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# One-Stage Procedure of Synthesis of Highly Reactive α-Chloro-β-ketoacetals. 4-Chloropyrazoles from α-Chloro-β-ketodimethoxyacetals

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**Abstract**—Conditions were developed where the reaction of alkyl 1,2-dichlorovinyl ketones with alcohols and 1,2-dihydroxybenzenes led to the formation of the corresponding open-chain and cyclic α-chloro-β-ketoacetals. The reaction of α-chloro-β-alkylketodimethoxyacetals with alkyl-, benzyl-, and arylhydrazines resulted in 1,3-substituted 4-chloropyrazoles in 70–90% yields demonstrating that primarily formed 2,2-dimethoxy-1-chloroethyl alkyl ketones hydrazones underwent heterocyclization.

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α-Chloro-β-ketoacetals are building blocks for organic synthesis, promising polydentate ligands for designing metal complex catalysts, and also models for solving fundamental theoretical problems [1, 2]. Owing to their high reactivity and different activity of the reaction sites they underlie syntheses of versatile classes of compounds [1].

At the same time α-chloro-β-ketoacetals are insufficiently used in the organic synthesis for the methods of their preparation and isolation are very laborous. Nowadays convenient and efficient preparation methods are developed for α-halogen-con-taining diketones and ketoesters [2]. α-Chloro-β-keto-acetals are obtained mainly from very labile α-chloro-β-ketoaldehydes, and among them only formyl deriva-tives of aryl methyl ketones and hydroxymethylene ketones with a substituent (alkyl or nitro group) at the α-carbon atom are relatively stable [1, 2].

In continuation of the research on the reactivity of the synthesized 1,2-dichlorovinyl alkyl ketones [3] we involved them into a reaction with alcohols and phenols in the presence of an equimolar quantity of NaOH. Both alkanols and DMSO, DMF were used as solvents.

1,2-Dichlorovinyl alkyl ketones reacted with methanol in the presence of 1 equiv of alkali at 30–40°C giving the corresponding ketoacetals **IIa–IIc**; therewith the intermediate alkoxyvinyl ketones **Ia–Ic** were not isolated in an individual state except for ketone **Id**.

$$ROH + R'C(O)CCl{=}CHCl$$

$$\xrightarrow{NaOH} \underset{\textbf{Ia–Id}}{R'C(O)CCl{=}CH{-}OR} \longrightarrow \underset{\textbf{IIa–IIc}}{R'C(O)CClHCH(OR)_2}$$

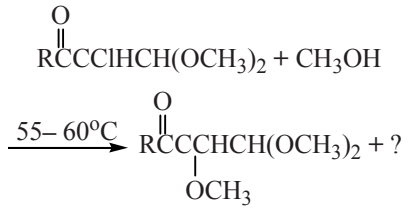
R = Me, R' = Me (**a**), Et (**b**), Pr (**c**); R = Ph, R' = Pr (**d**)

The yields of α-chloro-β-ketoacetals sharply decreased in going from methanol to ethanol, and in the reaction of 1,2-dichlorovinyl alkyl ketones with alcohols like propanol and 2-methylpropanol was a mixture obtained (as shown by $^1$H NMR data) of compounds where the content of the target α-chloro-β-ketoacetal was 20–30%. The distillation of these reaction mixtures led to the decomposition of the products mixtures.

Yet the reaction of phenol with 1,2-dichlorovinyl ketones in aprotic solvents (DMSO, DMF) without heating stopped at the stage of the corresponding (phenoxy)chlorovinyl propyl ketone (**Id**). The addition of the second phenol molecule with simultaneous formation of an intractable mixture of products occurres only at heating of the reagents for 5–6 h at 50–60°C.

