Compound IVb was similarly obtained in 97% yield from quinoneimine Vb.

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1-SUBSTITUTED AZIRIDINE-2,2-DICARBOXYLIC ACID ESTERS

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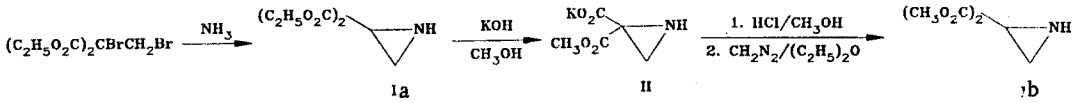
UDC 547.71:542.91

The synthesis and chemical properties of aziridine-2,2-dicarboxylic acid esters were investigated. The activation parameters of the inversion of the nitrogen atom in 1-substituted aziridine-2,2-dicarboxylic acid esters were determined. The σ_{inv} values of a number of substituents attached to the nitrogen atom were established.

1-Substituted aziridine-2,2-dicarboxylic acid esters are among the most suitable subjects for the investigation of the inversion of the nitrogen atom [1]. However, because of the lack of a method for the synthesis of aziridine-2,2-dicarboxylic acid ester, many of the 1-substituted derivatives have been virtually inaccessible. Attempts to obtain aziridine 2,2-dicarboxylic acid ester under conditions similar to those in the known syntheses of esters of 1-alkoxy-, 1-methyl-, and 1-phenylaziridine-2,2-dicarboxylic acids [1] from α,β-dibromomethylmalonic acid ester and ammonia under various temperature conditions were unsuccessful. However, carrying out the reaction in absolute ethanol at 20°C for 2 days made it possible to obtain, for the first time, diethyl aziridine-2,2-dicarboxylate (Ia) [2]:



Ia II Ib

The transesterification of aziridine Ia was carried out in order to remove the very small amounts of bromo derivative impurities that catalyze the decomposition of aziridines at high temperatures and interfere with the determination of the activation parameters of the inversion of the nitrogen atom, as well as to ensure the more accurate determination of the coalescence temperatures (T_c) from the singlet signals of the protons of the methoxycarbonyl groups.

Aziridine Ia is readily acylated by acid chlorides, phenyl isocyanate, and pheny isothiocyanate:

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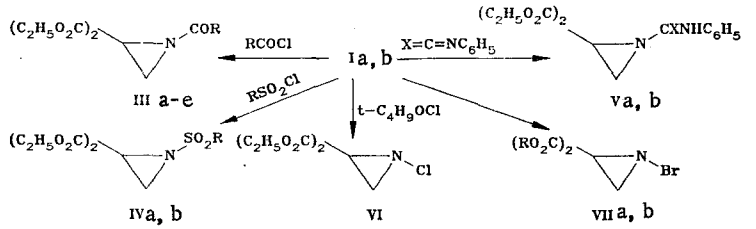
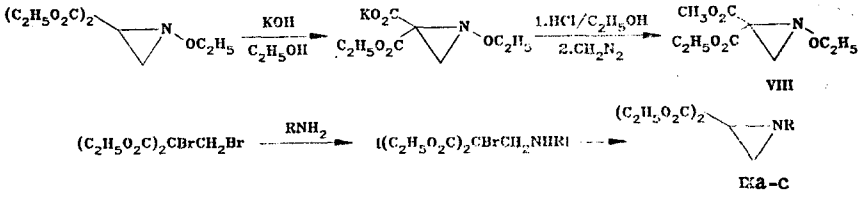


III a R=CH_3; b R=C_2H_5; c R=i-C_3H_7; d R=t-C_4H_9; e R=C_6H_5; IV a R=CH_3; b R=C_6H_5; V a X=O; b X=S; VII a R=C_2H_5; b R=CH_3

The reaction of aziridines Ia,b with halogenating agents, viz., tert-butyl hypochlorite, N-bromosuccinimide (NBS), or an aqueous solution of sodium hypobromite, leads, in good yields, to 1-halo derivatives VI and VIIa,b, which have increased (as compared with other 1-halo-aziridines) thermal stabilities. For example, 1-chloroaziridine VI underwent vacuum fractionation without decomposition [3] and was able to be stored for a long unrestricted time at 20°C, 1-bromoaziridines VIIa,b were stable at 0-5°C, whereas solutions of 1-bromo-2-methyl-aziridine decompose at −5°C to −10°C.

