH), 7.84 (s, 1H, H_a or H_b), 8.15 (s, 1H, H_a or H_b), 9.00 (s, 1H, NH)
III-5	$CDCl_3$	1.10 (s, 9H, $(CH_3)_3$), 4.21 (d, 2H, H_5 and $H_{5'}$), 5.92 (t, 1H, H_4), 7.22–8.30 (m, 3H, PhH), 8.02 (s, 1H, H_a or H_b), 8.26 (s, 1H, H_a or H_b), 8.68 (s, 1H, NH)

(*continued*)

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Table 2. Continued.

No.	Solvent	Shift (δ ppm)
III-6	$CDCl_3$	1.08 (s, 9H, $(CH_3)_3$), 4.21 (d, 2H, H_5 and $H_{5'}$), 5.92 (t, 1H, H_4), 7.34–8.04 (m, 3H, PhH), 7.70 (s, 1H, H_a or H_b), 7.92 (s, 1H, H_a or H_b), 8.50 (s, 1H, NH)
III-7	DMSO[a]	1.10 (s, 9H, $(CH_3)_3$), 4.24 (dd, 1H, H_5 or $H_{5'}$), 4.48 (t, 1H, H_5 or $H_{5'}$), 6.24 (dd, 1H, H_4), 7.16–7.52 (m, 5H, PhH), 8.08 (s, 1H, H_a or H_b), 8.81 (s, 1H, H_a or H_b)
III-8	DMSO[a]	0.98 (s, 9H, $(CH_3)_3$), 4.20 (dd, 1H, H_5 or $H_{5'}$), 4.40 (t, 1H, H_5 or $H_{5'}$), 4.78 (m, 2H, CH_2), 6.20 (dd, 1H, H_4), 7.31–7.34 (m, 5H, PhH), 8.05 (s, 1H, H_a or H_b), 8.78 (s, 1H, H_a or H_b)
III-9	DMSO[a]	1.00 (s, 9H, $(CH_3)_3$), 4.20 (dd, 1H, H_5 or $H_{5'}$), 4.48 (t, 1H, H_5 or $H_{5'}$), 6.28 (dd, 1H, H_4), 7.23–7.56 (m, 4H, PhH), 8.07 (s, 1H, H_a or H_b), 8.82 (s, 1H, H_a or H_b)
III-10	DMSO[a]	1.00 (s, 9H, $(CH_3)_3$), 3.75 (s, 3H, OCH_3), 4.24 (dd, 1H, H_5 or $H_{5'}$), 4.44 (t, 1H, H_5 or $H_{5'}$), 6.24 (dd, 1H, H_4), 6.92–7.34 (dd, 4H, PhH), 8.08 (s, 1H, H_a or H_b), 8.80 (s, 1H, H_a or H_b)
III-11	DMSO[a]	1.04 (s, 9H, $(CH_3)_3$), 4.28 (dd, 1H, H_5 or $H_{5'}$), 4.52 (t, 1H, H_5 or $H_{5'}$), 6.32 (dd, 1H, H_4), 7.52–7.92 (m, 7H, naphthyl H), 8.11 (s, 1H, H_a or H_b), 8.84 (s, 1H, H_a or H_b)
III-12	DMSO[a]	1.01 (s, 9H, $(CH_3)_3$), 4.24 (dd, 1H, H_5 or $H_{5'}$), 4.48 (t, 1H, H_5 or $H_{5'}$), 6.28 (dd, 1H, H_4), 7.41–7.88 (m, 4H, PhH), 8.08 (s, 1H, H_a or H_b), 8.82 (s, 1H, H_a or H_b)
III-13	$CDCl_3$	1.15 (s, 9H, $(CH_3)_3$), 5.32 (d, 1H, H_5), 5.84 (d, 1H, H_4), 7.04–7.42 (m, 8H, PhH), 7.74 (d, 2H, H_a and H_b), 8.14 (s, 1H, NH)
III-14	$CDCl_3$	1.14 (s, 9H, $(CH_3)_3$), 2.27 (s, 3H, *p*-CH_3), 5.32 (d, 1H, H_5), 5.86 (d, 1H, H_4), 7.05–7.35 (m, 8H, PhH), 7.73 (d, 2H, H_a and; H_b), 8.08 (s, 1H, NH)
III-15	$CDCl_3$	1.09 (s, 9H, $(CH_3)_3$), 5.40 (d, 1H, H_5), 5.52 (d, 1H, H_4), 7.11–8.06 (m, 7H, PhH), 8.20 (d, 2H, H_a and H_b), 8.80 (s, 1H, NH)

