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Synthesis, Structure, and Characteristics of 1,2-Dichlorovinyl Alkyl Ketones

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Abstract—A method of alkyl 1,2-dichlorovinyl ketones preparation from acyl halides and 1,2-dichloroethylene was developed. The configurational equilibrium and electronic structure of alkyl 1,2-dichlorovinyl ketones was investigated by IR, ^{1}H and ^{13}C NMR spectroscopy, by measuring dipole moments, and by quantum-chemical calculations using methods RHF and B3LYP in the basis 6-311++ G (*d,p*). Alkyl 1,2-dichlorovinyl ketones are stable in the *Z,s-cis*-configuration where the olefin proton is involved into an intramolecular hydrogen bond with the oxygen of the carbonyl group. Reaction of 1,2-dichlorovinyl ketones with alkylhydrazines afforded 1-alkyl-3-alkyl-4-chloropyrazoles. The reaction of alkyl 1,2-dichlorovinyl ketones with 1,1-dimethylhydrazine involved dehydrochlorination and afforded 1,1-dimethylhydrazinium hydrochloride and a mixture of compounds with uncertain structure.

Chlorovinyl ketones are extremely important and promising semiproducts for syntheses of quite a number of polyfunctional highly reactive and heterocyclic compounds [1]. With a goal to find a convenient procedure for preparation of a number of heterocyclic compounds, among them 1-alkyl-4-chlorosubstituted pyrazoles analogously to [2], and also to reveal the difference in the chemical properties of 1,2-dichlorovinyl ketones and their isostructural analogs, 2,2-dichlorovinyl ketones we have developed a method of synthesis for alkyl 1,2-dichlorovinyl ketones and report here on this method and the study of chemical properties and structure of these ketones. A comparative analysis of the structural parameters and reactivity of these compounds was also performed relative to similar data for 2-chloro- and 2,2-dichlorovinyl ketones

Prior to this study the following compounds were reported: dichloromethyl [3], phenyl 1,2-dichlorovinyl ketones [4], and a number of cyclic 2,3-dichloroenones-1 [1, 5]. The phenyl ketone was obtained by reaction of 1,2-dichloroacryloyl chloride with benzene in the presence of aluminum chloride [4]. It also was reported that this compound was prepared in an 80% yield as a result of transformation of the product of phenyl(dimethylamino)-acetonitrile dichlorovinylation by boiling for 15 min in ethanol in the presence of Cu(II) sulfate pentohydrate [6].

While up till now a single acyclic 1,2-dichlorovinyl ketone was known, dichloromethyl 1,2-dichlorovinyl ketone [3] obtained from the corresponding acyl chloride and *cis*-1,2-dichloroethylene in the presence of aluminum chloride at 35°C within 40 h, we developed in this study preparation procedure and synthesized metyl, ethyl, and propyl 1,2-dichlorovinyl ketones in up to 90% yield.

$$\mathrm{AlkCOCl} + \mathrm{CHCl{=}CHCl} \xrightarrow{\mathrm{AlCl_3}} \underset{\textbf{IV–VI}}{\mathrm{AlkC(O)CHClCHCl_2}}$$

$$\xrightarrow[-\mathrm{HCl}]{} \underset{\textbf{I–III}}{\mathrm{AlkC(O)CCl{=}CHCl}}$$

Alk = Me (**I, IV**), Et (**II, V**), Pr (**III, VI**).

Under conditions used in the synthesis of dichloromethyl 1,2-dichlorovinyl ketone [3] but applying the commercially produced mixture of *cis*- and *trans*-1,2-dichloroethenes methyl and propyl 1,2-dichlorovinyl ketones were obtained in the yield not exceeding 24%.

Under conditions we developed the reaction is carried out by heating for 6 h at 60°C the corresponding acyl chloride with the mixture of *cis*- and *trans*-1,2-dichloroethenes in the presence of anhydrous aluminum chloride at the reagents ratio 1:10:1. On completing the reaction the products were subjected to distillation to isolate and characterize the mixture of substances: the corresponding 1,2-dichlorovinyl ketones **I–III**, and 1,2,2-trichloroethyl alkyl ketones **IV–VI**. The treating of the reaction mixture with bases without heating or steam distillation analogously to preparation procedures for 2-chloro- and 2,2-dichlorovinyl ketones from 2,2-dichloro- and 2,2,2-trichloroethyl ketones [1, 7] did not result in a complete conversion of 1,2,2-trichloroethyl alkyl ketones **IV–VI** into 1,2-dichlorovinyl ketones. Exhaustive dehydrochlorination of 1,2,2-trichloroethyl alkyl ketones **IV–VI** succeeded on prolonged heating of the reaction mixture at 80–90°C in the presence of aqueous sodium carbonate.

At the same time these severe conditions were not fit for preparation of pure chloromethyl and trichloromethyl 1,2-dichlorovinyl ketones in reaction of monochloro- and trichloracetyl chlorides with 1,2-dichloroethylene. The trichloroethyl ketones formed in the first reaction stage when treated with bases at heating suffered hydrolysis involving the chloromethyl moiety and afforded a mixture of products containing among them the corresponding 1,2-dichlorovinyl derivatives as showed the resonances at 7.6–8.0 ppm in the ^{1}H NMR spectrum of the reaction mixture. We also failed to isolate pure products of the reaction with dichloroethylene of benzoyl and 4-chlorobenzoyl chlorides. The studies on the synthesis of chloromethyl and aryl 1,2-dichlorovinyl ketones are in progress.