Starting aziridine Ia is formed quantitatively in the reaction of 1-chloroaziridine VI with dimethylamine. Attempts to achieve the nucleophilic substitution of the chlorine atom in aziridine VI by reaction with an alcohol solution of sodium methoxide or sodium methylmercaptide were also unsuccessful.

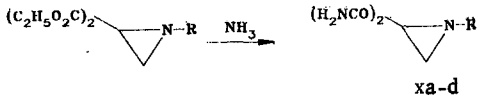
In order to obtain subjects for the investigation of the inversion of the nitrogen atom we synthesized unsymmetrical 1-ethoxyaziridine-2,2-dicarboxylic acid diester VII and 1-alkyl-aziridine-2,2-dicarboxylic acid esters IXa-c:



IX a R=CH_3; b R=C_2H_5; c R=i-C_3H_7

It was impossible to obtain 1-tert-butylaziridine-2,2-dicarboxylic acid ester via the scheme presented above because of the steric hindrance to cyclization to give the intermediately formed diethyl α-bromo-β-tert-butylaminomethylmalonate [4].

Esters of 1-substituted aziridine-2,2-dicarboxylic acids are amidated quantitatively by means of an alcohol solution of ammonia in the presence of traces of sodium methoxide:

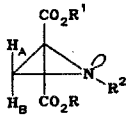


X a R=H; b R=CH_3; c R=$COCH_3$; d R=SO_2CH_3

However, removal of the acyl groups to give diamide Xa occurs in an attempt to recrystallize diamides Xc,d from methanol.

The compositions of all of the synthesized compounds were confirmed by the results of elementary analysis, and the structures were confirmed by data from the IR and PMR spectra (Table 1). The structure of aziridine-2,2-dicarboxylic diamide was established by x-ray diffraction analysis of the crystals that we obtained [5].

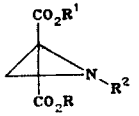
For a number of the investigated aziridines we determined the activation parameters of inversion of the nitrogen atom (Table 2). However, the T_c temperatures could not be reached for 1-acyl-(IIIa-e) and 1-isopropylaziridines (IXc) when solutions of them in CD_2Cl_2 were cooled to −110°C; the significant decrease in the inversion barriers is explained by conjugation of the carbonyl group of the acyl residue with the unshared pair of electrons of the nitrogen atom (IIIa-e) or by the increase in the steric interactions that stabilize the planar transition state of the inversion (IXc). In the case of aziridines IVa and Va,b we were unable to determine the T_c values because of their low solubilities at reduced temperatures, whereas we were unable to determine T_c for 1-chloroaziridine VI as a consequence of the impossibility of attaining it because of the high barrier to inversion of the nitrogen atom.

