ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 8, pp. 1194–1199. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © G.V. Bozhenkov, V.A. Savosik, L.V. Klyba, E.R. Zhanchipova, A.N. Mirskova, G.G. Levkovskaya, 2008, published in Zhurnal Organicheskoi Khimii, 2008, Vol. 44, No. 8, pp. 1207–1212.

1-Alkylpyrazoles and 1-Alkyl-5-chloropyrazoles from Halovinyl Ketones and 1,1-Dialkylhydrazines

G. V. Bozhenkov, V. A. Savosik, L. V. Klyba, E. R. Zhanchipova, A. N. Mirskova, and G. G. Levkovskaya

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: ggl@irioch.irk.ru

Received January 5, 2008

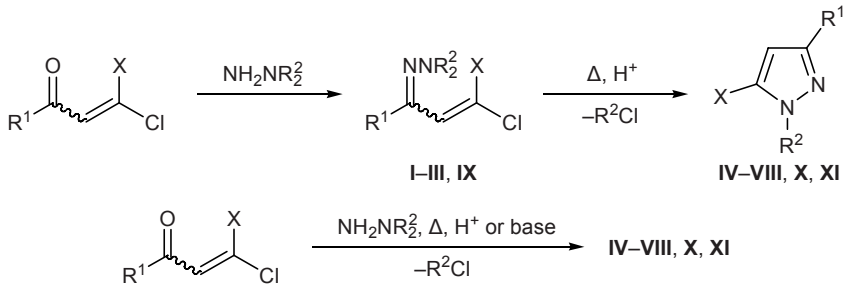
Abstract—Regioselective heterocyclization of alkyl 2-chloro- and 2,2-dichlorovinyl ketones with 1,1-dialkylhydrazines to 1,3-dialkyl-1*H*-pyrazoles and 1,3-dialkyl-5-chloro-1*H*-pyrazoles involves intermediate formation of the corresponding dialkylhydrazones. Fragmentation pattern of chlorine-containing pyrazoles, 3-chloromethyl-1-methyl-1*H*-pyrazole and 5-chloro-1-methyl-3-propyl-1*H*-pyrazole, depends on the position of the halogen atom.

DOI: 10.1134/S1070428008080150

Development of the chemistry of pyrazoles on the whole and specifically of halogen-containing pyrazoles is stimulated by broad spectrum of useful properties of these compounds. For example, they are used as intermediate products in the synthesis of dyes, materials for optoelectronics, pesticides, medicines, etc.; in addition, they attract interest due to diversity of their chemical transformations [1–8].

Systematic studies in the field of reactivity of halovinyl ketones showed that 1,3-dialkyl- and 1-alkyl-5-chloro(bromo)-3-alkyl(aryl, chloroalkyl, perfluoroalkyl)pyrazoles are formed by reactions of the corresponding methyl, ethyl, and chloromethyl 2-chlorovinyl ketones with 1,1-dimethyl-, 1,1-diethyl-, and 1,1-dibutylhydrazines [9, 10], as well as from 2,2-dichloro(bromo)vinyl ketones and 1,1-dimethylhydrazine [11]. The proposed mechanism of this reaction involved initial formation of the corresponding halo enone dimethyl- and alkylhydrazones, followed by intramolecular nucleophilic attack by the dimethyl(alkyl)amino group on the β-carbon atom of the vinyl group [9–11]. An alternative mechanism with initial formation of quaternary 1-(1-halo-2-acylvinyl)-1-dimethylhydrazinium halides and subsequent heterocyclization seemed to be improbable, for quaternary salts obtained from 1,1-dimethylhydrazine and bromoacetylenic ketones, 1-[1-bromo-2-benzoyl(2-thenoyl)vinyl]-1,1-dimethylhydrazinium bromides (their structure was determined by X-ray analysis), failed to undergo cyclization to pyrazoles [12]. It should be emphasized that neither dialkylhydrazones nor dihydropyrazolium salts were isolated or detected in the

Scheme 1.