We did not isolate individual tichloroethyl ketones **IV–VI** for they decomposed during distillation, but the compounds were characterized by IR and ^{1}H NMR spectra. In the IR spectra of compounds **IV–VI** the frequency and intensity of the absorption bands of carbonyl stretching vibrations are higher than in the corresponding spectra of 1,2-dichlorovinyl ketones. In the ^{1}H NMR spectra of ketones **IV–VI** appeared two characteristic proton doublets from $CHCl_2$ and CHCl groups and the signals from the protons of alkyl moieties.

The synthesized 1,2-dichlorovinyl ketones **I–III** are colorless liquids that in contrast to 2-chloro- and 2,2-dichlorovinyl ketones are relatively stable, do not turn dark at storage for a month under common conditions and do not undergo at long storage the dehydrochlorination to afford pyrones [8]. The structure of ketones **I–III** was established by physicochemical methods and confirmed by elemental analysis.

In the ^{1}H NMR spectra of 1,2-dichlorovinyl ketones **I–III** as also in those of 2,2-dichlorovinyl ketones and 2,2-dibromovinyl fluoromethyl ketone [9, 10] a singlet from olefin proton is observed. Note that the chemical shift of the olefin proton in the spectrum of phenyl 1,2-dichlorovinyl ketone (δ 6.39 ppm) reported in [6] is not in agreement with the chemical shifts of =CH in alkyl ketones **I–III** (δ 7.54–7.56 ppm) observed in the present study.

The singlet of the β-proton in the ^{1}H NMR spectra and also the single narrow absorption band of the carbonyl group in the IR spectra of 1,2-dichlorovinyl ketones **I–III** evidence their geometrical and in all likelihood conformational uniformity.

We previously studied conformational structure of important organic compounds, alkyl(aryl) 2,2-dichlorovinyl ketones and trifluoromethyl 2,2-dibromovinyl ketones by means of quantum-chemical calculations along SCF MO LCAO method using semiempirical CNDO/2 procedure, method B3LYP/6-311 G (*d,p*), calculations of atomic oscillations, measurements of dipole moments, IR, UV, ^{1}H NMR, and ^{35}Cl NQR spectroscopy [9–12].

In the present research the structure of alkyl 1,2-dichlorovinyl ketones **I–III** and the conformational equilibrium in their molecules were investigated by IR and ^{1}H NMR spectroscopy, measurements of dipole moments, and by quantum-chemical calculations using methods RHF and B3LYP in the basis 6-311++ G (*d,p*) [13] (Tables 1 and 2). The results obtained were compared with previous calculations for the 2,2-dichloro(bromo)vinyl ketones [12].

In the ^{1}H NMR spectra of 1,2-dichlorovinyl ketones **I–III** is observed a singlet from the β-protone displaced downfield by ≈1 ppm with respect to the singlet from the α-vinyl proton in the ^{1}H NMR spectrum of the 2,2-di-chlorovinyl analogs [10], and its chemical shift is close to the values of the signal from the β-olefin proton in the spectrum of methyl 2-chlorovinyl ketone (**XIV**) [^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.26 d (=CHCl, 1H, *J* 13.9 Hz), 6.45 d (=CH, 1H, *J* 13.9 Hz), 2.25 s (CH_3, 3H)] and chloromethyl 2-chlorovinyl ketone (**XV**) [^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.49 d (=CHCl, 1H, *J* 13.9 Hz), 6.76 d (=CH, 1H, *J* 13.9 Hz), 4.19 s (CH_2Cl, 2H)].

The more downfield chemical shift of the olefin proton in the ^{1}H NMR spectrum of ketones **I–III** is well consistent with the known trend to downfield displacement

Table 1. Experimentally measured and calculated [B3LYP/6-311++G(*d,p*), RHF/6-311++G(*d,p*)] dipole moments and chemical shifts of ^{1}H and ^{13}C for *E*- and *Z*-isomers of 1,2-dichlorovinyl ethyl ketone

Isomer	Method	Parameters								
		μ, D	^{1}H NMR spectrum, δ, ppm (*J*, Hz)			^{13}CNMR spectrum, δ, ppm (*J*, Hz)				
			=C–H	CH_2	CH_3	C^{β}	C^{α}	C=O	CH_2	CH_3
Obtained experimentally	Experiment	2.6[a]	7.54 s,[b] 8.08 s,[c] (*J* 7.2)	2.80 q, 2.82 q, (*J* 7.2)	1.13 t, 1.03 t	130.53	134.56	192.95	32.27	7.57
Z	B3LYP	1.34	7.98	2.76	1.06	148.1	147.20	200.90	38.90	9.26
Z	RHF	1.47	8.02	2.35	1.13	145.66	138.81	194.29	33.20	9.62
E	B3LYP	2.65	6.27	2.76	1.11	127.8	145.20	207.0	39.40	8.71
E	RHF	2.96	6.25	2.25	1.17	126.42	143.06	195.95	33.14	9.16

[a] Measured in benzene at 20°C. [b] Registered in $CDCl_3$. [c] Registered in DMSO-d_6.