TABLE 1. Aziridine-2,2-dicarboxylic Acid Derivatives 

Compound	bp [mp], °C (pressure, mm)	n_D^{28}	IR spectrum (microlayer), ν, cm⁻¹		PMR spectrum (in CCl_4), δ, ppm						N found, %	Empirical formula	N calc., %	Yield, %
			C=O	ring CH_2	H_A[a]	H_B	R(R¹) (J=7.0 Hz) CH_3	R(R¹) (J=7.0 Hz) CH_2	R^2 CH_3	R^2 CH_2[b]				
Ia	82 (1,5)	1,4403	1739	3088	2,23		1,33	4,38	—	1,90	7,5	$C_8H_{13}NO_4$	7,4	37
Ib	86—88 (2)	(n_D^{18}, 1,4506)	1740	3085	2,40		3,77 (3,72)	—	—	2,10	8,9	$C_6H_9NO_4$	8,9	67
IIIa	126 (2,5)	1,4434	1757	3085	2,81		1,34	4,42	2,13	—	6,1	$C_{10}H_{15}NO_5$	6,1	68
IIIb	130 (2,5)	1,4430	1757	3078	2,81		1,36	4,46	1,14	2,48	5,7	$C_{11}H_{17}NO_5$	5,8	75
IIIc	137 (2,5)	1,4427	1757	3085	2,63		1,27	4,22	1,05; 1,15	2,33	5,4	$C_{12}H_{19}NO_5$	5,4	66
IIId	139 (2)	1,4455	1757	3078	2,68		1,25	4,20	1,16	—	5,1	$C_{13}H_{21}NO_5$	5,2	88
IIIe	—	—	1755	3072	2,89		1,11	4,11	—	7,50	4,8	$C_{15}H_{17}NO_5$	4,8	48
IVa	—	1,4598	1750	3087	3,05		1,36	4,56	3,35	—	5,4	$C_9H_{15}NO_6S$	5,3	90
IVb	—	—	1743	3058	2,90		1,26	4,26	—	7,52	4,2	$C_{14}H_{17}NO_6S$	4,3	35
Va	[99—100]	—	1757[c], 1743	3092	2,84 (in$CDCl_3$)		1,21	4,26	—	7,25	8,8	$C_{15}H_{17}N_2O_5$	8,8	45
Vb	[104—106]	—	1757[c], 1740	3098	3,90 (in$CDCl_3$)		1,21	4,21	—	7,13	8,3	$C_{15}H_{17}N_2O_4S$	8,4	40
VI	67 (0,2)	—	1748	3087	2,80	2,95	1,40 (1,34)	4,39 (4,28)	—	—	6,3	$C_8H_{12}ClNO_4$	6,3	73
VIIa	—	—	1735	3085	2,81	2,97	1,40 (1,34)	4,40 (4,29)	—	—	5,2	$C_8H_{12}BrNO_4$	5,3	59
VIIb	—	—	1724	3084	2,67	2,79	3,82 (3,04)	—	—	—	5,9	$C_6H_8BrNO_4$	5,9	80
VIII	102 (3)	(n_D^{20}, 1,4432)	1740	3100	2,43	2,74	1,24 (3,65)	4,20	1,05	3,81	6,0	$C_9H_{16}NO_5$	6,0	90
IXa	80—81 (1,5)	1,4400	1739	3071	1,90	2,05	1,19	3,95	2,33	—	—	—	—	16
IXb	86—88 (1,5)	1,4367	1741	3051	2,19		1,33	4,35	1,16	2,69	6,5	$C_{10}H_{17}NO_4$	6,5	25
IXc	86—87 (1,5)	1,4348	1735	3058	2,19		1,22	4,22	1,06	2,22	6,1	$C_{11}H_{19}NO_4$	6,1	80
Xa	[171—173]	—	1685[c]	3095	—		—	—	—	—	32,6	$C_4H_7N_3O_2$	32,5	100
Xb	[156—157]	—	1685[c]	3095	—		—	—	—	—	29,4	$C_5H_9N_3O_2$	29,4	100
Xc	[170—172]	—	1685[c]	3095	—		—	—	—	—	24,6	$C_6H_9N_3O_3$	24,6	100
Xd	Dec. 120	—	1685[c]	3095	—		—	—	—	—	20,3	$C_5H_9N_3O_4S$	20,3	100

[a]For VI and VIIa,b, J_{AB} = 3.0 Hz, whereas for VIII, J_{AB} = 2.3 Hz (in C_2Cl_4). [b]For Ia,b, NH; for IIIc and IXc, CH; and for IIIe, IVb, and Va,b, C_6H_5, center of a multiplet. [c]KBr pellets.