Base = $NH_2NR^2_2$, NEt_3; **I**–**VIII**, X = H; **IX**–**XI**, X = Cl; **VI**, **IV**, R^1 = Me, R^2 = Bu; **II**, **V**, **XI**, R^1 = Pr, R^2 = Me; **III**, **VI**, **IX**, **X**, R^1 = Pr, R^2 = Bu; **VII**, $R^1 = R^2$ = Me; **VIII**, $R^1 = ClCH_2$, R^2 = Me.

reactions of halo enones with 1,1-dimethylhydrazine [9–11].

In the present work we continued our studies on reactions of 1-chloro- and 2,2-dichlorovinyl ketones with 1,1-dialkylhydrazines with a view to obtain new 1-alkyl-substituted pyrazoles and refine the mechanism of their formation. We were the first to find conditions for the synthesis of 2-chlorovinyl ketone dimethyl-(butyl)hydrazones **I**–**III** and isolate them as individual substances. The reactions were carried out by mixing equimolar amounts of the reactants in an organic solvent at –40 to 0°C (reaction time 1–3 h). Hydrazone **III** was also obtained by reaction of 1,1-dibutylhydrazine with an equimolar amount of 2-chlorovinyl propyl ketone in diethyl ether at room temperature. By reacting 2,2-dichlorovinyl propyl ketone with 1,1-dibutylhydrazine at –10 to 0°C we succeeded in obtaining the corresponding hydrazone **IX** containing no more than 5% of pyrazole **X** (Scheme 1). Presumably, the different conditions for the synthesis of 2-chloro- and 2,2-dichlorovinyl ketone dimethyl- and dibutylhydrazones are determined by steric factors.

In the reactions of 1,1-dimethylhydrazine with 2-chloro- and 2,2-dichlorovinyl ketones (reactant ratio 1:1) in alcohol, diethyl ether, and other solvents without cooling, the corresponding dimethylhydrazones were not isolated, and the products were 1-methylpyrazoles **IV**–**VIII**, **X**, and **XI**, while the conversion of the initial halo enone was not complete. No dimethylhydrazone was formed in the reaction of 2,2-dichlorovinyl propyl ketone with 1,1-dimethylhydrazine at –40°C; in this case, we isolated 5-chloro-1-methyl-3-propyl-1*H*-pyrazole (**XI**) in no more than 35% yield and the initial ketone.

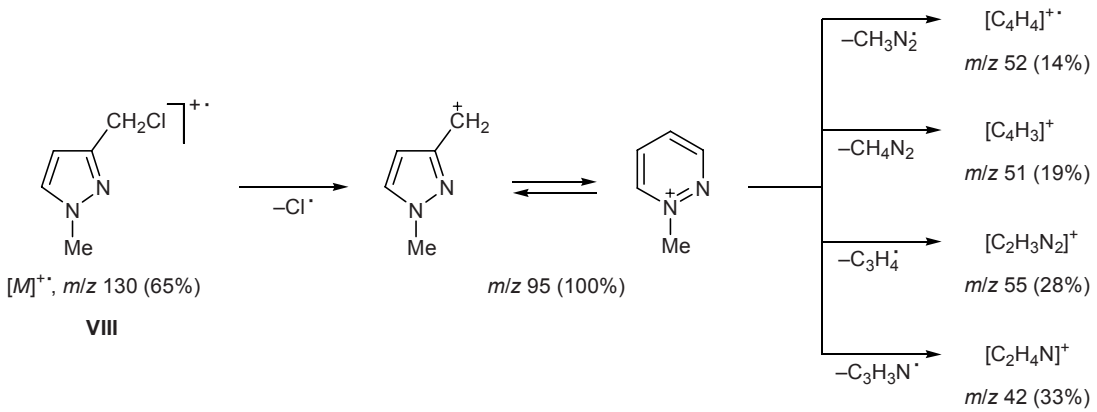
1,1-Dimethyl- and 1,1-dibutylhydrazones **I**–**III** and **IX** readily undergo intramolecular cyclization to the corresponding pyrazoles **IV**–**VIII** and **X** on heating in organic solvents in the presence of acids or in acetic acid. When hydrazones **I**–**III** and **IX** were heated in the absence of acid the reaction was accompanied by decomposition, and pyrazoles **IV**–**VI** and **X** were formed in a poor yield.