Table 2. Total charges on atoms (*Q*, e) and bond lengths (*l*, Å) calculated {B3LYP/6-311++G (D,P), RHF/6-311++G (*d, p*}for *E*- and *Z*-isomers of 1,2-dichlorovinyl ethyl ketone

Configuration	Atom	Q		*l*	
		B3LYP	RHF	B3LYP	RHF
Z,s-cis	C^1	–1.025	–0.981	C^2–C^1 1.347	C^2–C^1 1.337
	C^2	0.913	1.103	C^3–C^2 1.487	C^3–C^2 1.512
	C^3	–0.821	–0.806	C^4–C^3 1.500	C^4–C^3 1.515
	C^4	–0.260	–0.268	C^5–C^4 1.507	C^5–C^4 1.526
	C^5	–0.673	–0.741	Cl^6–C^1 1.678	Cl^6–C^1 1.720
	Cl^6	0.494	0.433	Cl^7–C^2 1.696	Cl^7–C^2 1.748
	Cl^7	0.533	0.452	O^8–C^3 1.237	O^8–C^3 1.214
	O^8	–0.258	–0.333	H^9–C^1 1.104	H^9–C^1 1.081
	H^9	0.303	0.340		
E,s-trans	C^1	–0.850	–0.846	C^2–C^1 1.326	C^2–C^1 1.326
	C^2	0.728	0.885	C^3–C^2 1.524	C^3–C^2 1.524
	C^3	–0.528	–0.393	C^4–C^3 1.512	C^4–C^3 1.512
	C^4	–0.196	–0.238	C^5–C^4 1.526	C^5–C^4 1.526
	C^5	–0.592	–0.642	Cl^6–C^1 1.745	Cl^6–C^1 1.745
	Cl^6	0.271	0.197	Cl^7–C^2 1.754	Cl^7–C^2 1.754
	Cl^7	0.322	0.232	O^8–C^3 1.206	O^8–C^3 1.206
	O^8	–0.169	–0.239	H^9–C^1 1.080	H^9–C^1 1.080
	H^9	0.231	0.264		

of the proton signal on the introduction of a geminal chlorine atom into the vinyl structure. The expected downfield shift of the olefin β-proton signal in going from 2-chlorovinyl ketones to 1,2-dichlorovinyl ketones was also registered.

The presence in the vibration spectra of alkyl 1,2-dichlorovinyl ketones **I–III** of narrow bands in the absorption region of C=O and C=C groups is likely caused by their existence in the form of a single isomer and a single rotational conformer. Therewith in the IR spectra of ketones **I–III** the observed stretching vibration bands of the carbonyl group (1690–1695 cm^{-1}) and the double bond are located in the region corresponding to the high-frequency component in the spectra of alkyl 2,2-dichlorovinyl ketones (1705 cm^{-1}) [12] belonging to the carbonyl vibrations of the *s-cis*-isomer. It was formerly

Z, s-cis *E, s-cis* *Z, s-trans* *E, s-trans*

established that the dichloro(bromo)vinyl ketones existed as a mixture of two *s-cis*-, *s-trans*-conformers [12]. It should be indicated that in the cyclic 1,2-dichloroenones with the fixed *Z,s-trans*-form the band of stretching vibrations $\nu_{C=O}$ is shifted by ≈ 40–50 cm^{-1} to the higher frequencies [5] compared with the analogous band in the IR spectra of ketones **I–III**.

The data of calculations performed in this study indicate that the planar *Z,s-cis*-structure of 1,2-dichlorovinyl ketone **II** is more favorable than non-planar ($\varphi OCC_\alpha C_\beta$ ~90°) *s-trans*-conformer of isomer of this compound by 4.57 (RHF) and 5.78 (B3LYP) kcal mol^{-1}.

It is presumable that in the *Z,s-cis*-structure **II** is present an intramolecular hydrogen bond (C=O···H) between the carbonyl oxygen and vinyl proton. This assumption is supported by the value of the distance between these atoms amounting to ~2.44 Å that is greater than the sum of their covalent radii (0.99 Å) [14] but less than the sum of the van der Waals radii (2.72 Å) [15] (Table 2). Besides the C=O and C–H bonds of this conformer are somewhat longer that those in the *s-trans*-conformer of the *E*-isomer (Table 2). The negative charge on the oxygen is larger in the planar *s-cis*- than in *s-trans*-conformer (Table 2). The same trend is observed in the change in the conformers of the positive charge on the hydrogen of the vinyl fragment thus facilitating the formation of the intramolecular hydrogen bond. For instance, the calculated chemical shift of the vinyl proton in the *Z,s-cis*-structure of ketone II is located in a weaker field than that of the *trans*-structure ($\Delta\delta_{calc}$ 1.71 ppm) (Table 1).