TABLE 2. Activation Parameters of the Nitrogen Atom in 1-Substituted Aziridine-2,2-Dicarboxylic Acid



Compound	R	R'	R²	Solvent	Observed group	T_c, °K	Δν, Hz	k_c,[a] sec⁻¹	$\Delta G_c^{\neq}$,[b] kJ/mole	$\Delta G_{298K}^{\neq}$,[c] kJ/mole	lg k_{298K}[d]	σ_{inv}
Ib	CH_3	CH_3	H	CD_2Cl_2	CO_2CH_3	306	3,0	6,79	70,2	70,4	0,48	0
IVb	C_2H_5	C_2H_5	$C_6H_5SO_2$	$(CD_3)_2CO$	CH_2 ring	190	30,4	67,46	39,2	38,3	6,08	1,6 [6]
VIIb	CH_3	CH_3	Br	C_2Cl_4	CO_2CH_3	448	7,8	17,23	100,7	102,0	−5,08	−2,2 [6]
VIII	C_2H_5	CH_3	C_2H_5O	C_6H_6	CO_2CH_3	373[a]	$12,4 \cdot 10^{-6}$ f	$6,3 \cdot 10^{-6}$ g	128,2	128,8	−9,94	−3,9
								$6,1 \cdot 10^{-6}$ h	128,9	129,6	−9,90	
IXa	C_2H_5	C_2H_5	CH_3	$CDCl_3$	CH_2 ring	320	13,5	29,97	69,5	69,9	0,55	−0,6 [6]
IXb	C_2H_5	C_2H_5	C_2H_5	CD_2Cl_2	CH_2 ring	311	13,7	30,43	67,5	67,6	0,95	−0,1
XI	C_2H_5	C_2H_5	CH_3O	C_6H_6	—	373 e [1]	—	$6,5 \cdot 10^{-6}$ i	128,9 [1]	130,4	−10,05	−3,95
XII	C_2H_5	C_2H_5	C_6H_5	$CHFCl_2$	CH_2 ring	228 [1]	25,0	55,5 f	47,7 [1]	46,4	4,67	1,3 [6]
XIII	CH_3	C_2H_5	p-$CH_3C_6H_4SO_2O$	C_6H_6	CO_2CH_3	392 i [8]	$5,5 \cdot 10^{-6}$ f	$2,73 \cdot 10^{-5}$ i	131,3 [8]	132,0	−10,34	−4,0
								$2,77 \cdot 10^{-6}$ i	131,2 [8]	132,0	−10,34	

[a]The rate constant for the inversion at T_c was determined from the formula $k_c = \pi \cdot \Delta\nu/\sqrt{2}$. [b]$\Delta G_c^{\neq} = 4.576T_c/10.319 + \log (T/k_c)$/ [7]. [c]$\Delta G_{298K}^{\neq} = \Delta G_c^{\neq} + R(T_c - 298)$ [6]. [d]Calculated from the Eyring equation [7] from the $\Delta G_{298K}^{\neq}$ value. [e]The temperature at which cis–trans isomerization was carried out. [f]The rate constant of cis–trans isomerization. Calculated by the method of least squares from the kinetic data. [g]The rate constant of the forward inversion reaction. [h]The rate constant of the reverse inversion reaction. [i]The rate constant of racemization of the optically active sample.