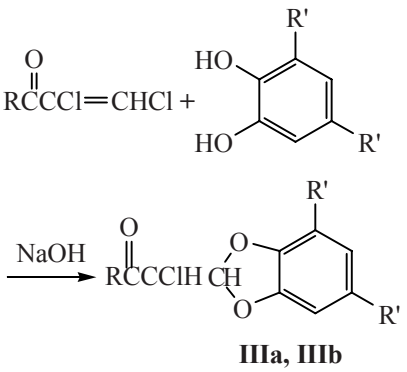
At raising the amount of alkali to the ratio ketone : NaOH = 1:2 the reaction carried out in alcohol involved also the chlorine atom in the α-position with respect to the carbonyl group. We failed to find the conditions for selective formation of trialkoxyethyl ketones: at varying

the process temperature, the content of alkali and alcohol we isolated only a mixture of trialkoxyethyl ketones (20–40%) with compounds of unknown structure as showed the data of $^1$H and $^{13}$C NMR spectra.



R = $CH_3$, $C_2H_5$, $C_3H_7$.

Alkyl 1,2-dichlorovinyl ketones reacted with 1,2-dihydroxybenzenes at 50–60°C in DMSO giving in good yield 2-(acyl)chloromethylbenzo-1,3-dioxoles, cyclic α-chloro-β-ketoacetals **IIIa** and **IIIb**.



**IIIa, IIIb**

R = Pr, R' = H (**a**); R = Et, R' = *t*-Bu (**b**).

The structure of compounds obtained was investigated by IR and NMR spectroscopy, the composition was confirmed by elemental analysis.

In the IR spectrum of 2-phenoxy-1-chlorovinyl propyl ketone (**Id**) absorption bands appeared of C=O, C=C, and C–H bonds of aromatic, alkyl, and olefin groups. In the $^1$H NMR spectrum of ketone **Id** alongside the characteristic resonances of the protons of the propyl and phenyl groups a downfield singlet was observed belonging to the olefin proton.

In the $^1$H NMR spectra of the products mixtures obtained in reactions of 1,2-dichlorovinyl alkyl ketones in the presence of 1 equiv of alkali with ethanol, propanol, butanol and 2-methylpropanol also the downfield singlet of the olefin proton was observed at 7.8–8.0 ppm.

In the IR spectra of compounds synthesized **IIa–IIc**, **IIIa**, and **IIIb** the absorption bands of the C=O group appeared in the region 1710–1720 cm$^{-1}$.

In the $^1$H NMR spectra of ketoacetals **IIa–IIc** the doublet signals of protons from CHCl and $CH(OR)_2$ groups appeared at 4.15–4.24 and 4.54–4.61 ppm respectively. It should be noted also that the methoxy groups of ketoacetals **IIa–IIc** are magnetically nonequivalent and therefore two singlet proton and carbon signals from $OCH_3$ groups are observed in the $^1$H and $^{13}$C NMR spectra ($\Delta\delta_H$ 0.4, $\Delta\delta_C$ 1.15–1.40 ppm).

The carbon of the carbonyl group in the $^{13}$C NMR spectra of obtained ketoacetals **IIa–IIc**, **IIIa**, and **IIIb** gives rise to a signal in the region 200.03–203.52 ppm, whereas the analogous carbon signal in the spectrum of propyl phenoxyvinyl ketone **Id** is shifted upfield by 6–9 ppm.

In the $^1$H NMR spectra of cyclic ketoacetals **IIIa** and **IIIb** the proton signal of CHCl group is shifted downfield ($\Delta\delta \sim 0.26$ ppm) compared to the analogous signal in the spectra of the corresponding dimethoxy-ketoacetals **IIa–IIc** and similarly to the protons of $CH(OR)_2$ group appears as two doublets: in the spectrum of cyclic acetal **IIIa** the coupling constants corresponding to the doublet proton signals of CHCl and $CH(O_2X)$ groups equal *J* 4.4 Hz. In the $^1$H NMR spectrum of compound **IIIb** the proton signals of groups CHCl and $CH(O_2X)$ give rise to two doublets with a coupling constant *J* 4.7 Hz.

This magnetic nonequivalence of protons and carbons of the methine and alkoxy groups in compounds **IIa–IIc**, **IIIa**, and **IIIb** revealed by the $^1$H and $^{13}$C NMR spectra originates from the presence in the structures of the molecules under investigation of one (**IIa–IIc** and **IIIa**) or two (**IIIb**) asymmetric centers.