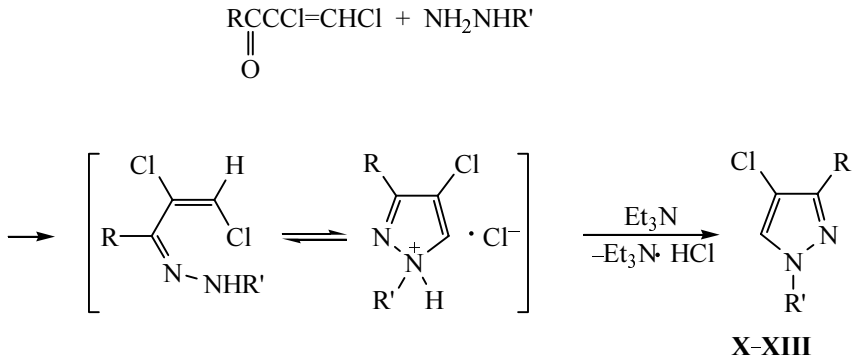
The calculated chemical shifts of ^{1}H for *Z,s-cis*-isomer of ketone II more often coincide with the experimental data (Table 1). For instance, the calculated chemical shift value for the vinyl proton in the *Z,s-cis*-structure of ketone **II** and also δ_C (C=O) are closer to the experimental data than the calculated δ_H (=C–H) and δ_C (C=O) for the *trans*-structure (Table 1). At the same time the experimentally measured chemical shift value for the β-carbon atoms δ_C (C^β) is in better agreement with that of the *E,s-trans*-isomer of ketone **II**. The dipole moment of ketone **II** measured in benzene solution under standard conditions and equal to 2.6 D corresponds to the calculated value for *trans*-isomer in an s-*cis*-form of compound **II** (Table 1). This deviation of calculated values from the experimental data requires independent determination of the structure and elucidation of the reason of this discrepancy (e.g., the influence of the medium should be taken into consideration).

The data of ^{1}H NMR spectra for methyl and chloromethyl 2-chlorovinyl ketones (**XIV** and **XV** respectively) that we prepared ftom acetylene and the corresponding acyl chlorides according to [1] also showed that in these ketones a single isomer was present, and the stabilization of the observed *E*-isomer (J_{H-H} ≈ 14 Hz) was apparently ensured by an intramolecular hydrogen bond.

The calculations obtained in this study evidence a significant polarization of the double bond to the direction of C^β in the *E,Z*-isomers of 1,2-dichlorovinyl ketones. The total charge on this atom in the *Z*-isomer is close to –1, and on the atom C^α it amounts to ~+1. A similar charge distribution on the respective atoms but with somewhat smaller absolute values is observed in the *E*-isomer. Interestingly, the calculation procedures applied suggest that in the *E*- and *Z*-isomers of ketone **II** the charges on the carbon atoms of the carbonyl group C^3 are negative, and on the both chlorine atoms they are positive; the charge distribution obtained for ketone **II** is virtually independent of the calculation procedure.

We studied the behavior of 1,2-dichlorovinyl ketones **I–III** in reactions with some nucleophiles aiming at elucidating the difference and analogy with the 2-chloro-, 2,2-dichloro(bromo)vinyl ketones.

Ketones **I–III** reacted with dinitrophenylhydrazine yielding the corresponding alkyl 1,2-dichlorovinyl ketones hydrazones **VII–IX**. In the ^{1}H NMR spectra of hydrazones **VII–IX** the signals of the benzene ring protons with the characteristic splitting were observed. The coupling of H^3–H^5 protons was also revealed. The olefin



X–XIII

X, R = Me, R' = C_7H_{15}; XI, R = R' = Et; **XII**, R = Et, R' = Bn; **XIII**, R = C_7H_{15}, R' = Et.

proton appeared as a singlet indicating the existence of nitrophenylhydrazones **VII–IX** in the form of a single isomer in contrast to the analogous 2,2-dichlorovinyl ketones hydrazones [16]. It was established that similarly to the 2,2-dichlorovinyl alkyl ketones dinitrophenylhydrazones [16] hydrazones **VII–IX** did not undergo cyclization into pyrazoles when treated with bases in alcohols, in DMSO, in DMF or at thermolysis.

In reaction of 1,2-dichlorovinyl ketones with alkylhydrazines we isolated 1-alkyl-4-chloropyrazoles **X–XIII** in reproducible high yields. No alkylhydrazones were obtained no matter under what conditions the process was carried out: in aprotic or proton-donor solvents, at different molar ratio of the reagents and at various low temperatures (from –70 to 20°C).

Pyrazoles **X–XIII** are liquids with a characteristic mould odor, soluble in organic solvents.

The structure of pyrazoles **X–XIII** was proved by physicochemical methods, the composition was confirmed by elemental analysis.

In the IR spectra of 1-alkyl-4-chloropyrazoles **X–XIII** the presence of a band should be indicated in the region 3125–3150 cm^{-1} characteristic of the stretching vibrations of the C^5–H bond of the heterocycle. The absorption bands of the C=C bonds of the heterocycle appeared in the IR spectra at 1470–1575 cm^{-1}.

In the ^1H NMR spectra of pyrazoles **X–XIII** the resonance signals of protons H^5 appear in the region 7.23–7.27 ppm with a downfield shift of 0.6–1.3 ppm as compared to the H^4 signals of their 5-chloro-substituted analogs (5.92–6.58 ppm). The dependence of the chemical shift for the protons in the NCH_2R' group is a lot weaker. In the ^1H NMR spectrum of 1-ethylpyrazoles **XI** and **XII** the proton signals from the methylene group at the nitrogen atom are located downfield with respect to the signals from NCH_2 group in 1-heptylpyrazole (**X**).

4-Chloropyrazoles are promising for manufacturing drugs, dyes, fluorescents, insecticides, insectoacaricides, and other biologically active compounds. For instance, the derivatives of 4-chloropyrazoles served for preparation of an acaricide tebufenpyrad, highly efficient preparation against herbivorous ticks at every stage of their development, and for preparation of an insecticide of wide application OMI-88 [17]. Thus the development of preparation procedures for 4-chloropyrazoles based on available products is obviously an important task.