Presumably, the role of acid in the cyclization of hydrazones to pyrazoles **IV**–**VIII** and **X** is not only promotion of isomerization of the *E-s-trans*-hydrazine conformer into *Z-s-cis* whose configuration is favorable for heterocyclization (as with halo enone dinitrophenylhydrazones [13]) but also electrophilic assistance to nucleophilic attack on the double bond by the amino nitrogen atom of the hydrazone fragment. Acid protonates the C=N nitrogen atom in the hydrazone, and electron-withdrawing effect of the $C=N^{+}H$ group is transmitted through the conjugated bond system to enhance electrophilicity of the β-carbon atom at the double C=C bond thus facilitating nucleophilic attack at that atom.

Pyrazoles **IV**–**VIII** and 5-chloropyrazole **X** can also be obtained in good yields by exothermic reaction of 2-chloro- and 2,2-dichlorovinyl ketones with 2 equiv of 1,1-dialkylhydrazine or in the presence of a base which is required to bind methyl or butyl chloride liberated during the heterocyclization process; as a result, the yield of the target pyrazoles increases.

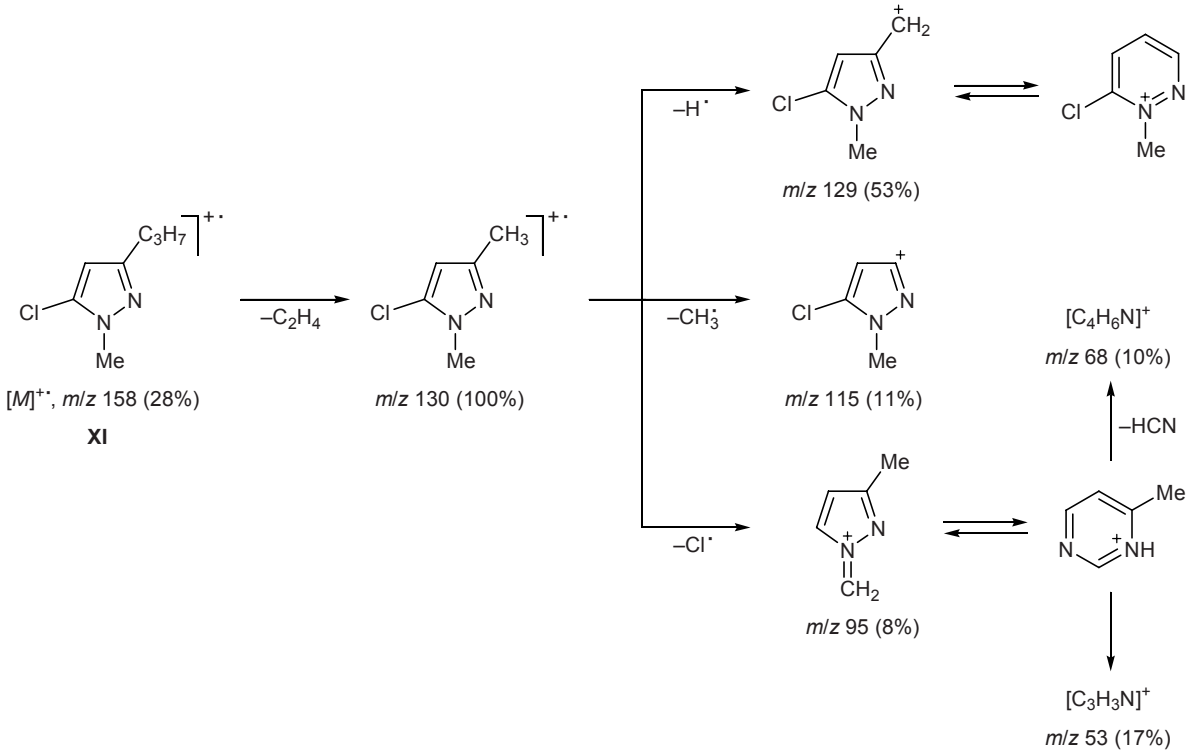
In the IR spectra of hydrazones **I**–**III** and **IX** we observed absorption bands due to vibrations of C=N, C=C, and aliphatic C–H bonds. Hydrazone **IX** showed in the ^{1}H NMR spectrum signals from protons in the alkyl groups and a singlet from the vinylic $CH=CCl_2$ proton. The ^{1}H NMR spectra of **I**–**III** contained two doublets from protons in the CH=CHCl group with a coupling constant ^{3}J of 14.1 Hz, indicating *trans*

Scheme 2.



