Russian Journal of Organic Chemistry, Vol. 39, No. 8, 2003, pp. 1069–1075. Translated from Zhurnal Organicheskoi Khimii, Vol. 39, No. 8, 2003, pp. 1140–1146.

Chloro(bromo)vinyl ketones and 2,2-Dichloroacrolein in Reactions with Hydrazines

G. V. Bozhenkov, G. G. Levkovskaya, A. N. Mirskova, G. V. Dolgushin, L. I. Larina, and P. E. Ushakov

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

Received August 2, 2002

Abstract—Reactions of 2,2-dichlorovinyl and 2,2-dibromovinyl ketones with alkylhydrazines afford respectively 1-R-3-alkyl(aryl)-5-chloro- or 5-bromopyrazoles in preparative yields. The dichloroacrolein forms with alkylhydrazines and dimethylhydrazine only the corresponding hydrazones. Quantum-chemical calculations were performed characterizing the structure of the obtained ketones and dichloroacrolein alkylhydrazones, of dichloroacrolein dimethylhydrazone, of 1-alkyl-5-chloropyrazolinium halides, and 1-alkyl-5-chloropyrazoles.

Pyrazoles attract great interest in connection with preparation of new pharmaceuticals, dyes, fluorescent dyes, insecticides, acaricides. For instance, the 1,3-dimethyl-5-chloropyrazole is an initial substance in production of new generation acaricide, Phenpyroxymate [1, 2]. 1,3-Dialkyl-5-chloropyrazoles are used in preparation of a series of antidepressants or semiproducts for their synthesis [3, 4], and their 4-acyl derivatives are components of fungicides [5]. Therefore the development of preparative methods of synthesis for pyrazoles, especially halopyrazoles is urgent.

We recently found a new reaction of purposeful heterocyclization affording 1-R-3-methyl-5*H*, 5-chloro(bromo)pyrazoles from accessible 2-chloro- and 2,2-dichlorovinyl ketones and trifluoromethyl 2,2-dibromovinyl ketone at treatment with 1,1-dimethylhydrazine [6]. Before our studies the known labor-consuming and multistage preparation methods for 5-chloro(bromo0pyrazoles [7, 8] involved the treatment of the corresponding pyrazol-5-ones with phosphorus oxychloride.

In order to test the general character and the rules governing the new heterocyclization reaction we used in this study in the process with 1,1-dimethylhydrazine the available dichloroacrolein [9], and also carried on the investigation of reactions between chloro(bromo)vinyl ketones with a number of alkyl hydrazines aiming at finding a convenient path for preparation of 1-alkyl-5-chloro(bromo)pyrazoles.

It was shown formerly that 2,4-dinitrophenylhydrazones of aliphatic 2,2-dichlorovinyl ketones did not undergo cyclization into the corresponding 5-chloropyrazoles in contrast to a similar 2,2-dichlorovinyl phenyl ketone 2,4-dinitrophenylhydrazone. This study unambiguously established that the heterocyclization process is governed by conformational structure of the ketone and by geometric *syn-anti* isomerism of the hydrazone [10, 11]. However the reaction between 2,2-dichlorovinyl ketones and alkylhydrazines was not investigated.

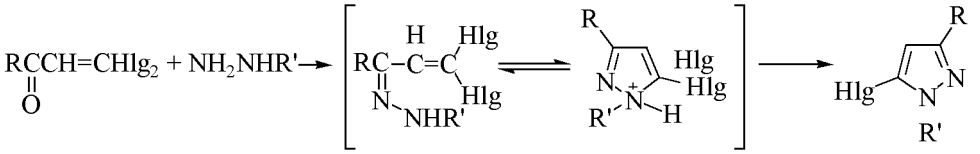
We have established in this research that in reacion of dichlorovinyl ketones with a series of alkylhydrazines form in a stable high yield 1-alkyl-3-alkyl-, chloroalkyl-, perfluoroalkyl, aryl-5-chloropyrazoles **I–X** (Scheme 1) (Tables 1, 2). The reactions were carried out at the reagents ratio 1 : 1 in the presence of an equimolar amount of triethylamine, or at a double excess of alkylhydrazine.

The reaction mechanism consists apparently in a primary formation of 2,2-dichloro(bromo)vinyl ketone alkylhydrazone followed by an intramolecular attack of the nucleophilic alkylamine moiety on the β-carbon of the vinyl group. Thus arising N-alkylpyrazolinium halide undergoes dehydrochlorination furnishing the target aromatic pyrazole.