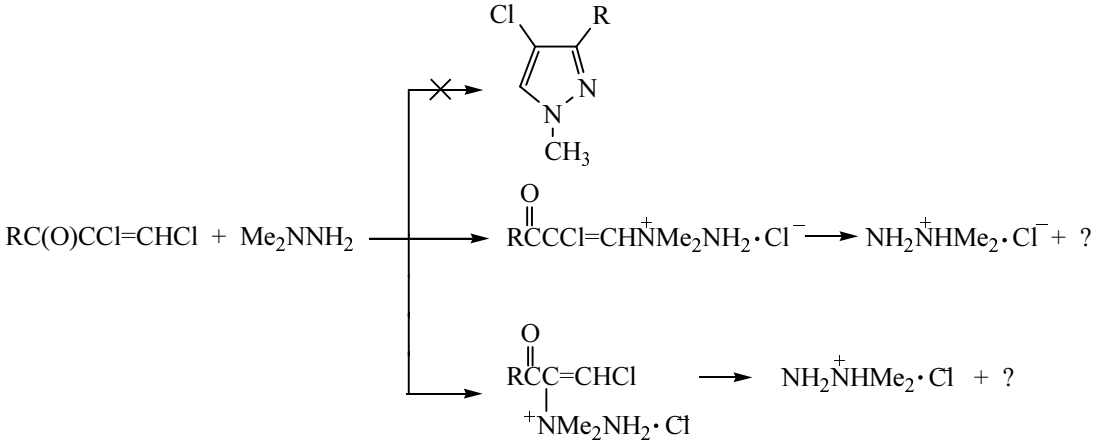
We recently found a new reaction of selective heterocyclization of the accessible 2-chloro-, 2,2-dichlorovinyl ketones and trifluoromethyl 2,2-dibromovinyl ketone effected by 1,1-dimethylhydrazine furnishing 1-methyl-3-R-pyrazoles and 1-methyl-3-R-5-chloro(bromo)pyrazoles [2, 9, 10]. In order to reveal the degree of generality and the rules governing the new reaction in this study we brought into the process with the 1,1-dimethylhydrazine the newly synthesized alkyl 1,2-dichlorovinyl ketones.

Unlike dichloroacrolein or 2,2-dichlorovinyl ketones [2, 18] the alkyl 1,2-dichlorovinyl ketones in the reaction with 1,1-dimethylhydrazine did not give rise either to ketones **I–III** dimethylhydrazones or to the corresponding 1-methyl-3-alkyl-4-chloropyrazoles.

The reaction of alkyl 1,2-dichlorovinyl ketones **I–III** with 1,1-dimethylhydrazine afforded a precipitate of 1,1-dimethylhydrazine hydrochloride (**XIV**) and an intractable mixture of substances, while in reaction of

unsymmetrical dimethylhydrazine with the isostructural analogs of the ketones under study, 2,2-dichlorovinyl ketones [2], were isolated trimethylhydrazinium chloride and 1-methyl-3-R-5-chloropyrazoles. In the IR spectrum of the isolated salt **XIV** appeared the bands of stretching vibrations of the CH (2950, 3000 cm^{-1}) and NH bonds (3130, 3250 cm^{-1}). The ^1H NMR spectrum of 1,1-dimethylhydrazine hydrochloride (**XIV**) in CD_3OD the methyl group protons appeared as a singlet at 2.96 ppm while in the ^1H NMR spectrum of trimethylhydrazinium chloride [19] in CD_3OD the methyl group protons were shifted downfield, δ_{Me} 3.41 ppm.

Inasmuch as in the ^1H NMR spectra of the reaction products obtained from ketones **I–III** and 1,1-dimethylhydrazine after separation of the dimethylhydrazine hydrochloride groups of signals were observed in the regions 3.6–4.0 and 7.2–7.5 ppm it is presumable that among the compounds of unknown structure were present 1-methyl-4-chloropyrazoles. The reaction carried out at cooling, in the presence of triethylamine, or at the double excess of the dimethylhydrazine also did not permit isolation of 1-methyl-4-chloropyrazoles or dimethylhydrazones. Since the 1-methyl-3-alkyl-4-chloropyrazoles are stable compounds the above findings indicate that



reactions between 1,1-dimethylhydrazine and 1-chloro-, 2,2-dichloro(bromo)vinyl ketones on the one hand and 1,2-dichlorovinyl ketones on the other hand follow different mechanisms. The 1,2-dichlorovinyl ketones in contrast to their isostractural analogs and 2,2-dibromo- and 2-chlorovinyl ketones in reaction with dimethylhydrazine first suffer a halogen atom substitution to give unstable 1,1-dimethyl-2-(2-acyl-2-chlorovinyl)-hydrazinium chlorides or 1,1-dimethyl-2-(1-acyl-2-chlorovinyl)-hydrazinium chlorides that decompose with separation of the dimethylhydrazine hydrochloride and a carbonyl compound of unknown structure. The investigation of the reaction is in progress.