VIII

Scheme 3.



configuration of the double bond. In the ^{13}C NMR spectra of hydrazones **I**–**III** and **IX**, the C=N carbon signal appears in a very weak field, at δ_C 196–199 ppm. The doublet signals from the olefinic protons in the ^1H NMR spectra of hydrazones **I**–**III** and **IX** are also displaced downfield relative to the corresponding signals of initial methyl and propyl 2-chloro(2,2-dichloro)vinyl ketones.

Pyrazoles **IV**–**VIII** and **X** are characterized by IR absorption at 3100–3130 cm^{-1}, belonging to stretching vibrations of the =C–H bonds. In the ^1H NMR spectra of **IV**–**VIII**, signals from 4-H and 5-H appear as two doublets at δ 5.9 and 7.2 ppm, respectively, with a coupling constant of 1.3–2.0 Hz. The 4-H proton in pyrazole **X** resonates as a singlet at δ 5.95 ppm.

The structure of pyrazoles **VIII** and **XI** was also studied by mass spectrometry. The main fragmentation pathway of 3-chloro-1-methyl-1*H*-pyrazole (**VIII**) under electron impact involves cleavage of the C–Cl bond in the molecular ion. Such behavior is typical of aromatic halogen derivatives, for which elimination of chlorine atom from the molecular ion is the main decomposition process [14]. Six-membered cyclic ions are known to be more stable than five-membered; therefore, it is quite possible that the $[M - Cl]^+$ ion with *m*/*z* 95 (100%) undergoes rearrangement with ring expansion as shown in Scheme 2. This process is related to cleavage of benzylic bond [15]. The structures of the primary rearranged ions derived from *N*- and *C*-methyl pyrazoles are different, and they determine further decomposition pattern with formation of lighter ions.

It is known that halogen atom generally does not leave stable molecular ions derived from 4-chloro(bromo)pyrazoles; these ions lose only two hydrogen cyanide molecules [16]. In fact, the mass spectrum of 5-chloro-1-methyl-3-propyl-1*H*-pyrazole (**XI**) obtained from 2,2-dichlorovinyl propyl ketone and 1,1-dimethylhydrazine according to the procedure described in [10] contained no $[M - Cl]^+$ ion peak. The base peak in the mass spectrum of **XI** was that corresponding to odd-electron 5-chloro-1,3-dimethyl-1*H*-pyrazolium ion with *m*/*z* 130 (100%) and products of its subsequent fragmentation (Scheme 3). Thus the fragmentation pattern of chlorine-containing pyrazoles **VIII** and **XI** is determined by the position of the halogen atom with respect to the heteroatom.

To conclude, the described procedure for selective synthesis of 1-alkylpyrazoles and 1-alkyl-5-chloropyrazoles from halogenated enones and 1,1-dialkylhydrazines makes these compounds accessible for further studies, while the use of 2-chloro- and 2,2-dichloro-

vinylketones and dialkylhydrazines ensures variation of the structure of the resulting pyrazoles and determines the presence of chlorine therein.

EXPERIMENTAL

The IR spectra were recorded in KBr or in thin films on a Specord 75IR spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on Bruker DPX-400 and Bruker AV-400 spectrometers at 400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C using tetramethylsilane as internal reference; the chemical shifts were determined with an accuracy of 0.01 and 0.02 ppm, respectively, and the coupling constants J_{HH} were determined with an accuracy of 0.1 Hz. The mass spectra were obtained on an LKB-2091 GC–MS system (SE-30 capillary column, 25 m; energy of ionizing electrons 60 eV; ion source temperature 250°C, injector temperature 240°C, oven temperature programming from 60 to 240°C at a rate of 10 deg/min).