An alternative reaction mechanism including a primary formation of a quaternary salt 1-(1-halo-2-acylvinyl)-1-alkylhydrazinium halide followed by heterocyclization is hardly probable. For instance, the quaternary salts of dimethylhydrazine, 1-[1-bromo-2-benzoyl(2-thienoyl)vinyl]-1,1-dimethylhydrazinium bromides, obtained from the corresponding bromoacetylene ketones and 1,1-dimethylhydrazine and

1070-4280/03/3908-1069$25.00 © 2003 MAIK "Nauka/Interperiodica"

Scheme 1.



Hlg = Cl, R = CH_3: R' = C_2H_5 (**I**); C_7H_{15} (**II**); R = C_3H_7, C_7H_{15} (**III**); R = *iso*-C_3H_7, R' = CH_3 (**IV**); R = CH_2Cl, R' = C_2H_5 (**V**); R = CF_3, R' = C_2H_5 (**VI**), R' = C_7H_{15} (**VII**); R = C_6H_5, R' = C_7H_{15} (**VIII**); R = 4-$NO_2C_6H_4$, R' = C_2H_5 (**IX**); Hlg = Br: R = CF_3, R' = C_2H_5 (**X**).

whose structure has been determined by X-ray diffraction analysis [12], are known not to undergo cyclization into pyrazoles.

Pyrazoles **I–VIII, X** are fluids with a characteristic mould odor, soluble in organic solvents. Compound **IX** is a crystalline substance.

At the same time we failed to prepare 1-alkyl-5-chloropyrazoles by reaction of 2,2-dichloroacrolein with alkylhydrazines and 1,1-dimethylhydrazine. Neither reaction carried out under conditions of synthesis of 1-methyl- and 1-alkyl-3R-5-chloro(bromo)-pyrazoles from dichloro(bromo)vinyl ketones and *N*,*N*-dimethylhydrazine [6] nor variation of temperature, time, and reagent ratio in the process resulted in heterocyclization and formation of 1-methyl(alkyl)-5-chloropyrazoles.

Scheme 2.

$$CCl_2{=}CHCHO + NH_2NRR' \longrightarrow CCl_2{=}CHCH{=}NNRR'$$

XI–XIII

R = H: R' = C_2H_5 (**XI**); C_7H_{15} (**XII**); R = R' = CH_3 (**XIII**).

Under all conditions tried (reagents ratio from equimolar to double excess of hydrazine, temperature from –70°C to the boiling of the reaction mixture, in the presence of 1-2-fold amount of triethylamine) the dichloroacrolein with dimethyl-, ethyl-, and heptylhydrazines afforded in 90% yield only the corresponding hydrazones **XI–XIII** (Scheme 2).

Hydrazones **XI, XIII** are liquids with a characteristic odor, soluble in organic solvents and water. Compound **XI** is a viscous oil.

Table 1. Yield, physical constants, and elemental analyses of 1-alkyl-3-R-5-chloropyrazoles **I**–**IX**, 1-ethyl-3-trifluoromethyl-5-bromopyrazole (**X**), and dichloroacrolein hydrazones **XI**–**XIII**

Compd. no.	Yield, %	bp, °C (*p*, mm Hg)	n_D^{20}	Found, %				Formula	Calculated, %			
				C	H	Cl	N		C	H	Cl	N
I	66	54–56(12)		50.03	6.14	24.44	19.60	$C_6H_9ClN_2$	50.03	6.14	24.44	19.60
II	80	75–80(3)	1.4710	61.53	8.92	16.51	13.05	$C_{11}H_{19}ClN_2$	61.62	8.95	16.31	13.11
III	82	100(1)	1.4740	64.31	9.55	14.60	11.54	$C_{13}H_{23}ClN_2$	64.25	9.59	14.70	11.55
IV[a]	80	76–77 (17)	1.4833	53.68	7.12	21.98	17.57	$C_7H_{11}ClN_2$	53.70	7.20	22.12	17.04
V	90	108–110(30)	1.5199	40.25	4.50	39.60	15.65	$C_6H_8Cl_2N_2$	40.18	4.35	39.22	15.26
VI	75	34(66)[b]		36.29	3.05	17.85	14.11	$C_6H_6ClF_3N_2$	36.39	3.01	17.93	14.13
VII	74	[c,d]		49.17	6.00	13.19	10.43	$C_{11}H_{16}ClF_3N_2$	49.21	6.01	13.22	10.49
VIII	90	[d,e]	1.5420	68.04	7.99	13.39	10.58	$C_{15}H_{21}ClN_2$	68.18	7.98	13.45	10.55
IX	91	[116–117]		52.50	4.00	14.09	16.70	$C_{11}H_{10}ClN_3O_2$	52.30	4.20	14.05	16.65
X	88	[d,e]	1.4515	29.65	2.49	–	11.53	$C_6H_6BrF_3N_2$	29.77	2.46	–	11.58
XI	63	[d]		35.95	4.83	42.45	16.77	$C_5H_8Cl_2N_2$	35.83	4.84	42.61	16.80
XII	50	[d]	1.5150	50.86	7.26	30.02	11.86	$C_{10}H_{17}Cl_2N_2$	50.76	7.22	30.012	11.81
XIII	68	51(2)	1.5770	35.95	4.83	42.45	16.77	$C_5H_8Cl_2N_2$	35.87	4.94	41.98	17.01

