Russian Journal of Organic Chemistry, Vol. 38, No. 10, 2002, pp. 1501–1506. Translated from Zhurnal Organicheskoi Khimii, Vol. 38, No. 10, 2002, pp. 1554–1559.

New Synthesis and Properties of 3-Alkyl-, 3-Chloroalkyl-, 3-Perfluoroalkyl-, and 3-Aryl-1-methyl-(5-halo)pyrazoles from Chloro(bromo)vinyl Ketones and *N*,*N*-Dimethylhydrazine

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Received November 7, 2001

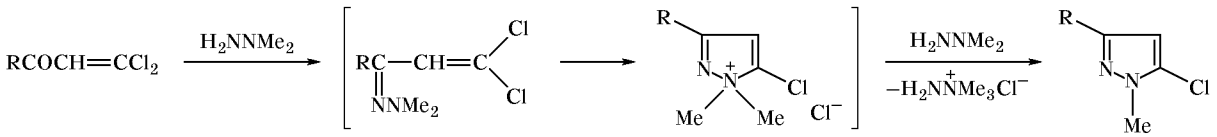
Abstract—A new regioselective heterocyclization was revealed in the reaction of 2-chloro- and 2,2-dichloro-(bromo)vinyl ketones with *N*,*N*-dimethylhydrazine to afford 3-substituted 1-methyl(5-halo)pyrazoles. The reaction is accompanied by elimination of methyl halide and formation of up to 90% of *N*,*N*,*N*-trimethylhydrazinium halide as the second product.

Pyrazoles, especially those having a halogen atom in position *5*, are promising initial compounds for the synthesis of drugs, dyes, fluorescent compositions, insecticides, insectoacaricides, and other biologically active substances [1–8]. For example, 5-chloro-1,3-dimethylpyrazole is used as starting compound for the preparation of a novel antiacaricide agent, Fenpyroximate [2, 3]. A series of pyrazolodiazocines and pyrazolodiazepines exhibiting antidepressant activity was obtained from 3-alkyl-5-chloro-5-methylpyrazoles [6, 7]; acylation of the latter gives the corresponding 4-acyl derivatives as components of fungicide compositions [8]. We can conclude that development of preparative procedures for synthesis of pyrazoles, specifically halogen-substituted pyrazoles, from accessible starting compounds is an important problem.

The known methods for synthesizing halopyrazole derivatives are laborious, they include a number of steps, and the yields of the final products are poor [4, 9–11]. 5-Chloro(bromo)pyrazoles are usualy obtained by reactions of acylacetic esters or those derived from alkylacetylenecarboxylic acids with hydrazine or methylhydrazine; 5-pyrazolones thus formed are treated with phosphorus halides [4, 9–11]. However, the reaction of methylhydrazine with acetylacetic esters gives 3-substituted 1-methylpyrazol-5-ones in low yield, and the process is accompanied by formation of isomeric products. It should also be noted that the possibilities for preparation of 3-alkyl-1-methylpyrazol-5-ones from methylhydrazine and methyl alkylacetylenecarboxylates are limited by difficulties in the synthesis of appropriate alkylacetylenecarboxylic acids.

We previously proposed a procedure for preparation of 1,3-disubstituted pyrazoles from 2-chlorovinyl ketones and arylhydrazines [12]. On the other hand, 2,2-dichlorovinyl ketones which are also fairly accessible products [12–14] failed to react with phenyl- or dinitrophenylhydrazine to give pyrazole derivatives;

Scheme 1.



I–XIII

I, R = Me; **II**, R = Et; **III**, R = Pr; **IV**, R = *i*-Pr; **V**, R = CH_2Cl; **VI**, R = CF_3; **VII**, R = Ph; **VIII**, R = 4-MeC_6H_4; **IX**, R = 4-$MeOC_6H_4$; **X**, 4-BrC_6H_4; **XI**, R = 4-ClC_6H_4; **XII**, R = 4-$NO_2C_6H_4$; **XIII**, R = 3-$NO_2C_6H_4$.