5-Chloro-1-methyl-3-propyl-1*H*-pyrazole (**XI**) was synthesized in 84% yield by reaction of 2,2-dichlorovinyl propyl ketone with 1,1-dimethylhydrazine in diethyl ether as described in [10].

4-Chlorobut-3-en-2-one dibutylhydrazone (I). 1,1-Dibutylhydrazine, 7.22 g (0.05 mol), was slowly added to a solution of 5.23 g (0.05 mol) of 4-chlorobut-3-en-2-one in 20 ml of methanol or ethanol on cooling to –10 to 0°C. The mixture was stirred for 3 h at that temperature, allowed to warm up to room temperature, and evaporated under reduced pressure. The dark red viscous oily residue was dried under reduced pressure until constant weight. Yield 10.9 g (95%). IR spectrum, ν, cm^{-1}: 1610 (C=N, C=C); 2965, 2930, 2875 (C–H_{Alk}), 3115 (=C–H). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.86 t (6H, CH_3, J = 7.7 Hz), 1.70 m and 1.25 m (8H, CH_2), 2.32 s (3H, CH_3), 3.68 t (4H, CH_2, J = 7.7 Hz), 6.62 d (1H, =CH, J = 13.9 Hz), 7.46 d (1H, =CH, J = 13.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.57 (CH_3), 19.03 (CH_2), 19.48 (CH_3), 23.93 (CH_2), 67.59 (CH_2), 127.91 (=CH), 146.88 (=CHCl), 196.45 (C=N). Found, %: C 62.25; H 10.15; Cl 15.29; N 12.04. $C_{12}H_{23}ClN_2$. Calculated, %: C 62.45; H 10.05; Cl 15.36; N 12.14.

1-Chlorohex-1-en-3-one dimethylhydrazone (II). 1,1-Dimethylhydrazine, 0.3 g (5 mmol), was slowly added dropwise under stirring to a solution of 0.66 g (5 mmol) of 1-chlorohex-1-en-3-one in 30 ml of carbon tetrachloride, maintaining the temperature at –30 to –40°C. The mixture was allowed to gradually warm up to room temperature and was stirred for 1 h. The solution was separated by decanting, and the residue was dried under reduced pressure. Yield 0.8 g (92%), oily substance. IR spectrum, ν, cm^{-1}: 1630 (C=N, C=C); 2955, 2925, 2870 (C–H_{Alk}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.83 t (3H, CH_3, J = 7.1 Hz), 1.51 m (2H, CH_2, J = 7.1 Hz), 2.65 t (2H, CH_2, J = 7.1 Hz), 3.56 s (6H, CH_3), 6.86 d (1H, =CH, J = 13.9 Hz), 7.66 d (1H, =CHCl, J = 13.9 Hz). Found, %: C 54.95; H 8.86; Cl 20.27; N 16.09. $C_8H_{15}ClN_2$. Calculated, %: C 55.01; H 8.66; Cl 20.30; N 16.04.

1-Chlorohex-1-en-3-one dibutylhydrazone (III). 1,1-Dibutylhydrazine, 7.22 g (0.05 mol), was slowly added dropwise to a solution of 6.6 g (0.05 mol) of 1-chlorohex-1-en-3-one in 30 ml of methanol, maintaining the temperature below 20°C. The mixture was stirred for 3 h at room temperature, the solvent was removed under reduced pressure, and the dark red viscous oily residue was dried in a vacuum. Yield 12 g (93%). IR spectrum, ν, cm^{-1}: 1610 (C=N, C=C); 2965, 2930, 2875 (C–H_{Alk}); 3115 (=C–H). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.83 t (3H, CH_3, J = 7.1 Hz); 0.86 t (6H, CH_3, J = 7.7 Hz); 1.25 m, 1.50 m, and 1.70 m (10H, CH_2); 1.25 m (8H, CH_2); 2.32 t (2H, CH_2, J = 7.1 Hz); 3.68 t (4H, CH_2, J = 7.7 Hz); 6.62 d (1H, =CH, J = 13.9 Hz); 7.46 d (1H, =CH, J = 13.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.57 (CH_3), 19.03 (CH_2), 19.48 (CH_3), 23.93 (CH_2), 67.59 (CH_2), 127.91 (=CH), 146.88 (=CHCl), 196.45 (C=N). Found, %: C 64.85; H 10.45; Cl 13.49; N 10.90. $C_{14}H_{27}ClN_2$. Calculated, %: C 64.97; H 10.51; Cl 13.70; N 10.82.