Hence we for the first time developed conditions for preparation from 1,2-dichlorovinyl ketones of α-chloro-β-ketodimethoxyacetals and cyclic α-chloro-β-keto-acetal in 45–88% yield, that might underlie syntheses of versatile classes of compounds. But first of all the α-chloro-β-ketoacetals are valuable initial substances for the synthesis of heterocyclic compounds, in particular, of halogenated pyrazoles, similar to the other 2-halogen-containing 1,3-dicarbonyl compounds. For instance, the reaction of β-ketoesters, diketones, ketoaldehydes and their acetals with hydrazine and phenylhydrazine is known to be a convenient procedure for the synthesis of functionalized pyrazoles [1, 4, 5], but similar reactions of 2-haogen-containing β-dicarbonyl compounds are poorly documented [1, 2, 4, 5], evidently because of unavailability of the initial substances. It is known [4]

that 2-chloro- and 2-bromoacetoacetate react with phenylhydrazine to form 4-chloro-(bromo)-5-methyl-2-phenylpyrazol-3-one. From the reaction of 2-chloroacetoacetate with hydrazine at the temperature not exceeding –20°C was isolated in 35% yield 3(5)-hydroxy-4-chloro-5(3)-methylpyrazole [4]. Similarly reacted with hydrazine also the fluoroalkyl-containing 2-chloro-1,3-ketoesters giving the cor-responding pyrazolones in 35–60% yield [5]. A side reaction in this process was a reduction by hydrazines of the halogen-containing ketoesters and halopyrazoles and the formation of pyrazoles without halogen in the ring and halogen-free esters [4, 5].

We established that in the reaction of α-chloro-β-ketodimethoxyacetals **IIa–IIc** with alkyl- and arylhydrazines formed 1,3-substituted 4-chloropyrazoles **Va–Vf** in 70–90% yield. The reaction was carried out by heating the mixture of β-keto-α-chloroacetals **IIa–IIc** with hydrazines in methanol for 5 h (see the scheme).

The corresponding 1,5-disubstituted 4-chloropyrazoles were not detected indicating that the intramolecular heterocyclization occurred in the primary formed 2,2-dimethoxy-1-chloroethyl alkyl ketones hydrazones **IVa–IVg**. Therewith the reduction of the chlorine-containing products giving free of chlorine ketoacetals and pyrazoles similarly to reactions of ketoesters with hydrazines [4, 5] was not observed.

Hydrazones **IVa–IVf** were not isolated in pure state save 2,2-dimethoxy-1-chloroethyl methyl ketone 2,4-dinitrophenylhydrazone (**IVg**) whose structure proved the preliminary formation of hydrazones involving the keto group of ketoacetals **IIa–IIc** followed by the cyclization of the formed hydrazones **IVa–IVf** into the target 4-chloropyrazoles.

Pyrazoles **Va–Vf** were also obtained by a *one-pot* procedure without isolation of chloroketoacetals from the reaction mixture where the latter were formed.

The structure of compounds obtained was investigated by IR and NMR spectroscopy, the composition was confirmed by mass spectra and elemental analysis.

In the IR spectra of 1-alkyl-4-chloropyrazoles **Va–Vf** attention should be attracted by the absorption band in the region 3125–3150 $cm^{-1}$ characteristic of the stretching vibrations of the $C^5$–H bonds of the heterocycle. The absorption bands of C=C and C=N bonds of the heterocycle appeared in the IR spectra at 1470–1575 $cm^{-1}$.

In the $^1H$ NMR spectra of pyrazoles **Va–Vf** the signals of protons $H^5$ are observed in the region 7.23–7.27 ppm.