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Table 1. Yields, physical properties, and elemental analyses of pyrazoles **I**–**XVI**

Comp. no.	Yield, %	bp, °C (*p*, mm) [mp, °C]	d_4^{20} (n_D^{20})	Found, %				Formula	Calculated, %			
				C	H	Cl	N		C	H	Cl	N
I[a]	64	157.5–158	1.1400 (1.4855)	45.89	5.63	29.95	21.65	$C_5H_7ClN_2$	45.99	5.40	27.15	21.45
II[a]	71	40 (1)	1.1808 (1.4848)	50.03	6.14	24.44	19.60	$C_6H_9ClN_2$	49.84	6.27	24.52	19.37
III[a]	77	67 (2)	(1.4832)	53.00	6.99	22.35	17.66	$C_7H_{11}ClN_2$	52.79	7.23	22.49	17.54
IV	70	76 (17–18)	(1.4833)	53.68	7.12	21.98	17.57	$C_7H_{11}ClN_2$	52.79	7.23	22.49	17.54
V	77	[33–33.5]	–	36.38	3.69	43.10	16.84	$C_5H_6Cl_2N_2$	36.39	3.66	42.97	16.97
VI[b]	45	140–141	1.4927 (1.4184)	32.39	2.12	18.97	15.33	$C_5H_4ClF_3N_2$	32.54	2.18	19.21	15.18
VII[a]	62	[60–62]	–	62.81	5.00	18.71	14.27	$C_{10}H_9ClN_2$	62.35	4.71	18.40	14.54
VIII	89	[98.5–100.5]	–	63.33	5.11	17.75	15.39	$C_{11}H_{11}ClN_2$	63.93	5.36	17.15	15.55
IX	69	[74–77]	–	59.03	4.77	16.04	12.59	$C_{11}H_{11}ClN_2O$	59.33	4.98	15.92	12.58
X	66	[103–106]	–	44.13	3.09		9.59	$C_9H_8BrClN_2$	44.23	2.97	13.06	10.32
XI	89	[89–91]	–	53.00	3.45	30.98	12.38	$C_{10}H_8Cl_2N_2$	52.89	3.55	31.22	12.34
XII	65	[160–161]	–	51.04	3.22	14.87	17.97	$C_{10}H_8ClN_3O_2$	50.54	3.39	14.92	17.68
XIII	87	[105–106.5]	–	50.45	3.31	14.82	17.47	$C_{10}H_8ClN_3O_2$	50.54	3.39	14.92	17.68
XIV[c]	70	145	(1.5210)	26.34	1.79	–	12.43	$C_5H_4BrF_3N_2$	26.22	1.76	–	12.23
XV[a]	64	136	1.4674 (0.9626)	62.03	8.06	–	29.19	$C_5H_8N_2$	62.47	8.29	–	29.14
XVI	70	146–148	1.5275	45.78		5.24	21.47	$C_5H_7ClN_2$	45.99	5.40		21.45

[a] Compounds **I**–**III**, **VII**, and **XV** were described previously (see Experimental).

[b] Found, %: F 29.89. Calculated, %: F 30.88.

[c] Found, %: Br 34.89; F 24.89. Calculated, %: Br 34.62; F 25.00.

the corresponding pyrazole was obtained only by heating of dichlorovinyl phenyl ketone 2,4-dinitrophenylhydrazone at the melting point [15]. We also described a single example [16] of the isolation of a 3-methylpyrazole derivative in the reaction of methyl 2,2-dichlorovinyl ketone with excess hydrazine; however, this result has not received further confirmation.

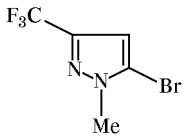
While performing the present study, we have found that alkyl, aryl, chloroalkyl, and perfluoroalkyl 2,2-dichlorovinyl ketones react with 1,1-dimethylhydrazine to afford the corresponding 3-substituted 5-chloro-1-methylpyrazoles **I**–**XIII** (Scheme 1) in good yields. The second reaction product is trimethylhydrazinium chloride. The reactions were carried out in an organic solvent: hexane, benzene, lower alcohols, diethyl ether, or acetonitrile; the reactant ratio was 1:2. The process was accompanied by heat evolution, and the products were isolated by standard techniques.