[a] Compound was previously described [6, 8].

[b] (**VI**) Found, %: F 29.89. Calculated, %: F 30.88.

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

[d] Compounds purified by column chromatography on SiO_2 (eluent hexane). Purity tested by GLC.

[e] (**X**) Found, %: F 23.45; Br 32.88. Calculated, %: F 23.45; Br 32.79.

Table 2. IR spectra (from microfilm) and ^{1}H NMR spectra (in $CDCl_3$) of 1-alkyl-3-alkyl-, chloroalkyl-, perfluoroalkyl-, aryl-5-bromo- and 5-chloropyrazoles **I**–**X** and dichloroacrolein hydrazones **XII, XIII**

Compd. no.	IR spectra, ν, cm^{-1}				^{1}H NMR spectra, δ, ppm (*J*, Hz)			
	C–Cl	C=C	N–CH_3, R = Alk	=C–H	N–CH_2R'	R'(R' = R'–NCH_2)	H^4	*3*-R
I	770	1510	2950	3125	4.09 t (7.2)	1.38 t (7.2)	5.95	2.21
II	770	1515	2925, 2960, 2850	3125	4.01 t (7.3)	1.78 m, 127 m, 0.87 t	5.93	2.20
III	765	1505	2860, 2920, 2950	3125	4.05 t	1.60 m 0.92 t	5.95	2.53 t, 1.27 m, 0.85 t
IV	775	1500	2860–2950	3120	3.73	–	5.99	1.20 d, 2.89 m
V	790	1575	2975	3135	4.13 q (7.23)	1.40 t (7.23)	6.25	4.51 s
VI	790	1505	2950, 2980	3150	4.22 q (11.64)	1.44 t (11.64)	6.45	
VII	790	1480	2960	3150	4.15 t[a]	1.84 m, 1.27 m, 0.87 t	6.44	
VIII	765, 700	1480, 1600	2850, 2940, 2980	3060, 3130	4.08 t (7.21)	1.82 m, 1.27 m, 0.86	6.41	7.24, 7.31, 7.71 m
IX	800	1510, 1600	2930, 2960, 2990	3070, 3135	4.24 q (7.22)	1.48 t	6.57	7.88 d, 8.22 d (1.0)
X	–	1475	2850, 2940, 2980	3140	4.25 q (11.64)	1.43 t (11.64)	6.52	
XII	760	1500, 1600; 1680 (C=N)	2850–2960; 3400 (br, NH)		4.094 t (7.2)	1.81 m, 1.27 m, 0.87 t	7.412 d, 7.131 d (2.0)	
XIII	760	1540; 1720 (C=N)			2.93 s		6.61 d[b], 6.81 d (8.57)	

[a] ^{1}H NMR spectrum in DMSO-d_6: 6.97 s (=C–H, 1H), 4.20 t (NCH_2, 2H), 1.80 m (CH_2, 2H), 1.27 m (CH_2, 8H), 0.86 t (CH_3, 3H).

[b] Chemical shifts of protons from the fragment –N=CH–CH= are presented for hydrazones (**XII, XIII**).