Hence we developed a procedure for preparation of 1,2-dichlorovinyl alkyl ketones from acyl chlorides and 1,2-dichloroethylene in the presence of aluminum chloride. The strudture of 1,2-dichlorovinyl alkyl ketones was investigated with the use of ^1H NMR and IR spectroscopy and quantum-chemical calculations. The similarity of their reactions with dinitro- and monoalkylhydrazines to the analogous reactions with 2,2-dichlorovinyl ketones was demonstrated. To reveal the limits of applicability of the developed synthetic procedure for 1,2-dichlorovinyl ketones and to disclosure the difference in the chemical properties of useful synthons, 1,2-dichlorovinyl ketones and their isostructural analogs 2,2-dichlorovinyl ketones is of primary importance.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were registered on spectrometer Bruker DPX-400 (400.13 and 100.61 MHz respectively), internal reference HMDS. IR spectra were recorded on spectrophotometer Specord IR-75 from samples as microfilms or KBr pellets. 1-Chlorovinyl ketones **XIV** and **XV** were prepared by known procedure [20].

Ethyl 1,2-dichlorovinyl ketone (II). To a stirred dispersion of 46.7 g (0.35 mol) of anhydrous aluminum chloride in 50.1 g (0.52 mol) of 1,2-dichloroethylene was slowly added 32.44 g (0.35 mol) of freshly distilled propionyl chloride. The reaction mixture was stirred and heated at reflux for 7–8 h. Then it was cooled and poured on 300–400 g of crushed ice. The organic layer was separated, the water layer was extracted with chloroform (2Ч50 ml). The combined organic solution was stirred at heating to 80–90°C with a water solution of Na_2CO_3 (pH 12) for 1 h. On cooling the organic layer was separated in a separating funnel and dried with $MgSO_4$. The vacuum distillation furnished 42.85 g(90%) of target reaction product **II**, bp 60°C (21 mm Hg), n_D^{20} 1.4945. IR spectrum, ν, cm^{-1}: 1560 (C=C), 1695 (C=O), 3080 (=C–H). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.54 s (1H, =CH), 2.80 q (2H, CH_2, *J* 7.16 Hz), 1.13 t (3H, CH_3, *J* 7.16 Hz); (DMSO-d_6): 8.27 s (1H, =CH), 2.85 q (2H, CH_2, *J* 7.2 Hz), 1.01 t (3H, CH_3, *J* 7.2 Hz). ^{13}C NMR spectrum, δ, ppm: 192.43 (C=O), 134.83 (=CCl), 130. 64 (=CHCl), 40.73 (CH_2), 17.50 (CH_2), 13.35 (CH_3). Found, %: C 39.62; H 3.95; Cl 46.31. $C_5H_6Cl_2O$. Calculated, %: C 39.48; H 3.98; Cl 46.02.

Methyl 1,2-dichlorovinyl ketone (I) was obtained in a similar way from 30.99 g (0.395 mol) of acetyl chloride, 52.64 g (0.395 mol) of aluminum chloride, and 40 ml of dichloroethylene. Yield 47.2 g (86%), bp 55–58°C (18 mm Hg), n_D^{20} 1.4965. IR spectrum, ν, cm^{-1}: 1510 (C=C), 1690 (C=O), 3070 (=C–H). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.56 s (1H, =CH), 2.45 s (3H, CH_3). ^{13}C NMR spectrum, δ, ppm: 189.95 (C=O), 135.09 (=CCl), 131.50 (=CHCl), 26.71 (CH_3). Found, %: C 35.03; H 3.14; Cl 51.44. $C_4H_4Cl_2O$. Calculated, %: C 34.57; H 2.90; Cl 51.02.

Propyl 1,2-dichlorovinyl ketone (III) was obtained in a similar way from 53.28 g (0.5 mol) of butyryl chloride, 66.67 g (0.5 mol) of aluminum chloride, and 100 g (1 mol) of dichloroethylene. Yield 62.6 g (75%), bp 68–70°C (9 mm Hg), n_D^{20} 1.4900. IR spectrum, ν, cm^{-1}: 1570 (C=C), 1695 (C=O), 3080 (=C–H). ^{1}H ($CDCl_3$), δ, ppm: 7.54 s (1H, =CH), 2.74 t (2H, CH_2, *J* 7.20 Hz), 1.66 m (2H, CH_2), 0.953 t (3H, CH_3, *J* 7.2 Hz). ^{13}C, δ, ppm: 192.43 (C=O), 134.83 (=CCl), 130.64 (=CHCl), 40.73 (CH_2), 17.15 (CH_2), 13.35 (CH_3). Found, %: C 43.15; H 4.85; Cl 42.49. $C_6H_8Cl_2O$. Calculated, %: C 43.14; H 4.83; Cl 42.45.

Synthesis of methyl 1,2,2-trichloroethyl ketone (IV) and methyl 1,2-dichlorovinyl ketone (I) mixture. To a stirred dispersion of 26.67 g (0.2 mol) of anhydrous aluminum chloride in 50 ml of dichloroethylene was slowly added dropwise 15.70 g (0.2 mol) of acetyl chloride. The reaction mixture was stirred for 7 h at reflux. Then it was cooled and poured on 300 g of crushed ice. The organic layer was separated, the water layer was extracted with chloroform. The combined organic solutions were dried on $CaCl_2$ and distilled in a vacuum collecting the fraction of bp 47–75°C (5 mm Hg) amounting to 20 g and consisting of methyl 1,2-dichlorovinyl ketone (**I**) and methyl 1,2,2-trichloroethyl ketone (**IV**) at a ratio 2:3. Compound **IV**. IR spectrum, ν, cm^{-1}: 1720 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.09 d (1H, $CHCl_2$, *J* 6.28 Hz), 4.60 d (1H, CHCl, *J* 6.28 Hz) 2.40 s (3H, CH_3).