The reaction mechanism is likely to involve initial formation of 2-chlorovinyl ketone dimethylhydrazone and subsequent intramolecular nucleophilic attack by the dimethylamino group on the β-carbon atom of the vinyl group. *N*,*N*-Dimethylpyrazolium chloride thus formed undergoes demethylation to give the final product (Scheme 1).

The structure of pyrazoles **I**–**XIII** was proved by spectral methods and elemental analysis (Tables 1–3). The second product, 1,1,1-trimethylhydrazinium chloride, is a crystalline water-soluble substance [17] from which dimethylhydrazine can be regenerated. On the other hand, trimethylhydrazinium chloride itself may be utilized in other chemical processes or used in medicine and agriculture [17, 18].

It is known [19, 20] that 1,1-dimetylhydrazine reacts with carbonyl compounds, including unsaturated ones, to give the corresponding hydrazones. Elokhina *et al.* [21] reported on the formation of a quaternary dimethylhydrazinum salt, 1-[1-bromo-2-benzoyl(2-thenoyl)vinyl]-1,1-dimethylhydrazinium bromide in the reaction of 1,1-dimethylhydrazine with bromoacetylenic ketones. According to the authors, this is the result of reaction of intermediate 2,2-dibromovinyl phenyl(thienyl) ketones with 1,1-dimethyl-

hydrazine. Contrastingly, by reaction of dimethylhydrazine with 2,2-dibromovinyl trifluoromethyl ketone [22] we obtained 5-bromo-1-methyl-3-trifluoromethylpyrazole (**XIV**) (Tables 1–3). The reaction was also accompanied by heat evolution and formation of 1,1,1-trimethylhydrazinium bromide.



XIV

Likewise, while studying the reaction of chlorovinyl ketones with dimethylhydrazine we discovered a new route to 3-substituted 1-methylpyrazoles. 2-Chlorovinyl methyl ketone and 2-chlorovinyl chloromethyl ketone reacted with 1,1-dimethylhydrazine to give the corresponding 1-methylpyrazoles **XV** and **XVI** in up to 70% yield and 1,1,1-trimethylhydrazinium chloride (Scheme 2). It should be emphasized that the reaction between equimolar amounts of mono- or dihalovinyl ketones with dimethylhydrazine also gives pyrazoles and trimethylhydrazinium halides, but unreacted initial ketone remains in the reaction mixture. This may be due to partial deactivation of dimethylhydrazine as a result of quaternization with liberated methyl chloride; on the other hand, demethylation of dimethylpyrazolium salts can also be effected by dimethylhydrazine which is thus converted into inactive hydrazinium halide.

Prior to our present study, 3-methyl-, 3-ethyl-, 3-propyl-, and 3-phenyl-5-chloro-1-methylpyrazoles have already been reported [4, 10, 11], but their chemical and physical properties have been studied poorly; in some cases only the boiling points are available [4]. We have examined the IR and NMR spectra of pyrazoles **I**–**XIV** and **XVI**, and studies of their chemical transformations (such as acylation, nitration, sulfonation, etc.) are now in progress.

The IR spectra of 5-bromo-, 5-chloro-, and 5-unsubstituted 1-methylpyrazoles are characterized by absorption in the region 3120–3150 cm^{-1}, which belongs to stretching vibrations of the C^4-H bond. The corresponding frequency increases in going to 3-arylpyrazoles **VII**–**XIII** and those having an electron-acceptor group on C^3 (compounds **V**, **VI**, and **XIV**). Absorption of the endocyclic C=C bond appears at 1480–1510 cm^{-1}.