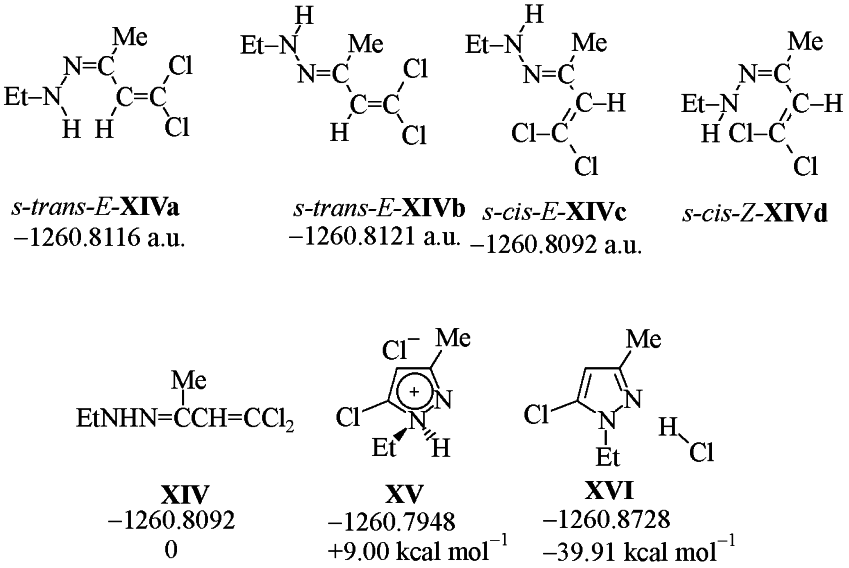
The structure of pyrazoles **I**–**X** and hydrazones **XI**–**XIII** was proved by physicochemical methods, the composition was confirmed by elemental analyses (Tables 1, 2) and by independent synthesis. For instance, the characteristics of 1-methyl-3-isopropyl-5-chloropyrazole obtained by reaction of isopropyl 2,2-dichlorovinyl ketone with dimethylhydrazine [6] are identical to those of the same pyrazole synthesized by treating with phosphorus oxychloride an appropriate pyrazole prepared by reaction of 2-methylpropanoylacetoacetic ester with methylhydrazine [8].

In the IR spectra of 1-alkyl-5-chloropyrazoles **I**–**IX** and of bromopyrazole **X** a presence of band in the region 3125–3150 cm^{-1} should be noted corresponding to the stretching vibrations of the C^4–H bond in the heterocycle. The frequency and intensity of the stretching vibrations of the C^4–H bond increases in going to pyrazoles containing the electronegative CF_3 group in *3* position (compounds **VI, VII, X**). The absorption bands of C=C bonds of the heterocycle appear in the IR spectra at 1470–1575 cm^{-1}.

In the ^{1}H NMR spectra of pyrazoles **I**–**X** the resonances of H^4 protons appear in the region 5.93–6.57 ppm; therewith in going from 3-alkyl derivatives **I**–**IV** (5.93–5.99 ppm) to pyrazoles with electron-acceptor (CH_2Cl, CF_3) (6.25–6.52 ppm) and aromatic substituents (C_6H_5, $C_6H_4NO_2$) (6.41, 6.57 ppm) in position *3* the signal shifts downfield. Similar but weaker trend is observed for protons of NCH_2R' groups. The strongest shift of H^4 signal occurs in 1-ethyl-5-bromopyrazole (**X**) compared to its analogs **VI, VII**, and in 1-ethyl-3-(4-nitrophenyl)-5-chloropyrazole (**IX**) (6.57 ppm). In the ^{1}H NMR spectra of 1-ethylpyrazoles **IX, X** the methylene protons signal is located downfield with respect to the resonance of the NCH_2 group in 1-ethyl-, 1-heptylpyrazoles **I**–**III, V**–**VIII** (Table 2).

Note that in the ^{1}H NMR spectrum of compound **VII** the signal of H^4 considerably shifts (by 0.5 ppm) downfield. The other signals of protons in compound **VII** either shift insignificantly ($\Delta\delta$ NCH_2Me, NCH_2Pt = 0.05 ppm) or remain intact at the change of the solvent (Table 2).

Scheme 3.



In the IR spectra of hydrazones **XI–XIII** we mention first of all the presence of a weak band of C=N bond vibrations, and in the spectra of hydrazones **XI, XII** the presence of a wide band of N–H in the region 3400 cm^{-1}. In the ^1H NMR spectra of hydrazones **XI, XII** appear doublet signals from the protons of dichlorovinyl and imino groups (Table 2) and the proton signals from alkyl groups. For instance, in the NMR spectrum of dichloroacrolein dimethylhydrazone are observed two doublets at 6.53 ppm (1H) and 6.83 ppm (1H) (*J* 8.6 Hz) and a singlet signal at 2.93 ppm (6H). It should be noted that at heating the hydrazone solution to 50°C the signals of the olefin and azomethine protons and also those of methyl groups split. Unlike the ^{13}C NMR spectra of 1-methyl-5-chloropyrazoles [6] in that of hydrazone **XIII** the carbon signals from methyl groups are shifted downfield. The chemical shifts of nitrogen signals in the ^{15}N NMR spectrum of hydrazone **XIII** (–17.9 and –267.3 ppm) significantly differ from those of pyrrole (–74 to –83 ppm) and pyrazole (–178 to –188 ppm) nitrogen signals in 1-methyl-5-chloropyrazoles [6].