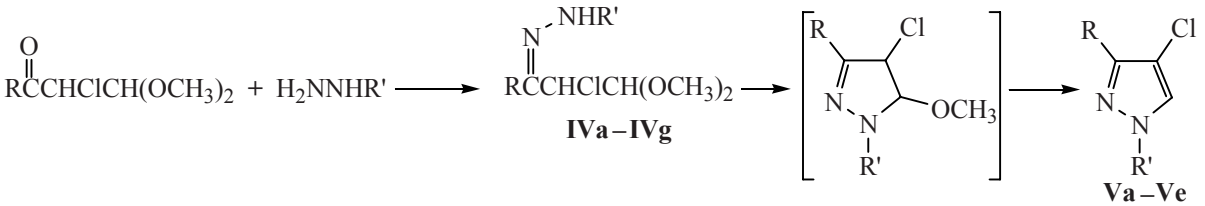
This chemoselective reaction of formation of 1,3-substituted 4-chloropyrazoles characterizes the potential of α-chloro-β-ketoacetals application to the synthesis of functionalized pyrazoles. For instance, after preliminary replacement of the chlorine in the initial α-chloro-β-ketoacetals by other functional groups the reaction with hydrazines can yield 4-organyloxy, -thio-, -aminopyrazoles that are widely used as semiproducts for production of dyes, fluorescent substances, efficient pesticides, and pharmaceuticals. They also possess a theoretical interest due to the wealth of the chemical transformations.

Therefore we developed a new method for the synthesis of α-chloro-β-ketoacetals, promising semiproducts for preparation of heteroatomic multifunctional systems and heterocyclic compounds, and for the first time showed the possibility to synthesize pyrazoles therefrom.

## EXPERIMENTAL

$^1H$ and $^{13}C$ NMR spectra were registered on a spectrometer Bruker DPX-400 (400.6 and 100.61 MHz respectively) from solutions in $CDCl_3$, $^1H$ NMR spectrum of compound Ivg was registered in DMSO-$d_6$. Chemical shifts of $^1H$ and $^{13}C$ were measured with respect to

**Scheme.**




R = $CH_3$, R' = $C_6H_5$ (**a**), $C_7H_{15}$ (**b**) $C_6H_3(NO_2)_2$-2,4 (**IVg**); R = $C_2H_5$, R' = $C_2H_5$ (**c**), $CH_2C_6H_5$ (**d**); R = $C_3H_7$, R' = $C_2H_5$ (**e**), $C_6H_5$ (**f**).

HMDS. IR spectra were recorded on spectrophotometer Specord IR75 from KBr pellets or thin films.

**1-Chloro-2-phenoxyvinyl propyl ketone (Id).** To a solution of 0.95 g (0.01 mol) of phenol and 0.4 g (0.01 mol) of NaOH in 15 ml of DMSO was added dropwise at stirring 1.67 g (0.01 mol) of propyl 1,2-dichlorovinyl ketone. The reaction mixture was stirred at room temperature for 5 h and was left standing overnight, then it was diluted with water and extracted with dichloromethane. The extract was dried with $MgSO_4$, the solvent, initial ketone and phenol were distilled off in a vacuum. Yield 0.68 g (30%), very viscous undistillable substance, $n_D^{20}$ 1.5540. IR spectrum, ν, cm$^{-1}$: 3075 (HC=), 2965, 2935, 2875 ($C_3H_7$), 1685 (C=O). $^1$H NMR spectrum, δ, ppm: 7.93 s (1H, =CH), 7.30 t, 7.13 t, 7.03 d (5H, $C_6H_5$), 2.63 t (2H, $CH_2$, *J* 7.2 Hz), 1.60 m (2H, $CH_2$, *J* 7.2 Hz), 0.89 t (3H, $CH_3$, *J* 7.2 Hz). Found, %: C 64.35; H 5.90; Cl 15.75. $C_{12}H_{13}ClO_2$. Calculated, %: C 64.15; H 5.83; Cl 15.78.

Under similar conditions in reactions of propyl 1,2-dichlorovinyl ketone with methanol, ethanol, propanol, 2-methylpropanol, and butanol were isolated mixtures of undistillable products whose $^1$H NMR spectra contained groups of signals in the region 7.89–8.01 ppm and two unresolved doublets in the region 4.20–4.60 ppm. In the IR spectra were observed wide bands in the region 3055–3070, 2970–2880, 1685 cm$^{-1}$.