Despite the fact that the logarithms of the inversion rate constants (log k_{298K}, Table 2) in aziridines Ib, IVb, VIIb, IXa, and XII were determined in different solvents, they display a satisfactory ($r = 0.989$, $\rho = 2.84 \pm 0.33$, $\log k_0 = 1.28 \pm 0.25$, $s = 0.742$) correlation with the substituent inversion constants (σ_{inv}) [6]. The observed correlation confirms the reliability of the proposed σ_{inv} values and, correspondingly, the possibility of their utilization for a preliminary evaluation of the barriers to inversion of the nitrogen atom. In conformity with the correlation data, the erroneous σ_{inv} value for the OCH_3 group (~ -2.5 [6]) should be corrected by a value of -3.95; for the $OSO_2C_6H_4CH_3$-p, OC_2H_5, and C_2H_5 groups, which were obtained for the first time, the σ_{inv} values should be -4.0, -3.9, and -0.1, respectively. It must also be noted that an increase in the electron-acceptor properties of the substituents attached to the carbon atom of the aziridine ring intensifies the effect on the barrier to inversion of the electronic properties of the substituents attached to the nitrogen atom: For the 1-substituted derivatives of 2,2-(R,R)-disubstituted aziridines the constants of the reaction series increase in the following order: R = CH_3 (2.5) [6] < R = H (2.7) [6] < R = CO_2R (2.84).

EXPERIMENTAL

The IR spectra of microlayers (for the liquid samples) and KBr pellets (for the solid samples) were recorded with UR-20 and Specord 75 IR spectrometers. The PMR spectra were measured with RYa-2305 (60 MHz) and Tesla BS-487 C (80 MHz) spectrometers with hexamethyldisiloxane (HMDS) as the internal standard.

The activation parameters of the inversion of the nitrogen atom were determined from the T_c values of the signals of the protons of the methyoxycarbonyl groups (aziridines Ib and VIIb) and the aziridine ring (IVb and IXa,b) or from the kinetic data for the thermal cis–trans isomerization (aziridine VIII); monitoring of the kinetics of the isomerization of the thermal cis–trans isomerization (aziridine VIII); monitoring of the kinetics of the isomerization in the case of heating (100 ± 0.1°C) in sealed evacuated ampuls was accomplished by measuring the integral intensities of the PMR signals of the methoxycarbonyl groups. In order to eliminate the effect of proton exchange on the barrier to inversion of the nitrogen atom the T_c of aziridine Ib was determined after prior drying of a solution of the aziridine in benzene with calcium hydride for a week. The T_c of the unstable (at high temperatures) 1-bromoaziridine VIIb was established via brief heating ($\sim$ 5 min) in a heated (to T_c) sensor after prior determination of T_c in other experiments with other samples of aziridine VIIb. In the recording of the dynamic PMR spectra the error in the determination of T_c was ±1.0°C and the error in the determination of $\Delta\nu$ was ±0.1 Hz. The errors, correspondingly, in the determination of the rest of the activation parameters of the inversion of the nitrogen atom were ±0.22 sec^{-1} for k_c, 0.22-0.28 kJ/mole for $\Delta G^{\neq}$, and ±0.04 for log k_{298K}.

The characteristics of the synthesized compounds are presented in Table 1.

Diethyl Aziridine-2,2-dicarboxylate (Ia). A solution of 33.2 g (0.1 mole) of diethyl α,β-dibromomethylmalonate in 100 ml of absolute ethanol was added with stirring and cooling to a solution of 5.1 g (300 mmoles) of ammonia in 150 ml of absolute ethanol, and the mixture was maintained at 20°C for 2 days. The solvent was removed at reduced pressure, and the product was extracted with ether. The solvent was removed, and the residue was distilled *in vacuo* to give 6.0 g (33%) of aziridine Ia.

Dimethyl Aziridine-2,2-dicarboxylate (Ib). A 2.0-g (11 mmoles) sample of aziridine Ia was added to a solution of 0.6 g (11 mmoles) of KOH in 10 ml of absolute methanol, and the mixture was maintained at 20°C for 24 h. The solvent was then removed, and the crystalline precipitate was washed with absolute ether. The isolated monopotassium salt II was dissolved in 20 ml of methanol, an equimolar amount of a solution of HCl in methanol was added, and the mixture was treated with an excess amount of an ether solution of diazomethane. The solvent was removed, and the residue was extracted with ether. The ether was removed, and the reaction product was distilled *in vacuo* to give 1.1 g (67%) of aziridine Ib.