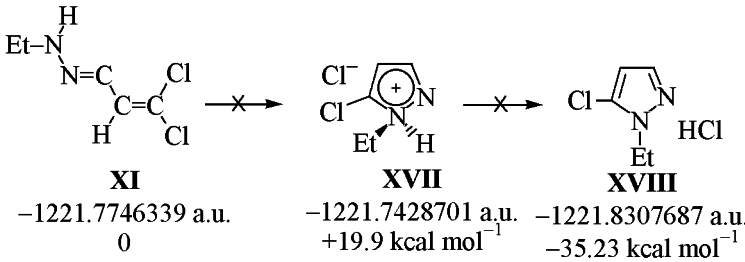
We also attempted to carry out heterocyclization of hydrazones **XI–XIII** by heating from 100 to 200°C or in the presence of bases; however we failed to isolate 1-alkyl-5-chloropyrazoles from these reaction mixtures. We observed only hydrazones decomposition with gas liberation.

It was formerly established [10, 11] in the study of stereochemistry of 2,4-dinitrophenylhydrazones obtained from 2,2-dichlorovinyl ketones and 2,2-dichloroacrolein that these hydrazones existed as a mixture of *Z*- and *E*-isomers with the latter prevailing. The dichloroacrolein 2,4-dinitrophenylhydrazone is pure *E*-isomer, whereas in the respective hydrazones of aromatic ketones prevails the *Z*-form. These results provided an understanding of the capability of aromatic ketones to undergo cyclization into pyrazoles. The most convenient for cyclization is the cisoid *Z,s*-form. The 2,4-dinitrophenylhydrazones of aromatic ketones exist in the *Z*-form, and in those of ketones with alkyl groups dominate the *E*-forms. The energy barrier to *Z*-*E*-transitions was established to be relatively high [11]. However although the 4,4,1-trichloro-3-buten-2-one 2,4-dinitrophenylhydrazone as the dichloroacrolein 2,4-dinitrophenylhydrazone exists as the *E*-isomer, in reaction with dimethylhydrazine [6] and as is established in the present study also with ethylhydrazine this ketone affords the corresponding pyrazoles in good yields.

The incapability of dichloroacrolein hydrazones to undergo heterocyclization is probably due both to high energy barrier to the first process stage, the formation of the respective pyrazolinium halides, and to the lesser stabilization of these salts because of the lack of a substituent in the *3* position of the pyrazole ring.

In the light of the above facts we deemed as urgent the investigation by means of quantum-chemical calculations of geometrical and energy parameters of alkyl and dimethylhydrazones of dichloroactolein and methyl 2,2-dichlorovinyl ketone ethylhydrazone, of the corresponding presumed intermediates of the

Scheme 4.



XI −1221.7746339 a.u. 0

XVII −1221.7428701 a.u. +19.9 kcal mol^{-1}

XVIII −1221.8307687 a.u. −35.23 kcal mol^{-1}

hetrocyclization (pyrazolinium halides), and also of products of decomposition of the latter.

In order to refine the understanding of the mechanism of the pyrazoles formation from dihalovinyl ketones and alkylhydrazines we performed *ab initio* calculations of methyl 2,2-dichlorovinyl ketone ethylhydrazone (**XIV**), of the presumed intermediate of its hetrocyclization (pyrazolinium chloride **XV**), and also of products of decomposition of the latter, adduct of 2-ethylpyrazole (**I**) with HCl (Scheme 1).

We took in account that ethylhydrazone **XIV** can exist in four geometric forms: *s-trans-Z*, *s-trans-E*, *s-cis-Z*, *s-cis-E*. However the optimization of a structure with an *s-cis-Z*-configuration resulted in compound of *s-trans-Z*-form.

The indicated energy values show that for ethylhydrazone **XIV** the most energetically favorable configuration is *s-trans-E*-isomer **XIVb**: its energy is lower by 0.32 and 1.83 kcal mol^{-1} than those of *s-trans-Z*- (**XIVa**) and *s-cis-E*- (**XIVc**) forms, and the latter configuration is the least energetically favorable form of hydrazone **XIV**. As was previously demonstrated, among the isomers of methyl 2,2,-dichlorovinyl ketone 2,4-dinitrophenylhydrazone prevailed the *Z*-form [10].