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III-16	$CDCl_3$	1.15 (s, 9H, $(CH_3)_3$), 5.32 (d, 1H, H_5), 5.92 (d, 1H, H_4), 7.04–7.83 (m, 7H, PhH), 7.74 (d, 2H, H_a and H_b), 8.16 (s, 1H, NH)
III-17	$CDCl_3$	1.15 (s, 9H, $(CH_3)_3$), 5.68 (d, 1H, H_5), 6.27 (d, 1H, H_4), 7.03–8.19 (m, 7H, PhH), 7.61 (s, 1H, H_a or H_b), 7.76 (s, 1H, H_a or H_b), 8.55 (s, 1H, NH)
III-18	$CDCl_3$	1.02 (s, 9H, $(CH_3)_3$), 5.74 (d, 2H, H_5 and H_4), 6.89–7.41 (m, 7H, PhH), 7.97 (s, 1H, H_a or H_b), 8.20 (s, 1H, H_a or H_b), 9.86 (s, 1H, NH)
III-19	$CDCl_3$	1.07 (s, 9H, $(CH_3)_3$), 5.67 (d, 1H, H_5), 5.80 (d, 1H, H_4), 6.97–8.20 (m, 6H, PhH), 8.25 (s, 1H, H_a or H_b), 8.80 (s, 1H, H_a or H_b), 9.22 (s, 1H, NH)
III-20	$CDCl_3$	1.05 (s, 9H, $(CH_3)_3$), 5.42 (d, 1H, H_5), 5.75 (d, 1H, H_4), 6.94–7.73 (m, 6H, PhH), 8.03 (d, 2H, H_a and H_b), 8.27 (s, 1H, NH)
III-21	$CDCl_3$	1.09 (s, 9H, $(CH_3)_3$), 5.69 (d, 1H, H_5), 6.27 (d, 1H, H_4), 6.85–8.65 (m, 6H, PhH), 8.21 (s, 1H, H_a or H_b), 9.43 (s, 1H, H_a or H_b), 9.81 (s, 1H, NH)
III-22	DMSO[a]	1.08 (s, 9H, $(CH_3)_3$), 6.14 (t, 1H, H_5), 6.80 (d, 1H, H_4), 7.26–8.24 (m, 10H, PhH), 8.55 (s, 1H, H_a or H_b), 8.80 (s, 1H, H_a or H_b)
IV	$CDCl_3$	1.09 (s, 9H, $(CH_3)_3C$,), 2.39 (s, 3H, CH_3), 4.17 (m, 2H, H_5 and $H_{5'}$), 6.00 (m, 1H, H_4), 6.70–7.43 (m, 5H, PhH), 7.95 (s, 1H, H_a or H_b), 8.26 (s, 1H, H_a or H_b)

[a]The peak of N–H could not be seen in the picture of ^{1}H NMR when used DMSO as the solvent.

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compounds could be dissolved only in DMSO. The peak of N–H could be seen in the picture of ^{1}H NMR when used $CDCl_3$ as the solvent, but not be seen when used DMSO as the solvent.

EXPERIMENTAL

General

^{1}H NMR spectra were recorded with a Bruker AC-P200 spectrometer; reported chemical shifts were in ppm (δ) relative to TMS (δ 0.00). Infrared spectra were recorded on a Shimadzu corporation chart 200-91527 instrument, using KBr plate. Mass spectra were made with a MS-7070 mass spectrometer using the EI method. Melting point were determined by using a Thomas–Hoover apparatus and uncorrected. Elemental analyses were carried out with Yanaco CHN Corder MT-3 elemental analyzer.