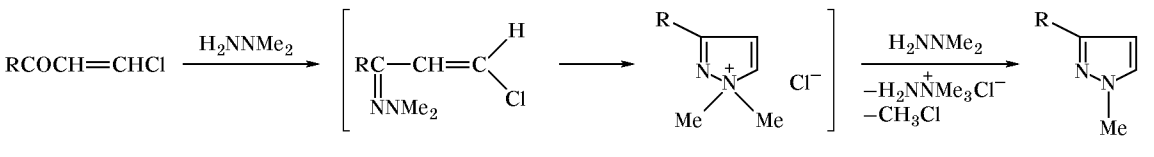
In the ^1H NMR spectra of pyrazoles **I**–**XIII**, resonance signals of the 4-H proton are observed in the

Table 2. IR spectra of pyrazoles **I**–**XIV** and **XVI**[a]

Comp. no.	C–Cl	C=C	N–CH_3 (R = Alk)	=C–H
I	770	1510	2950	3125
II	770	1510	2925	3120
III	770	1510	2860, 2920, 2950	3120
IV	775	1500	2860–2950	3120
V	770, 790	1505	2940, 2975	3130
VI	790	1480	2960	3150
VII	780	1490	2940	3127, 3060, 3030
VIII	780	1490	2920	3145
IX	790	1500, 1600	2840, 2910, 2940, 2950	3130
X	790	1500	2950	3130
XI	790	1500	2950	3135, 3060, 3090
XII	770	1510, 1600	2940	3140, 3100, 3080, 3050
XIII	760	1500	2940	3100, 3130, 3050, 3070
XIV	–	1470	2950	3145
XVI	760	1510	2930, 2950	3130

[a] The IR spectra of compounds **I**–**IV**, **VI**, **XIV**, and **XVI** were recorded from samples prepared as thin films, and of **V** and **VII**–**XIII**, from samples pelleted with KBr.

Scheme 2.



XV, XVI

XV, R = Me; **XVI**, R = CH_2Cl.

Table 3. ^{1}H, ^{13}C, ^{15}N, and ^{19}F chemical shifts (δ, ppm) and coupling constants (*J*, Hz) in the NMR spectra of pyrazoles **I**–**XIV** and **XVI** in $CDCl_3$

Comp. no.	^{1}H			^{15}N		^{13}C				
	NCH_3	5-H	3-R	N^2	N^1	C^3	C^4	C^5	NCH_3	others
I	3.72	5.94	2.19			148.13	103.87	127.16	35.66	13.80 (CH_3)
II	3.73	5.92	0.91 t, 2.45 q							
III	3.74	5.97	0.93 t, 1.61 m, 2.51 t	–78.4	–188.2	152.95	103.10	127.09	35.84	22.79, 30.69, 13.86 (C_3H_7)
IV	3.73	5.99	1.20 d, 2.89 m							
V	3.78	6.24	4.48	–74.4	–183.8	118.40	103.97	127.86	35.99	38.61 (CH_2Cl)
VI[a]	3.88	6.46		–74.3	–178.5	141.80 q ($^{2}J_{CF}$ = 38.7)	103.40	128.88	36.78	121.69 q (CF_3) ($^{1}J_{CF}$ = 169.1)
VII	3.81	6.44	7.29–7.64 m			150.94	101.84	128.00	36.34	
VIII	3.85	6.44	2.34 (CH_3), 7.17 d, 7.59 d (8.1)	–81.6	–184.8	150.96	101.63	128.09	36.30	125.28, 130.10, 129.43, 137.92
IX	3.79	6.39	3.82 (CH_3O), 6.89 d, 7.63 d (8.8)	–82.8	–185.3	150.75	101.30	128.05	36.20	55.34 (OCH_3); 126.65, 114.13, 132.78, 159.68
X	3.85	6.44	7.48 d, 7.57 d (8.4)	–80.3	–183.2	149.54	101.66	128.26	36.24	131.69, 121.86, 126.76
XI	3.81	6.40	7.28 d, 7.19 d (8.7)	–81.6	–184.8	149.81	101.86	128.00	36.42	133.91, 131.45, 128.95, 126.66
XII[b]	3.90	6.58	7.87 d, 8.23 d (8.7)	–76.8	–180.0	148.45	102.83	129.11	36.66	124.05, 124.18, 125.78, 139.04, 147.40
XIII[b]	3.90	6.58	7.55 d.d (8.0), 8.13 d (8.0), 8.06 d.d (8.0, 1.8), 8.51 d (1.8)	–78.0	–181.3	148.51	102.31	129.73	36.63	120.30, 122.68, 128.85, 131.00, 134.72, 148.65
XIV		3.91	6.54 ($^{2}J_{CF}$ = 39.1)	–	–	142.57 q	107.13	114.62	38.19	120.67 q ($^{1}J_{CF}$ = 268.7)
XVI	3.86	6.27 d (1.6)	4.58 (CH_2Cl); 7.32 d (4-H, 1.6)	–74.8	–181.2	148.37	105.08	130.97	38.62	76.83