Synthesis of ethyl 1,2,2-trichloroethyl ketone (V) and ethyl 1,2-dichlorovinyl ketone (II) mixture. Likewise from 18.51 g (0.2 mol) of propionyl chloride, 26.67 g (0.2 mol) of anhydrous aluminum chloride, and 50 ml of dichloroethylene was obtained 26.7 g of a mixture of ethyl 1,2-dichlorovinyl ketone (**II**) and ethyl 1,2,2-trichloroethyl ketone (**V**) at a ratio 1:7, bp 92–98°C (30 mm Hg). Compound **V**. IR spectrum, ν, cm^{-1}: 1720 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.09 d (1H, $CHCl_2$, *J* 6.57 Hz), 4.59 d (1H, CHCl, *J* 6.57 Hz), 2.75 q (2H, CH_2, *J* 7.13 Hz), 1.09 t (3H, CH_3, *J* 7.13 Hz).

Synthesis of propyl 1,2,2-trichloroethyl ketone (VI) and propyl 1,2-dichlorovinyl ketone (III) mixture. Likewise from reaction products of 21.31 g (0.2 mol) of butyryl chloride, 26.67 g (0.2 mol) of anhydrous aluminum chloride, and 50 ml of dichloroethylene was isolated a fraction of bp 52–65°C (2–3 mm Hg) weighing 26 g composed of 1,2-dichlorovinyl propyl ketone (**III**) and propyl 1,2,2-trichloroethyl ketone (**VI**) at a ratio 1:5 respectively. Compound **VI**. IR spectrum, ν, cm^{-1}: 1720 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.08 d (1H, $CHCl_2$, *J* 6.84 Hz), 4.57 d (1H, $CHCl_2$, *J* 6.84 Hz), 2.74 t (2H, CH_2, *J* 7.27 Hz), 1.69 m (2H, CH_2), 0.94 t (3H, CH_3, *J* 7.33 Hz).

1,2-Dichlorovinyl methyl ketone 2,4-dinitrophenylhydrazone (VII). To a solution of 1.98 g (0.01 mol) of 2,4-dinitrophenylhydrazine in 50 ml of anhydrous methanol and 0.5 ml of concn. H_2SO_4 was added at stirring 1.37 g (0.01 mol) of ketone **I**. After the heat evolution ended the solution was stirred for 15 min at 60°C. The separated precipitate was filtered off and dried. Yield 2.30 g (98%), mp 205–206°C. IR spectrum, ν, cm^{-1}: 1300, 1330, 1430,

1500, 1580 (NO_2), 1600 (C=N), 3080 (=C–H), 3320 (NH). ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 11.18 s (1H, NH), 9.02 d (1H, H^3, ^4J 2.6 Hz), 8.48 d.d (1H, H^5, ^3J 9.5, ^4J 2.6 Hz), 8.13 d (1H, H^6, ^3J 9.5 Hz), 7.53 s (1H, =CH), 2.41 c (3H, CH_3). Found, %: C 38.05; H 2.80; Cl 22.58; N 18.55. $C_{10}H_8Cl_2N_4O_4$. Calculated, %: C 37.64; H 2.53; Cl 22.22; N 17.56.

1,2-Dichlorovinyl ethyl ketone 2,4-dinitrophenylhydrazone (VIII) was obtained similarly from 0.4 g (2 mmol) of 2,4-dinitrophenylhydrazine in a mixture of 2 ml H_2SO_4 and 10 ml of ethanol and from 0.31 g (2 mmol) of 1,2-dichlorovinyl ethyl ketone. Yield 0.6 g (98%), mp 204°C. IR spectrum, ν, cm^{-1}: 1300, 1330, 1575 (NO_2), 1490 (C=C), 1620 (C=N), 3300 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 11.15 s (1H, NH), 8.92 d (1H, H^3, ^4J 2.6 Hz), 8.43 d.d (1H, H^5, ^3J 9.5, ^4J 2.6 Hz), 8.02 d (1H, H^6, ^3J 9.5 Hz), 7.68 s (1H, =CH), 2.78 q (2H, CH_2, *J* 7.6 Hz), 1.20 t (3H, CH_3, *J* 7.6 Hz). Found, %: C 39.97; H 3.41; Cl 20.28; N 18.63. $C_{11}H_{10}Cl_2N_4O_4$. Calculated, %: C 39.66; H 3.03; Cl 21.28; N 16.82.

1,2-Dichlorovinyl propyl ketone 2,4-dinitrophenylhydrazone (IX) was obtained from 0.49 g (2.5 mmol) of 2,4-dinitrophenylhydrazine and 4.17 g (2.5 mmol) of 1,2-dichlorovinyl propyl ketone in 2 ml of H_2SO_4 and 10 ml of methanol. Yield 8.60 g (98%), mp 75°C. IR spectrum, ν, cm^{-1}: 1300, 1330, 1575 (NO_2), 1490 (C=C), 1620 (C=N), 3300 (NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 11.42 s (1H, NH), 9.13 d (1H, H^3, ^4J 2.6 Hz), 8.39 d.d (1H, H^5, ^3J 9.5, ^4J 2.6 Hz), 8.06 d (1H, H^6, ^3J 9.5 Hz), 7.01 s (1H, =CH), 2.64 t (2H, CH_2, *J* 12.9 Hz), 1.77 m (2H, CH_2), 1.13 t (3H, CH_3, *J* 11.6 Hz). Found, %: C 41.70; H 3.60; Cl 21.00; N 16.10. $C_{12}H_{12}Cl_2N_4O_4$. Calculated, %: C 41.52; H 3.48; Cl 20.42; N 16.14.