The intramolecular cyclization of compound **XIV** into structure **XV** causes increase in the energy of the system by 10.52, 10.84 and 9.00 kcal mol^{-1} compared to the energy of the corresponding geometrical isomers of the initial hydrazone, **XIVa, XIVb**, and **XIVc** respectively. Further at elimination of a proton from pyrazolium chloride **XV** resulting in formation of two neutral molecules (structure **XVI**) the energy of the system diminishes by 0.0636011 au (39.91 kcal mol^{-1}) as compared to that of the initial hydrazone. The energy gain at decomposition of the pyrasolium salt **XV** into adduct of 1-ethyl-2-methyl-5-chloropyrazol with HCl (**XVI**) amounts to 30.91 kcal mol^{-1} with respect to the initial hydrazone suggesting that the heterocyclization is favorable.

The study of heterocyclization of dichloroacrolein ethylhydrazone (**XI**) into the corresponding pyrazolium chloride **XVII** and then into adduct of HCl and 1-ethyl-5-chloropyrazole (**XVIII**) (Scheme 4) revealed that the energy loss at the first stage of the heterocyclization is approximately twice as great as at the analogous heterocyclization of methyl 2,2,-dichlorovinyl ketone ethylhydrazone (**XIV**), and further proton elimination from **XVII** to give **XVIII** is also less feasible than transformation **XV** → **XVI**.

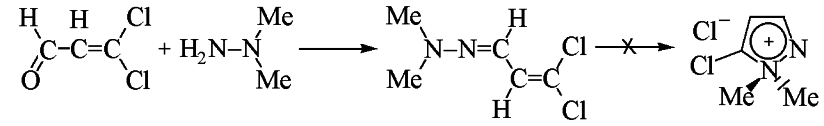
The energy gain at heterocyclization of dichloroacrolein ethylhydrazone (**XI**) till formation of adduct of HCl with 1-ethyl-5-chloropyrazole (**XVIII**) amounts only to 15.33 kcal mol^{-1} compared to the energy of the initial hydrazone; therewith at the first stage should arise energetically unfavorable pyrazolium chloride (19.9 kcal mol^{-1}). Therefore the process stops at the stage of hydrazone **XI** formation.

Obviously in heterocyclization of dichlorovinyl ketones dimethylhydrazones the stabilization of the corresponding pyrazolium chlorides should involve methyl chloride elimination and separation of 1-methyl-5-chloropyrazoles [6]. In the case of dichloroacrolein hydrazone it should have resulted in unsubstituted 1-methyl-5-chloropyrazole (**XX**) (Scheme 5).

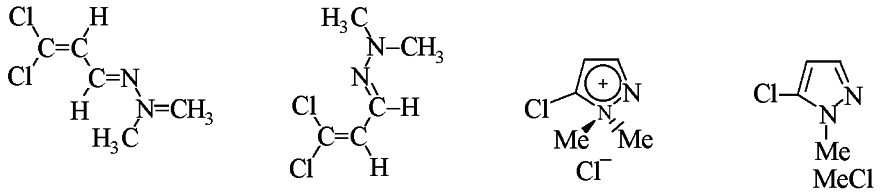
Ab initio calculations of *s-cis*- and *s-trans*-configurations of dichloroacrolein dimethylhydrazone (**XIII**) and of the product of its intramolecular cyclization show the energy preference for *2-trans*-isomer that apparently originates from the minimal deformation of the bond angles and conservation of the planar skeleton structure at this molecular geometry; the planar structure is feasible for conjugations existing in the molecule.

The *s-cis*-isomer has intermediate energy that is by 3.9 kcal mol^{-1} higher then that of the *s-trans*-isomer and by 6.44 kcal mol^{-1} lower than the energy of 1,1-dimethylpyrazolium chloride. Evidently the overall energy gain at formation of 1-methyl-5-chloro-

Scheme 5.