[a] $\delta_F(CF_3)$ –63.4 ppm (relative to CCl_3F).

[b] $\delta_N(NO_2)$ –11.2 (**XII**), –11.1 ppm (**XIII**) (relative to CH_3NO_2).

region δ 5.6–6.9 ppm. In going from 3-alkylpyrazoles **I**–**IV** to derivatives containing electron-acceptor (CF_3, CH_2Cl) or aryl group on C^3, the 4-H signal shifts downfield. An analogous but less distinct tendency is observed for signals from the NCH_3 protons. The 4-H signal of 5-bromo-1-methyl-3-trifluoromethylpyrazole (**XIV**) is also displaced slightly downfield relative to the corresponding signal of its 5-chloro analog **VI**. In the ^{1}H NMR spectra of 5-unsubstituted pyrazoles **XV** and **XVI**, the 5-H signal appears in a much weaker field than 4-H (Table 3).

The positions of the C^4 and C^5 signals in the ^{13}C NMR spectra of compounds **I**–**XIII** change only slightly ($\Delta\delta_C$ ~3 ppm) on variation of the substituent on C^3. Their chemical shifts fall into the same regions as those found for 1-methylpyrazole (δ_C 105.7 and 128.7 ppm, respectively) [23]. Naturally, the chemical shift of C^3 changes over a wider range ($\Delta\delta_C$ ~35 ppm;

Table 3). Variations of the N^1 and N^2 chemical shifts in the ^{15}N NMR spectra of 5-chloropyrazoles **I**–**XIII** are about 10 and 8 ppm, respectively. Electron-acceptor substituents in position *3* induce a downfield shift of the N^1 signal (Table 3). It is known that shielding of the pyrrole-type nitrogen atom in azoles is much stronger, as compared to the pyridine-type nitrogen atom [24]. In fact, the chemical shifts of N^1 fall into the range from –178 to –188 ppm, while the N^2 signals are displaced downfield by ~100 ppm.

Pyrazoles **I**–**XI** and **XIV**–**XVI** are colorless liquids or crystalline powders having a specific mould odor which is typical of pyrazole and its derivatives. Nitrophenyl-substituted pyrazoles **XII** and **XIII** are light orange powders. The products are readily soluble in organic solvents and insoluble in water.

Thus the proposed procedure for preparation of 3-alkyl-, 3-aryl-, 3-chloroalkyl-, and 3-perfluoroalkyl-5-chloro-1-methylpyrazoles and [5-chloro(bromo)]-1-methyl-3-trifluoromethylpyrazoles utilizes readily accessible initial compounds or those produced on a large scale; it requires neither special equipment nor catalyst and is simple; therefore, it can be applied for large-scale syntheses. We are now studying the scope of application of this procedure. It seems important to examine the effect of ketone conformation, dialkylhydrazine structure, and nature of the halogen atom in initial halovinyl ketones on the reaction direction.