Diethyl 1-Acetylaziridine-2,2-dicarboxylate (IIIa). A solution of 0.39 g (5 mmoles) of acetyl chloride in 5 ml of absolute ether was added slowly with stirring to a solution of 0.93 g (5 mmoles) of aziridine Ia and 0.51 g (5 mmoles) of triethylamine in 20 ml of absolute ether, after which the mixture was maintained at 20°C for 2 h. The precipitate was removed by filtration, the filtrate was evaporated at reduced pressure, and the residue was distilled *in vacuo* to give 1.0 g (68%) of aziridine IIIa.

Compounds IIIb-d. These compounds were similarly obtained.

Diethyl 1-Benzoylaziridine-2,2-dicarboxylate (IIIe). A solution of 1.41 g (10 mmoles) of benzoyl chloride in 5 ml of absolute pyridine was added gradually with stirring to a cooled (to 0°C) solution of 0.93 g (5 mmoles) of aziridine Ia and 0.56 g (5.5 mmoles) of triethylamine in 10 ml of absolute pyridine, after which the mixture was maintained at 0°C for 0.5 h. It was then poured into 50 g of ice, and the resulting aqueous mixture was extracted with methylene chloride. The extract was washed with 0.2 N hydrochloric acid until the wash liquid was acidic, after which it was washed with water and dried with magnesium sulfate. After removal of the solvent, the product was purified by chromatography with a column (silica gel L 100/160μ, CH_2Cl_2) to give 0.7 g (48%) of aziridine IIIe (Table 1).

Compounds IVa,b. These compounds were similarly obtained.

Diethyl 1-Phenylcarbamoylaziridine-2,2-dicarboxylate (Va). A solution of 0.95 g (5 mmoles) of aziridine Ia and 0.6 g (5 mmoles) of phenyl isocyanate in 10 ml of benzene was maintained at 20°C for 24 h, after which it was refluxed for 3 h, and the solvent was removed at reduced pressure. The product was purified by column chromatography (silica gel L 100/160μ, CH_2Cl_2) and subsequent crystallization from a mixture of ether and hexane to give 0.71 g (45%) of aziridine Va.

Compound Vb. This substance was similarly obtained.

Diethyl 1-Chloroaziridine-2,2-dicarboxylate (VI). A solution of 0.34 g (3.1 mmoles) of tert-butyl hypochlorite in 5 ml of absolute ether was added gradually with stirring to a solution of 0.57 g (3 mmoles) of aziridine Ia in 5 ml of absolute ether, after which the mixture was maintained at 20°C for 0.5 h. The solvent was then removed at reduced pressure, and the residue was extracted with carbon tetrachloride. The solvent was removed, and the product was distilled *in vacuo* to give 0.5 g (73%) of aziridine VI.

Diethyl 1-Bromoaziridine-2,2-dicarboxylate (VIIa). A) A 0.93-g (5 mmoles) sample of aziridine Ia was added gradually to a solution of NaOBr obtained from 0.4 g (10 mmoles) of NaOH and 0.8 g (5 mmoles) of bromine in 3 ml of water, and the resulting mixture was maintained at 0°C for 0.5 h. It was then extracted with ether, and the extract was washed with water until the wash waters were neutral. The extract was then dried with sodium sulfate, and the ether was removed at 20°C to give 0.78 g (59%) of aziridine VIIa.

B) A 0.97 g (6 mmoles) sample of N-bromosuccinimide (NBS) was added to a solution of 0.93 g (5 mmoles) of aziridine Ia in 20 ml of absolute ether, and the mixture was maintained at 20°C for 24 h. The precipitate was removed by filtration, and the filtrate was evaporated at reduced pressure. The residue was extracted with carbon tetrachloride, and the solvent was removed to give 0.77 g (58%) of aziridine VIIa.