**α-Chloro-β-ketodimethoxyacetals IIa–IIc.** *General procedure*. To a solution of 0.4 g (0.01 mol) of NaOH in 30 ml of methanol was added dropwise at stirring 0.01 mol of alkyl 1,2-dichlorovinyl ketone. The reaction mixture was heated at 30–40°C for 3 h, and on cooling it was diluted with 100 ml of water, extracted with $CH_2Cl_2$, the extract was dried with $MgSO_4$ and distilled.

At heating of a mixture of equimolar amounts of alkyl 1,2-dichlorovinyl ketones and alkali in ethanol, propanol, 2-methylpropanol, and butanol at 50–60°C for 3 h were isolated mixtures of undistillable products whose $^1$H NMR spectra contained signals of groups CHCl, $CH(OAlk)_2$ and of protons from fragments RC(O) and AlkO. In the IR spectra were observed wide bands in the region 2970–2880, 1690–1710 cm$^{-1}$.

**1,1-Dimethoxy-2-chlorobutan-2-one (IIa).** Yield 1 g (60%), bp 62–64°C (20 mm Hg), $n_D^{20}$ 1.4340. IR spectrum, ν, cm$^{-1}$: 2935, 2830 ($CH_3$), 1710 (C=O). $^1$H NMR spectrum, δ, ppm: 4.61 d (1H, CH, *J* 6.3 Hz), 4.24 d (1H, CHCl, *J* 6.3 Hz), 3.45 (3H, $OCH_3$), 3.41 (3H, $OCH_3$), 2.30 (3H, $CH_3$). $^{13}$C NMR spectrum, δ, ppm: 200.63 (C=O), 104.09 (CH), 61.58 (CHCl), 55.83 ($OCH_3$), 54.68 ($OCH_3$), 27.55 ($CH_3$). Found, %: C 43.30; H 6.60; Cl 21.26. $C_6H_{11}ClO_3$. Calculated, %: C 43.26; H 6.65; Cl 21.28.

**1,1-Dimethoxy-2-chloropentan-3-one (IIb).** Yield 1.63 g (45%), bp 70–72°C (5 mm Hg), $n_D^{20}$ 1.4685. IR spectrum, ν, cm$^{-1}$: 2975, 2935, 2835 (Alk), 1720 (C=O). $^1$H NMR spectrum, δ, ppm: 4.56 d (1H, CH, *J* 6.7 Hz), 4.20 d (1H, CHCl, *J* 6.7 Hz), 3.38 s (3H, $OCH_3$), 3.34 s (3H, $OCH_3$), 2.60 t (2H, $CH_2$, *J* 7.1 Hz), 1.01 t (3H, $CH_3$, *J* 7.1 Hz). $^{13}$C NMR spectrum, δ, ppm: 203.52 (C=O), 104.30 (OCHO), 60.66 (CHCl), 56.05, 54.60, 34.00 ($CH_2$), 7.54 ($CH_3$). Found, %: C 46.48; H 7.33; Cl 19.65. $C_7H_{13}ClO_3$. Calculated, %: C 46.55; H 7.25; Cl 19.63.

**1,1-Dimethoxy-2-chlorohexan-3-one (IIc).** Yield 1.94 g (50%), bp 75–80°C (5 mm Hg), $n_D^{20}$ 1.4409. IR spectrum, ν, cm$^{-1}$: 2970, 2950, 2870, 2840 (Alk), 1720 (C=O). $^1$H NMR spectrum, δ, ppm: 4.54 d (1H, CH, *J* 6.7 Hz), 4.14 d (1H, CHCl, *J* 6.7 Hz), 3.36 s (3H, $OCH_3$), 3.32 s (3H, $OCH_3$), 2.50 t (2H, $CH_2$, *J* 7.4 Hz), 1.54 m (2H, $CH_2$, *J* 7.4 Hz), 0.83 t (3H, $CH_3$, *J* 7.4 Hz). $^{13}$C NMR spectrum, δ, ppm: 202.22 (C=O), 103.56 (OCHO), 59.99 (CHCl), 55.36, 53.90, 41.82 ($CH_2$), 16.19 ($CH_2$), 11.01 ($CH_3$). Found, %: C 50.26; H 7.80; Cl 18.17. $C_8H_{15}ClO_3$. Calculated, %: C 49.36; H 7.77; Cl 18.21.