EXPERIMENTAL

The ^1H, ^{13}C, ^{15}N, and ^{19}F NMR spectra were recorded on Bruker DPX-400 (400.6, 100.61, 40.56, and 376 MHz, respectively) and Jeol FX-90Q instruments (90 MHz for ^1H and 84 MHz for ^{19}F). Hexamethyldisiloxane was used as internal reference for ^1H and ^{13}C NMR spectra. The IR spectra were measured on a Specord 75IR spectrometer.

5-Chloro-1,3-dimethylpyrazole (I). 4,4-Dichloro-3-buten-2-one, 13.9 g (0.1 mol), was slowly added in a dropwise manner to a solution of 12.0 g (0.2 mol) of *N*,*N*-dimethylhydrazine in 50–100 ml of dry hexane. When the exothermic reaction was over, the mixture was stirred for 1–2 h, and the precipitate of 1,1,1-trimethylhydrazinium chloride was filtered off and dried under reduced pressure over P_2O_5. Yield 9.68 g (88%). mp 261–262°C; published data [17]: mp 245°C (decomp.; from EtOH–EtOAc). IR spectrum, ν, cm^{-1}: 3200, 3100, 3005, 2700 (N–H); 2950 (CH_3); 1480, 1630 (C–N). ^1H NMR spectrum (CD_3OD), δ, ppm: 3.41 (NMe). Found, %: C 32.58; H 10.24; Cl 31.97; N 25.37. $C_3H_{11}ClN_2$. Calculated, %: C 32.58; H 10.03; Cl 32.06; N 25.33. The filtrate was distilled to obtain 8.36 g of pyrazole **I**. bp 156–157.5°C; published data [10, 11]: bp 158°C, $n_D^{17.6}$ = 1.4841, $d_4^{17.6}$ = 1.1367.

When the reaction of *N*,*N*-dimethylhydrazine with 2,2-dichlorovinyl methyl ketone (reactant ratio 2 : 1) was performed in benzene, ether, acetonitrile, or lower alcohols (metanol, ethanol, or 2-propanol), other conditions being equal, pyrazole **I** was obtained in 63–68% yield. Pyrazoles **II**–**XIV** were synthesized in a similar way (Tables 1–3).

5-Chloro-3-ethyl-1-methylpyrazole (II) was synthesized from 7.54 g (0.125 mol) of *N*,*N*-dimethylhydrazine and 8.72 g (0.0627 mol) of 4,4-dichloro-3-penten-2-one. 1,1,1-Trimethylhydrazinium chloride, 8.85 g (80%), was isolated. Yield of pyrazole **II** 6.4 g; published data [4]: bp 82–83°C (28 mm).

5-Chloro-1-methyl-3-propylpyrazole (III) was synthesized from 12 g (0.2 mol) of *N*,*N*-dimethylhydrazine and 16.7 g (0.1 mol) of 1,1-dichloro-1-hexen-2-one in 50 ml of 2-propanol. Yield 13 g. Published data [4]: bp 78–79°C (10 mm).

5-Chloro-3-isopropyl-1-methylpyrazole (IV) was obtained from 12 g (0.2 mol) of *N*,*N*-dimethylhydrazine and 16.7 g (0.1 mol) of 1,1-dichloro-4-methyl-1-penten-3-one in 100 ml of diethyl ether. Yield 12.7 g.

5-Chloro-3-chloromethyl-1-methylpyrazole (V) was synthesized from 12 g (0.2 mol) of *N*,*N*-dimethylhydrazine and 17.3 g (0.1 mol) of 1,4,4-trichloro-3-buten-2-one in 100 ml of benzene. Yield 13 g.

5-Chloro-1-methyl-3-trifluoromethylpyrazole (VI) was synthesized from 7.44 g (0.1238 mol) of *N*,*N*-dimethylhydrazine and 10.97 g (0.0619 mol) of 4,4-dichloro-1,1,1-trifluoro-3-buten-2-one in 40–50 ml of anhydrous acetonitrile. Yield 5.46 g.