1,3-Diethyl-4-chloropyrazole (XI). (a) To a solution of 1.2 g (0.02 mol) of ethylhydrazine in 15 ml of anhydroushexane was added dropwise at stirring 1.53 g (0.01 mol) of ethyl 1,2-dichlorovinyl ketone. After the end of heat evolution the reaction mixture was stirred for 1–2 h. The precipitated ethylhydrazine hydrochloride was filtered off and dried in a vacuum over P_2O_5. The distillation of filterate afforded 1.27 g (80%) of pyrazole, bp 77–80°C (14–15 mm Hg). IR spectrum, ν, cm^{-1}: 1560 (C=C), 2860, 2940, 2960 (Alk), 3130 (=C–H). ^{1}H NMR spectrum ($CDCl_3$), 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.

(b) To a solution of 0.6 g (0.01 mol) of ethylhydrazine and 1.01 g (0.01 mol) of triethylamine in 15 ml of anhydrous ethanol was added dropwise at stirring a solution of 1.53 g (0.01 mol) of ethyl 1,2-dichlorovinyl ketone in 5 ml of anhydrous ethanol, and the mixture was stirred for 2 h. From filtrate by distilling off the solvents 1.34 g (80%) of pyrazole **XI** was isolated.

1-Heptyl-3-methyl-4-chloropyrazole (X) was prepared similarly from 1.3 g (0.01 mol) of heptylhydrazine, 1.01 g (0.01 mol) of triethylamine, and 1.39 g (0.01 mol) of 1,2-dichlorovinyl methyl ketone. 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}: 1540 (C=C), 2860, 2930, 2960 (Alk), 3140 (=C–H). ^{1}H NMR spectrum ($CDCl_3$), 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 16.54; N 12.59. $C_{11}H_{19}ClN_2$. Calculated, %: C 61.53; H 8.92; Cl 16.51; N 13.05.

1-Benzyl-3-ethyl-4-chloropyrazole (XII) was prepared similarly from 1.22 g (0.01 mol) of benzylhydrazine, 1.01 g (0.01 mol) of triethylamine, and 1.53 g (0.01 mol) of 1,2-dichlorovinyl ethyl ketone. Yield 1.98 g (90%), viscous fluid, purified by column chromatography on silica gel, eluent hexane, n_D^{20} 1.5610. IR spectrum, ν, cm^{-1}: 1520 (C=C), 2870, 2940, 2970 (Alk), 3140 (=C–H). ^{1}H NMR spectrum ($CDCl_3$), 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 (XIII) was prepared in the same way from 0.6 g (0.01 mol) of ethylhydrazine, 1.01 g (0.01 mol) of triethylamine, and 1.67 g (0.01 mol) of 1,2-dichlorovinyl propyl ketone. Yield 1.29 g (75%), bp 70°C (5 mm Hg), n_D^{20} 1.4838. IR spectrum, ν, cm^{-1}: 1520 (C=C), 2860, 2940, 2960 (Alk), 3140 (=C–H). ^{1}H NMR spectrum ($CDCl_3$), 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.

The reactions of alkylhydrazines with 1,2-dichlorovinyl ketones at the reagents ratio 1:1 (in the presence of triethylamine) and 2:1 in ether, hexane, benzene, lower alcohols (methanol, ethanol, 2-propanol) under similar conditions also gave rise to pyrazoles **X–XIII** in 60–80% yield.

Reaction of 1,2-dichlorovinyl ethyl ketone with 1,1-dimethylhydrazine. To a solution of 1.67 g (0.01 mol) of 1,2-dichlorohex-1-en-3-one in anhydrous ether cooled to –78°C was slowly added 1.20 g (0.02 mol) of 1,1-dimethylhydrazine. After the end of heat evolution the precipitate of dimethylhydrazinium hydrochloride was filtered off and dried in a vacuum over P_2O_5. Yield of the salt 0.86 g (89%), mp 60°C (publ.: mp 81–82°C [18]). IR spectrum, ν, cm^{-1}: 1470, 1620, 2520, 2700, 2950, 3000, 3130, 3250. ^1H NMR spectrum (CD_3OD), δ, ppm: 2.96 s. Found, %: C 23.58; H 10.24; Cl 35.97; N 29.37. $C_2H_9ClN_2$. Calculated, %: C 24.99; H 9.44; Cl 36.41; N 29.16.

After the solvent was distilled off from the filtrate the oily substance that fast darkened was passed through a column (eluent $CHCl_3$), the solvent was removed, the residue was dried in a vacuum. IR spectrum, ν, cm^{-1}: 1460, 1570, 1600, 1640, 1650, 2860, 2960, 3000, 3130. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.87 t, 2.57 m, 3.01 m, 7.26 s. A large number of weak signals was observed in the regions 2.13–3.12, 3.5–3.9, 7.47–8.12 ppm

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