**2-(1-Chloro-2-oxopentyl)benzo-1,3-dioxole (IIIa).** To a solution of 1.1 g (0.01 mol) of pyrocatechol and 0.4 g (0.01 mol) of NaOH in 15 ml of DMSO was added dropwise at stirring 1.67 g (0.01 mol) of propyl 1,2-dichlorovinyl ketone. The reaction mixture was stirred at 50–60°C for 3 h, then it was diluted with water and extracted with dichloromethane. The extract was dried with $MgSO_4$, the solvent was distilled off in a vacuum. Yield 1.45 g (60%), very viscous undistillable substance. IR spectrum, ν, cm$^{-1}$: 3065 (C=O), 2960, 2925, 2875 ($C_3H_7$), 1710 (C=O). $^1$H NMR spectrum, δ, ppm: 6.80 m (4H, $C_6H_4$), 6.45 d (1H, CH, *J* 4.4 Hz), 4.46 d (1H, CHCl, *J* 4.4 Hz), 2.68 t (2H, $CH_2$, *J* 7.2 Hz), 1.61 m (2H, $CH_2$, *J* 7.2 Hz), 0.90 t (3H, $CH_3$, *J* 7.2 Hz). $^{13}$C NMR spectrum, δ, ppm: 202.17 (C=O), 146.69, 121.99, 120.32, 115.32, 108.62, 107.96, 61.97 (CHCl), 42.41 ($CH_2$), 16.51 ($CH_2$), 13.27 ($CH_3$). Found, %: C 59.90; H 5.50; Cl 14.70. $C_{12}H_{13}ClO_3$. Calculated, %: C 59.88; H 5.44; Cl 14.73.

**2-(1-Chloro-2-oxobutyl)-4,6-di-*tert*-butylbenzo-1,3-dioxole (IIIb)** was obtained in the same way as compound **IIIa** from 1.56 g (7 mmol) of 3,5-di-*tert*-butylpyrocatechol, 0.28 g (7 mmol) of NaOH, and 1.07 g (7 mmol) of ethyl 1,2-dichlorovinyl ketone in 10 ml of

DMSO. Yield 1.18 g (50%). IR spectrum, ν, cm$^{-1}$: 3085 (C–$H_{Ar}$), 2950, 2900, 2870 (Alk), 1710 (C=O). $^1$H NMR spectrum, δ, ppm: 6.85 s, 6.75 s (2H, $C_6H_2$), 6.43 d (1H, CH, *J* 4.5 Hz), 4.48 d (1H, CHCl, *J* 4.5 Hz), 2.75 q (2H, $CH_2$, *J* 7.2 Hz), 1.39 s (9H, $C_4H_9$), 1.30 s (9H, $C_4H_9$), 1.09 t (3H, $CH_3$, *J* 7.2 Hz). Found, %: C 68.10; H 8.20; Cl 10.24. $C_{19}H_{27}ClO_3$. Calculated, %: C 67.34; H 8.03; Cl 10.46.