Synthesis of Intermediates

3,3-Dimethyl-1-(1,2,4-triazol-1-yl)-2-butanone,1-(2-chlorophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl)-1-penten-3-one (**I_2**) and 1-(2,4-dichlorophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl)-1-penten-3-one (**I_3**) were bought.

4,4-Dimethyl-2-(1,2,4-triazol-1-yl)-1-penten-3-one (I_1): Mixed 90.0 g. of 3,3-dimethyl-1-(1,2,4-triazol-1-yl)-2-butanone (0.5 mole) and 130 mL of aqueous formaldehyde (37–40%), in 30 mL water, refluxed for 4 h. After cooling the precipitate white solid formed. Collected the white solid and dried. Mixed 42.8 g of above solid (0.2 mol) and 150 mL of acetic anhydride, stirrered and heated to 106–109°C for 3 h, moved the acetic anhydride, distilled in reduced pressure. Collected 90–2°C/0.2 mm Hg 31.2 g of distillation, yielding 36%.

Synthesis of the Product II–IV

3-*t*-Butyl-5-(2,4-dichlorophenyl)-4-(1,2,4-triazol-1-yl)-2-pyrazoline (II): A mixture of 32.4 g (0.1 mol) of 1-(2,4-dichlorophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl)-1-buten-3-one (**I_3**) and 17.7 g (0.30 mol) of hydrazine hydrate in 100 mL ethanol, was refluxed for 4 h, moved the solvent, after

cooling, the precipitate white solid collected and washed with cold ether. Yield 80.3%, m.p. 132–134°C.

3-*t*-Butyl-5-(2,4-dichlorophenyl)-1-(3,4-dichlorophenylcarbamoyl)-4-(1,2,4- triazol-1-yl)-2-pyrazoline (III): To stirred suspension of 6.8 g of **II** (0.02 mol) in 50 mL of dry ether, 4.0 g of 3,4-dichlorophenyl isocyanate (0.02 mol) was added. The solution became clear and a precipitate of the reaction mixture appeared. After stirring for 2 h, the precipitate was collected and dried, recrystallized with acetonitrile, yielding 9.3 g (88.5%), of compound **III**, m.p. 216–218°C. IR: $\nu_{CO} = 1672\,cm^{-1}$, $\nu_{NH} = 3379\,cm^{-1}$, $\nu_{CH} = 3089$ and $2954\,cm^{-1}$. MS: m/z 253 (100%).

3-*t*-Butyl-1-(*N*-phenyl-*N*-methyl)thiocarbamoyl-4-(1,2,4-triazol-1-yl)-2-pyrazoline (IV): To a solution of 6.6 g of **III** (0.02 mol), in 50 mL of dimethylformamide, 1.4 g of powered potassium hydroxide (0.025 mol) was added, and stirred for 15 min, then 2.8 g of methyl iodide (0.02 mol) was added. After stirred for 0.5 h, the reaction mixture was poured into ice water. The resulting precipitate was stirred for another 2 h, and washed with methanol and petroleum ether, recrystallized with acetonitrile, yielding 70%, m.p. 104–106°C.

REFERENCES

1. Mulder, R.; Wellinga, K.; Van Daalen, J.J. Naturwissenschaften **1975**, *62*, 531–532.
2. Wellinga, K.; Grosscurt, A.C.; Van Hes, R. J. Agric. Food Chem. **1977**, *25*, 987–992.
3. Van Hes, R.; Wellinga, K.; Grosscurt, A.C. J. Agric. Food Chem. **1978**, *26*, 915–918.
4. Ozawa, K.; Nakayima, Y.; Tsugeno, M., et al. EP 058424, 1982.
5. Neh, H.; Bühmann, U.; Wegner, P., et al. EP 227055, 1987.
6. Rainer, F.; Bernd, G.; Christoph, E., et al. Pestic. Sci. **1997**, *50* (4), 333–337.
7. Grosscurt, A.C.; Van Hes; Wellinga, K. J. Agric. Food Chem. **1979**, *27*, 406–408.
8. Jacobson, R.M. US 4,663,341, 1987.
9. Chuchi Tang; Yuchang Li; Bing Chen, et al. Pestic. Chem. **1997**, 432.

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