5-Chloro-1-methyl-3-phenylpyrazole (VII) was synthesized from 12 g (0.2 mol) of *N*,*N*-dimethylhydrazine and 20.2 g (0.1 mol) of 3,3-dichloro-1-phenyl-2-propen-1-one in 100 ml of dry diethyl ether. Yield 5.46 g. mp 60–62°C [9].

5-Chloro-1-methyl-3-(4-tolyl)pyrazole (VIII) was synthesized from 12 g (0.2 mol) of *N*,*N*-dimethylhydrazine and 21.1 g (0.1 mol) of 3,3-dichloro-1-(4-tolyl)-2-propen-1-one in 100 ml of anhydrous diethyl ether. Yield 18.39 g, mp 60–62°C [9].

5-Chloro-3-(4-methoxyphenyl)-1-methylpyrazole (IX) was synthesized from 12 g (0.2 mol) of *N*,*N*-dimethylhydrazine and 22.9 g (0.1 mol) of 3,3-dichloro-1-(4-methoxyphenyl)-2-propen-1-one in 100 ml of anhydrous ether. Yield 15.36 g.

3-(4-Bromophenyl)-5-chloro-1-methylpyrazole (X) was synthesized from 12 g (0.2 mol) of *N*,*N*-di-

methylhydrazine and 27.9 g (0.1 mol) of 1-(4-bromophenyl)-3,3-dichloro-2-propen-1-one in 100 ml of anhydrous ether. Yield 17.92 g.

5-Chloro-3-(4-chlorophenyl)-1-methylpyrazole (XI) was synthesized from 4.6 g (0.02 mol) of 2,2-dichlorovinyl 4-chlorophenyl ketone and 2.4 g (0.04 mol) of *N*,*N*-dimethylhydrazine in 50 ml of anhydrous ether. Yield 4.04 g.

5-Chloro-1-methyl-3-(4-nitrophenyl)pyrazole (XII) was synthesized from 4.92 g (0.02 mol) of 2,2-dichlorovinyl 3-nitrophenyl ketone and 2.4 g (0.04 mol) of *N*,*N*-dimethylhydrazine in 50 ml of anhydrous ether. Yield 3.90 g.

5-Chloro-1-methyl-3-(3-nitrophenyl)pyrazole (XIII) was synthesized from 4.92 g (0.02 mol) of 2,2-dichlorovinyl 3-nitrophenyl ketone and 2.4 g (0.04 mol) of *N*,*N*-dimethylhydrazine in 50 ml of anhydrous ether. Yield 4.12 g.

5-Bromo-1-methyl-3-trifluoromethylpyrazole (XIV) was synthesized in a similar way from 2.70 g (9.5 mmol) of 2,2-dibromovinyl trifluoromethyl ketone and 1.2 g (1.9 mmol) of *N*,*N*-dimethylhydrazine. Yield 1.5 g. The product was purified by distillation.

1,3-Dimethylpyrazole (XV). Likewise, from 1.2 g of *N*,*N*-dimethylhydrazine and 1.04 g of 4-chloro-3-buten-2-one in 50–100 ml of anhydrous hexane we obtained 0.9 g of 1,1,1-trimethylhydrazinium chloride and 0.84 g (64%) of pyrazole **XV**. bp 136–138°C, n_D^{20} = 1.4674, d_4^{20} = 0.9626; published data [25]: bp 136°C, $n_D^{16.2}$ = 1.46769, $d_4^{16.2}$ = 0.9628.

3-Chloromethyl-1-methylpyrazole (XVI). From 1.20 g of *N*,*N*-dimethylhydrazine and 1.39 g of 1,4-dichloro-3-buten-2-one in 50–100 ml of anhydrous ether we obtained 0.96 g (88%) of 1,1,1-trimethylhydrazinium chloride. The filtrate was purified by column chromatography on silica gel to isolate pyrazole **XVI**. Yield 0.91 g.

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