**Methyl 1-chloro-2,2-dimethoxyethyl ketone 2,4-dinitrophenylhydrazone (IVg).** To a solution of 0.98 g (5 mmol) of 2,4-dinitrophenylhydrazine in 30 ml of methanol and 7 ml of 25% sulfuric acid was poured at stirring 0.83 g (5 mmol) of methyl 1-chloro-2,2-dimethoxyethyl ketone (**IIa**). The reaction mixture was stirred at room temperature for 4 h and was left standing overnight, then it was diluted with 50 ml of water, the separated precipitate was filtered off and dried. Yield 1.5 g (88%), mp 93–95°C. IR spectrum, ν, cm$^{-1}$: 3300 (NH), 3090 ($CH_{Ar}$), 2930, 2840 ($CH_3$), 1610, 1585 (C=N, C=C), 1510, 1325 ($NO_2$). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 10.80 (1H, NH), 8.84 d (1H, H$^{3'}$, $^4J$ 2.3 Hz), 8.40 d.d (1H, H$^{5'}$, $^4J$ 2.3, 9.5 Hz), 7.89 d (1H, H$^{6'}$, $^4J$ 9.5 Hz), 4.84 d (1H, CH, $^3J$ 7.3 Hz), 4.77 d (1H, CHCl, $^3J$ 7.3 Hz), 3.41 s (3H, $OCH_3$), 3.34 s (3H, $OCH_3$), 2.13 (3H, $CH_3$). Found, %: C 41.60; H 4.26; Cl 10.25; N 16.19. $C_{12}H_{15}ClN_4O_6$. Calculated, %: C 41.57; H 4.36; Cl 10.23; N 16.16.

**4-Chloropyrazoles Va–Vf**. **General procedure.** *a*. To a solution of 0.01 mol of an appropriate α-chloro-β-ketoacetal in 30 ml of methanol was added dropwise 0.01 mol alkyl(aryl)hydrazine. The reaction mixture was boiled for 5 h, diluted with water, extracted with ether, the extract was dried with $CaCl_2$ and subjected to distillation.

*b*. To a solution of ketoacetals **IIa–IIc** prepared in 30–40 ml of methanol from 0.01 mol of an appropriate alkyl 1,2-dichlorovinyl ketone in the presence of 0.4 g (0.01 mol) of NaOH without isolation of ketoacetal from the reaction mixture was added at stirring 0.01 mol of alkyl(aryl)hydrazine. Further process and workup were performed as described in procedure *a*.

**1-Phenyl-3-methyl-4-chloropyrazole (Va).** *a*. Yield 1.49 g (77%), bp 125°C (4 mm Hg). IR spectrum, ν, cm$^{-1}$: 3130, 3050 (=CH), 2950, 2920 ($CH_3$), 1595 (C=C). $^1$H NMR spectrum, δ, ppm: 7.76 s (1H, H$^5$), 7.55 d, 7.37 t, 7.20 t (5H, $C_6H_5$), 2.28 (3H, $CH_3$). Found, %: C 62.30; H 4.75; Cl 18.38; N 14.52. $C_{10}H_9ClN_2$. Calculated, %: C 62.35; H 4.71; Cl 18.40; N 14.54.

**1-Heptyl-3-methyl-4-chloropyrazole (Vb).** *a*. Yield 1.83 g (85%), viscous fluid, purified by column chromatography on silica gel, eluent hexane. $n_D^{20}$ 1.4800. IR spectrum, ν, cm$^{-1}$: 3140 (=C–H), 2960, 2930, 2860 (Alk), 1540 (C=C). $^1$H NMR spectrum, δ, ppm: 7.26 s (1H, =C–H), 3.96 t (2H, $CH_2$, *J* 7.1 Hz), 1.78 m (2H, $CH_2$), 1.26 m [8H, $(CH_2)_4$], 0.86 t (3H, $CH_3$, *J* 7.1 Hz). $^{13}$C NMR spectrum, δ, ppm: 144.8 (C$^3$), 126.7 (C$^5$), 108.0 (C$^4$), 52.3, 31.4, 30.0, 28.5, 26.2, 23.3, 13.7 ($C_7H_{15}$). Found, %: C 60.78; H 8.91; Cl 12.59; N 18.54. $C_{11}H_{19}ClN_2$. Calculated, %: C 61.53; H 8.92; Cl 16.51; N 13.05.