1-Butyl-3-methyl-1*H*-pyrazole (IV). A mixture of 0.92 g (4 mmol) of 4-chlorobut-3-en-2-one dibutylhydrazone (**I**), 20 ml of methanol, and 0.5 ml of acetic acid was heated for 5 h under reflux. The mixture was cooled and poured into water, the aqueous solution was neutralized with a solution of Na_2CO_3 and treated with diethyl ether. The extract was dried over $CaCl_2$ and evaporated under reduced pressure, and the oily residue was dried in a vacuum. Yield 0.25 g (45%). IR spectrum, ν, cm^{-1}: 1510 (C=C); 2945, 2920, 2855 (C–H_{Alk}), 3100 (=CH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.87 t (3H, CH_3, J = 7.3 Hz), 1.24 m (2H, CH_2, J = 7.3 Hz), 1.75 m (2H, CH_2, J = 7.3 Hz), 2.22 s (3H, CH_3), 3.96 t (2H, CH_2, J = 7.3 Hz), 5.91 d (1H, 4-H, J = 2.0 Hz), 7.17 d (1H, 5-H, J = 2.0 Hz). Found, %: C 69.50; H 10.24; N 20.30. $C_8H_{14}N_2$. Calculated, %: C 69.52; H 10.21; N 20.27.

1-Methyl-3-propyl-1*H*-pyrazole (V) was synthesized in a similar way from 1.75 g (0.01 mol) of 1-chlorohex-1-en-3-one dimethylhydrazone (**II**). Yield 0.77 g (62%), bp 125–130°C (12 mm). IR spectrum, ν,

cm^{-1}: 1515 (C=C); 2940, 2920, 2855 (C–H_{Alk}); 3110 (=C–H). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.97 t (3H, CH_3, J = 7.7 Hz), 1.31 m (2H, CH_2, J = 7.7 Hz), 2.56 t (2H, CH_2, J = 7.7 Hz), 3.80 s (3H, CH_3), 5.99 d (1H, 4-H, J = 1.6 Hz), 7.21 d (1H, 5-H, J = 1.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.72, 22.95, 38.23, 45.84, 103.86, 130.31, 153.15. Found, %: C 67.30; H 9.68; N 22.49. $C_7H_{12}N_2$. Calculated, %: C 67.70; H 9.74; N 22.56.

1-Butyl-3-propyl-1*H*-pyrazole (VI). 1-Chlorohex-1-en-3-one, 1.33 g (0.01 mol), and triethylamine, 1.01 g (0.01 mol), were slowly added dropwise to a solution of 1.44 g (0.01 mol) of 1,1-dibutilhydrazine in 15 ml of ethanol. The mixture was heated for 5 h under reflux, cooled, poured into water, and extracted with diethyl ether. The extract was dried over $CaCl_2$, the solvent was distilled off, and the residue was distilled in a vacuum. Yield 1 g (60%), bp 83–85°C (12 mm), n_D^{20} = 1.4710. IR spectrum, ν, cm^{-1}: 1525, 1515 (C=C, C=N); 2950, 2925, 2870 (C–H_{Alk}); 3100 (=C–H). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.89 t (3H, CH_3, J = 7.3 Hz), 0.97 t (3H, CH_3, J = 7.7 Hz), 1.31 m (2H, CH_2, J = 7.7 Hz), 1.65 m (2H, CH_2, J = 7.3 Hz), 1.76 m (2H, CH_2, J = 7.3 Hz), 2.56 t (2H, CH_2, J = 7.7 Hz), 4.00 t (2H, CH_2, J = 7.3 Hz), 5.96 d (1H, 4-H, J = 1.8 Hz), 7.37 d (1H, 5-H, J = 1.8 Hz). Found, %: C 72.28; H 11.07; N 16.78. $C_{10}H_{18}N_2$. Calculated, %: C 72.24; H 10.91; N 16.85.