XIII **XIX**



XX

HF = –1221.7641 a.u. 0 kcal mol^{-1} HF = –1221.7538 a.u. +6.44 kcal mol^{-1} HF = –1221.7476 a.u. +10.3 kcal mol^{-1} HF = –1221.8180 a.u. –33.9 kcal mol^{-1}

pyrazole and methyl chloride is insufficient for *s-trans*-isomer of dichloroacrolein dimethylhydrazone to transform into the *s-cis*-form with subsequent cyclization. The most unfeasible from the energy viewpoint is the cyclic structure, dimethypyrazolium chloride **XIX**: its energy is by 10.3 kcal mol^{-1} higher than that of *s-trans*-isomer. The elimination of methyl chloride from salt **XIX** decreases the energy of the system by 23.6 kcal mol^{-1}. Apparently this energy gain does not ensure heterocyclization and formation of 1-methyl-5-chloropyrazole. We are planning further to investigate in detail by means of quantum-chemical methods the routes of heterocyclization of dichloroacrolein and dichlorovinyl ketones hydrazones.

Thus the formation of cyclic reaction products in the case of alkyl- and dialkylhydrazones of dichloroacrolein is energetically unfeasible. The divinyl ketones alkylhydrazones undergo cyclization into the corresponding 1,3-dialkyl-5-chloropyrazoles with a significant energy gain.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered on spectrometers Bruker DPX-400 (at 400 and 100.61 MHz respectively) and Jeol FX-90Q (at 90 and 22.4 MHz respectively), internal reference HMDS. Calculations *ab initio* (RHF 6-31G*) were carried out with the use of Gaussian-98 software [13].

IR spectra were recorded on spectrophotometer Specord 75 IR from samples pelletized with KBr or from thin film.

Preparation of 1-alkyl-5-chloro(bromo)pyrazoles from 2,2-dichloro(bromo)vinyl ketones and alkylhydrazines (general procedure). (a) To a solution of 0.1 mol of alkylhydrazine and 0.1 mol of triethylamine in 50–100 ml of anhydrous ethyl ether was slowly added dropwise at stirring 0.1 mol of 2,2-dichloro(bromo)vinyl ketone. On completion of the exothermic reaction the reaction mixture was stirred for 2–3 h more. The precipitated triethylammonium halide was filtered off. The target pyrazoles were obtained from the filtrate either by distillation (compounds **I–VI**, **IX**) or by evaporation followed by recrystallization (compounds **VII, VIII, X**), or by reprecipitation with hexane from an alcoholic solution (compounds **VII, VIII, X**), and also by column chromatography on silica gel L 100/160 (eluent hexane) or by evaporation with subsequent recrystallization.

(b) By adding 0.1 mol of dihalovinyl ketone to a solution of 0.2 mol of alkyl hydrazine in 100–150 ml of ethyl ether, hexane, benzene, methanol, ethanol, 2-propanol under above described conditions the target pyrazoles **I–X** also were prepared.

1-Ethyl-3-methyl-5-chloropyrazole (I) was obtained in amount of 0.64 g from 1.39 g (0.01 mol) of 1,1-dichloro-1-buten-2-one, 1.20 g (0.02 mol) of ethylhydrazine.

1-Heptyl-3-methyl-5-chloropyrazole (II). Obtained from 1.4 g (0.01 mol) of 1,1-dichloro-1-buten-2-one and 2.6 g (0.02 mol) of heptylhydrazine in 50–100 ml of 2-propanol. Yield 2 g.

1-Heptyl-3-propyl-5-chloropyrazole (III). Obtained from 1.67 (0.01 mol) of 1,1-dichloro-1-hexen-2-one, 0.6 g (0.01 mol) of ethylhydrazine and 1.01 g (0.01 mol) of triethylamine in 20 ml of 2-propanol. Yield 2 g.

1-methyl-3-isopropyl-5-chloropyrazole (IV). Obtained from 0.96 g (0.02 mol) of methylhydrazine and 1.67 g (0.01 mol) of 1,1-dichloro-4-methyl-1-penten-3-one in 20 ml of diethyl ether. Yield 1.27 g, bp 76°C (17–18 mm Hg), n_D^{20} 1.4833 [6]; bp 72–74°C (10 mm Hg) [8]).

1-Ethyl-3-chloromethyl-5-chloropyrazole (V). Obtained from 0.6 g (0.01 mol) of ethylhydrazine, 1.73 g (0.01 mol) of 1,4,4-trichloro-3-buten-2-one and 1.01 g (0.01 mol) triethylamine in 50 ml of ether. Yield 1.5 g.

1-Ethyl-3-trifluoromethyl-5-chloropyrazole (VI). Obtained from 1.93 g (0.01 mol) of 2,2-dichlorovinyl trifluoromethyl ketone, 0.6 g (0.01 mol) of ethylhydrazine and 1.01 g (0.01 mol) of triethylamine in 20 ml of 2-propanol. Yield 2 g.