**1,3-Diethyl-4-chloropyrazole (Vc).** *b*. Yield 1.27 g (80%), bp 77–80°C (14–15 mm Hg). IR spectrum, ν, cm$^{-1}$: 3130 (=C–H), 2960, 2940, 2860 (Alk), 1560 (C=C). $^1$H NMR spectrum, δ, ppm: 7.27 s (1H, =C–H), 4.03 q (2H, $CH_2$, *J* 7.3 Hz), 2.61 q (2H, $CH_2$, *J* 7.7 Hz), 1.41 t (3H, $CH_3$, *J* 7.3 Hz), 1.23 t (3H, $CH_3$, *J* 7.7 Hz). Found, %: C 53.10; H 7.51; Cl 22.30; N 17.89. $C_7H_{11}ClN_2$. Calculated, %: C 53.00; H 6.99; Cl 22.35; N 17.66.

**1-Benzyl-3-ethyl-4-chloropyrazole (Vd).** *a*. Yield 1.98 γ (90%), viscous fluid, purified by column chromatography on silica gel, eluent hexane. $n_D^{20}$ 1.5610. IR spectrum, ν, cm$^{-1}$: 3140 (=C–H), 2970, 2940, 2870 (Alk), 1520 (C=C). $^1$H NMR spectrum, δ, ppm: 7.21 s (1H, =C–H), 7.32–7.20 m (5H, $C_6H_5$), 5.17 s (2H, $CH_2$), 2.68 q (2H, $CH_2$, *J* 7.6 Hz), 1.29 t (3H, $CH_3$, *J* 7.6 Hz). Found, %: C 67.05; H 6.00; Cl 15.27; N 12.08. $C_{12}H_{13}ClN_2$. Calculated, %: C 67.10; H 5.63; Cl 15.23; N 12.04.

**1-Ethyl-3-propyl-4-chloropyrazole (Ve).** *a*. Yield 1.29 g (75%), bp 70°C (5 mm Hg), $n_D^{20}$ 1.4838. IR spectrum, ν, cm$^{-1}$: 3140 (=C–H), 2960, 2940, 2860 (Alk), 1520 (C=C). $^1$H NMR spectrum, δ, ppm: 7.27 s (1H, =C–H), 4.03 q (2H, $CH_2$, *J* 7.3 Hz), 2.56 t (2H, $CH_2$, *J* 7.5 Hz), 1.66 m (2H, $CH_2$), 1.40 t (3H, $CH_3$, *J* 7.3 Hz), 0.94 t (3H, $CH_3$, *J* 7.5 Hz). $^{13}$C NMR spectrum, δ, ppm: 148.8 (C$^3$), 126.1 (C$^5$), 107.7 (C$^4$), 27.5, 15.1, 13.5 ($C_3H_7$). Found, %: C 55.60; H 7.45; Cl 20.58; N 16.31. $C_8H_{13}ClN_2$. Calculated, %: C 55.65; H 7.59; Cl 20.53; N 16.22.

**1-Phenyl-3-propyl-4-chloropyrazole (Ve**). *a*. Yield 1.55 g (70%), bp 155°C (8 mm Hg), $n_D^{20}$ 1.5766. IR spectrum, ν, cm$^{-1}$: 3140, 3050 (=CH), 2950, 2925, 2870 ($C_3H_7$), 1595 (C=C). $^1$H NMR spectrum, δ, ppm: 7.76 (1H, H$^5$), 7.57 d, 7.37 t, 7.21 t (5H, $C_6H_5$), 2.65 t (2H, $CH_2$, *J* 7.4 Hz), 1.73 m (2H, $CH_2$, *J* 7.4 Hz), 0.98 t (3H, $CH_3$, *J* 7.4 Hz). $^{13}$C NMR spectrum, δ, ppm: 151.46 (C$^3$),

139.83 ($C^{1'}$), 129.41 ($C^{3',5'}$), 126.36 ($C^{5}$), 124.84 ($C^{4'}$), 118.59 ($C^{2',6',4'}$), 27.89 ($CH_2$), 21.89 ($CH_2$), 13.87 ($CH_3$). Found, %: C 65.35; H 6.00; Cl 16.08; N 12.66. $C_{12}H_{13}ClN_2$. Calculated, %: C 65.31; H 5.99; Cl 16.06; N 12.69.

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