1,3-Dimethyl-1*H*-pyrazole (VII). 1,1-Dimethylhydrazine, 1.2 g (0.02 mol), was added under stirring to a solution of 1.04 g (0.01 mol) of 4-chlorobut-3-en-2-one in 35 ml of anhydrous diethyl ether. The mixture was stirred for 5 h at room temperature and poured into water, the organic layer was separated, and the aqueous phase was extracted with diethyl ether, The extracts were combined with the organic phase, dried over $CaCl_2$, and evaporated, and the residue was distilled under reduced pressure. Yield 0.84 g (64%), bp 136°C, n_D^{20} = 1.4674. Found, %: C 62.30; H 8.37; N 29.12. $C_5H_8N_2$. Calculated, %: C 62.47; H 8.39; N 29.14. The product was identical in physical properties to a sample described in [9, 11].

3-Chloromethyl-1-methyl-1*H*-pyrazole (VIII). 1,4-Dichlorobut-3-en-2-one, 1.39 g (0.01 mol), was slowly added in small portions to a solution of 1.20 g (0.02 mol) of 1,1-dimethylhydrazine in 30 ml of anhydrous diethyl ether so that to avoid boiling of the mixture. When the exothermic reaction was over, the mixture was stirred for 0.5–2 h, and the precipitate of trimethylhydrazinium chloride, 0.96 g (89%, mp 261–262°C), was filtered off. The filtrate was evaporated, and the residue was purified by passing through a column charged with silica gel or by distillation. Yield 0.91 (70%), bp 146–148°C, n_D^{20} = 1.5275. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.86 (NCH_3), 4.58 (CH_2Cl), 6.278 and 6.274 (4-H), 7.324 and 7.319 (5-H). ^{13}C NMR spectrum, δ_C, ppm: 38.62 (CH_3N), 76.838 (CH_2Cl), 105.084 (C^4), 130.97 (C^3), 148.37 (C^5). Found, %: C 45.78; H 5.24; N 21.47. $C_5H_7ClN_2$. Calculated, %: C 45.99; H 5.40; N 21.45. The physical properties of the product were consistent with published data [10].

1,1-Dichlorohex-1-en-3-one dibutylhydrazone (IX). 1,1-Dichlorohex-1-en-3-one, 4.17 g (0.025 mol), was added dropwise to a solution of 3.60 g (0.025 mol) of dibutylhydrazine in 15 ml of ethanol on cooling to –10 to 0°C. The mixture was stirred for 3 h on cooling, allowed to warm up to room temperature, and evaporated under reduced pressure. Yield 5.57g (95%), dark red oily substance containing 5% of 1-butyl-5-chloro-3-propyl-1*H*-pyrazole (**X**). IR spectrum, ν, cm^{-1}: 1610 (C=N); 2965, 2930, 2875 (C–H_{Alk}); 3100 (=C–H). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.91 t, 0.92 t, and 0.93 t (3H each, CH_3); 1.35 m and 1.65 m (10H, CH_2); 2.20 t (2H, CH_2, J = 7.2 Hz); 3.00 t (4H, CH_2, J = 7.4 Hz); 6.64 s (1H, =CH). Found, %: C 57.30; H 8.79; Cl 24.17; N 9.53. $C_{14}H_{26}Cl_2N_2$. Calculated, %: C 57.34; H 8.94; Cl 24.18; N 9.55.