1-Heptyl-3-trifluoromethyl-5-chloropyrazole (VII). Obtained from 1.93 g (0.01 mol) of 2,2-dichlorovinyl trifluoromethyl ketone and 1.3 g (0.01 mol) heptylhydrazine and 1.01 g (0.01 mol) triethylamine in 20 ml of 2-propanol. Yield 2 g.

1-Heptyl-3-phenyl-5-chloropyrazole (VIII). Obtained from 2.01 g (0.01 mol) of 1,1-dichlorovinyl phenyl ketone, 1.3 g (0.01 mol) of heptylhydrazine and 1.01 g (0.01 mol) of triethylamine in 50 ml of 2-propanol. Yield 2.5 g.

1-Ethyl-3-(4-nitrophenyl)-5-chloropyrazole (IX). Obtained from 2.46 g (0.01 mol) of 2,2-dichlorovinyl 4-nitrophenyl ketone, 0.6 g (0.01 mol) of ethylhydrazine and 1.01 g (0.01 mol) of triethylamine in 20 ml ethyl ether. Yield 2.15 g.

1-Ethyl-3-trifluoromethyl-5-bromopyrazole (X). Obtained from 2.8 g (0.01 mol) of trifluoromethyl 2,2-dibromovinyl ketone, 0.6 g (0.01 mol) of ethylhydrazine and 1.01 g (0.01 mol) of triethylamine in 20 ml ethyl ether. Yield 2.15 g.

2,2-Dichloroacrolein dimethylhydrazone (XIII). To a solution of 12.0 g (0.2 mol) of *N*,*N*-dimethylhydrazine in 50–100 ml of ether was slowly added dropwise 12.5 g (0.1 ml) of 3,3-dichloro-3-propenal. On completion of the exothermic reaction the reaction mixture was stirred for 1–2 h more. Yield 1.04 g.

Hydrazones **XI, XII** were prepared in a similar way.

The authors are grateful to Professor V. A. Lopyrev for the help in performing the calculations.

REFERENCES

1. Granov, A.F., *Usp. khim.,* 1999, vol. 68, p. 773.
2. Nazarinia, M., Sharifian, A., and Shafiee, A., *J. Heterocyclic. Chem.*, 1995, vol. 32, p. 223.
3. US Patent 2955108, 1960; *Chem. Abstr.,* 1961, vol. 55, p. 5544f.
4. Japan Patent 5824522, 1992; *Ref. Zh. Khim.*, 1993, 7Zh 108.
5. Russian Patent 2072991, 1977; *Byull. Izobr.*, 1997, no. 4; *Ref. Zh. Khim.,* 1998, 19O 370P.
6. Levkovskaya, G.G., Bozhenkov, G.V., Larina, L.I., and Mirskova, A.N., *Zh. Org. Khim.*. 2002, vol. 38, p. 1554.
7. Michaelis, A. and Dorn, N., *Ber.,* 1907, vol. 2343, p. 179; *Lieb. Ann. Chem.,* 1907, vol. 352, p. 169; Auwers, K., and Hollmann, N., *Ber.,* 192643, 4459, p. 601; Butler, D.E. and De Ward, H.A., *J .Org. Chem.,* 1971, vol. 36, p. 2542; Auwers, K. and Niemyer, F., *J. Prakt. Chem.,* 1925, vol. 110, p. 153; Habraken, C.L. and Moore, J.A., *J. Org. Chem.,* 1965, vol. 30, p. 1892.
8. Butler, D.E. and De Ward, H.A., *J. Org. Chem.*, 1971, vol. 36, p. 2542.
9. Zakharkin, L.I., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1956, p. 313.
10. 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.
11. 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.
12. Elokhina, V.N., Nakhmanovich, A.S., Larina, L.I., Shishkin, O.V., Baumer, V.N., and Lopyrev, V.A., *Izv. Akad. Nauk, Ser. Khim.,* 1999, p. 1536.
13. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Zakrzewski, V.G., Montgomery, J.A., Stratmann, R.E., Burant, J.C., Dapprich, S., Millam, J.M., Daniels, A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J. B., Cioslowski, J., Ortiz, J.V., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nana yakkara A., Gonzalez, C., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Andres, J.L., Gonzalez, C., Head-Gordon, M., Replogle, E.S., and Pople, J.A., *Gaussian 98, Revision A.6,* Gaussian, Inc., Pittsburgh PA, 1998.