1-Butyl-5-chloro-3-propyl-1*H*-pyrazole (X). A solution of 5.86 g (0.02 mol) of 1,1-dichlorohex-1-en-3-one dibutylhydrazone (**IX**) in 30 ml of ethanol containing 0.5 ml of acetic acid was heated for 5 h under reflux. The solution was cooled, neutralized with a solution of sodium carbonate, and extracted with diethyl ether. The extract was dried over $CaCl_2$ and evaporated, and the residue was distilled in a vacuum. Yield 2.40 g (60%) [11]. IR spectrum, ν, cm^{-1}: 1610 (C=N, C=C); 2945, 2920, 2855 (C–H_{Alk}); 3130 (=C–H). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.89 m (3H, CH_3, J = 7.3 Hz), 0.94 t (3H, CH_3, J = 7.5 Hz), 1.25 m (2H, CH_2, J = 7.3 Hz), 1.66 m (2H, CH_2, J = 7.5 Hz), 1.76 m (2H, CH_2, J = 7.3 Hz), 2.58 t (2H, CH_2, J = 7.5 Hz), 4.05 t (2H, CH_2, J = 7.3 Hz), 5.95 (1H, =CH). Found, %: C 59.82; H 8.51; Cl 17.63; N 13.94. $C_{10}H_{17}ClN_2$. Calculated, %: C 59.84; H 8.54; Cl 17.66; N 13.96.

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 05-03-97202).

REFERENCES

1. Pawer, A. and Patil, A.A., *Indian J. Chem*., 1994, vol. 33, p. 156.

2. Grapov, A.F., *Usp. Khim*., 1999, vol. 68, p. 773.
3. Nazarinia, M., Sharifian, A., and Shafiee, A., *J. Heterocycl. Chem*., 1995, vol. 32, p. 223.
4. Suzuki, F., Iwazawa, Y., Sato, T., Igai, T., and Oguchi, T., JPN Patent no. 06-56792, 1994; *Chem. Abstr*., 1995, vol. 122, no. 31573f.
5. Butler, D.E. and De Ward, H.A., *J. Org. Chem*., 1971, vol. 36, p. 2542.
6. De Wald, H.A., US Patent no. 3823157, 1974; *Ref. Zh., Khim*., 1975, no. 12O253P.
7. De Wald, H.A., FRG Patent no. 2423642, 1974; *Chem. Abstr*., 1975, vol. 83, no. 206345.
8. Shen, A., Pejn'e, R., Vor, Zh.-P., Mort'e, Zh., Kantegrij, R., and Kruaza, D., Russian Patent no. 2072991, 1997; *Byull. Izobret*., 1997, no. 4.
9. Ioffe, B.V. and Zelenina, N.L., *Khim. Geterotsikl. Soedin*., 1970, p. 1414.
10. Levkovskaya, G.G., Bozhenkov, G.V., Larina, L.I., and Mirskova, A.N., *Russ. J. Org. Chem*., 2002, vol. 38, p. 1501.
11. Levkovskaya, G.G., Bozhenkov, G.V., Malyushenko, R.N., and Mirskova, A.N., *Russ. J. Org. Chem*., 2001, vol. 37, p. 1795.
12. Elokhina, V.N., Nakhmanovich, A.S., Larina, L.I., Shishkin, O.V., Baumer, V.N., and Lopyrev, V.A., *Izv. Ross. Akad. Nauk, Ser. Khim*., 1999, p. 1536.
13. Kalikhman, I.D., Lavlinskaya, L.I., Levkovskaya, G.G., Mirskova, A.N., Atavin, A.S., and Pestunovich, V.A., *Izv. Akad. Nauk SSSR, Ser. Khim*., 1974, p. 1402; Kalikhman, I.D., Levkovskaya, G.G., Lavlinskaya, L.I., Mirskova, A.N., and Atavin, A.S., *Izv. Akad. Nauk SSSR, Ser. Khim*., 1973, p. 2235.
14. Ponomarev, D.A., Takhistov, V.V., and Temnikova, T.I., *Zh. Org. Khim*., 1973, vol. 9, p. 2446.
15. Krasnoshchek, A.P., Khmel'nitskii, R.A., Polyakova, A.A., Grandberg, I.I., and Minkin, V.I., *Zh. Org. Khim*., 1968, vol. 4, p. 1690.
16. Vul'fson, N.S., Zaikin, V.G., and Mikaya, A.I., *Mass-spektrometriya organicheskikh soedinenii* (Mass Spectrometry of Organic Compounds), Moscow: Khimiya, 1986.