Compound VIIb. This substance was similarly obtained.

trans-Methyl cis-Ethyl 1-Ethoxyaziridine-2,2-dicarboxylate (VIII) and Diethyl 1-Methylaziridine-2,2-dicarboxylate (IXa). These compounds were obtained by the method in [1].

Compounds IXb,c. These substances were similarly obtained.

Aziridine-2,2-dicarboxylic Acid Diamide (Xa). A solution of 0.17 g (10 mmoles) of ammonia in 10 ml of absolute methanol containing traces of sodium methoxide was added to a solution of 0.93 g (5 mmoles) of aziridine Ia in 1.0 ml of absolute methanol, and the mixture was maintained at 20°C for 5 days. The solvent was removed, and the residue was crystallized from ethanol. Aziridine Xa was obtained in quantitative yield.

Compounds Xb-d. These substances were similarly obtained.

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REACTION OF α-α'-DICHLORO-SUBSTITUTED 1,5-DIKETONES WITH AMMONIA AND AMMONIUM ACETATE

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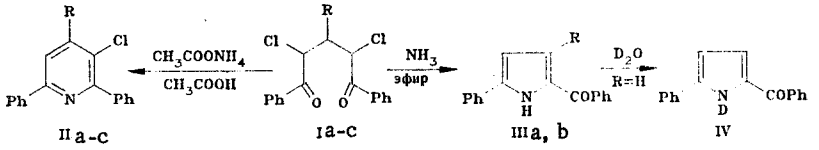
Under the influence of ammonia or ammonium acetate, α-α'-dichloro-substituted 1,5-diketones undergo heterocyclization to give β-chloropyridines or 2-benzoylpyrrole derivatives. The structure of the final product depends on the reagent and the character of the substituent in the 3 position of the starting dichloro diketones.

Products of the pyridine series are formed in the reaction of acyclic 1,5-diketones with ammonia and ammonium acetate [1]. The literature does not contain any information relative to the utilization of chloro-substituted 1,5-diketones in the indicated reaction, inasmuch as the latter, prior to our research, were unknown and were recently obtained by the reaction of acyclic diketones with chlorine [2]. A new active center, which probably opens up new aspects of the chemistry of this class of compounds, develops when a chlorine atom is introduced into the 1,5-diketone structure.

In the present research we studied the reactions of α-α'dichloro-substituted 1,5-diketones Ia-c with ammonia and ammonium acetate in order to ascertain the effect of the chlorine atom on the direction of the transformation. We found that the character of the products of the reaction of chloro-substituted diketones Ia-c with nucleophilic reagents is determined by the competitive reactivities of the active centers:



IIa-c Ia-c IIIa, b IV

I—III a R=H; b R=CH_3; c R=Ph

The Chichibabin reaction of diketones Ia-c with ammonium acetate (by heating in acetic acid at 60-80°C) proceeds most smoothly and unambiguously. In this case the attack of the nucleophilic reagent, as assumed, is realized at the C=O groups and leads to the formation of β-chloropyridines IIa-c in up to 90% yields. The structure of the β-chloropyridines is confirmed by the presence in the IR spectra of absorption bands of a pyridine ring at 1540 cm^{-1}. In the PMR spectrum of IIa (Fig. 1) the signal of the 4-H proton is found at weak field at 7.83 ppm in the form of doublet (J = 8.5 Hz). The splitting of the signal is the result of coupling with the 5-H proton, the signal of which also appears in the form of a doublet at 7.46 ppm. In the spectra of IIb and IIc, which have substituents in the 4 position, the signal of the 5-H proton is present in the form of a singlet at 7.53 and 7.63 ppm, respectively.

The reaction of dichloro-substituted 1,5-diketones Ia-c with ammonia in ether at room temperature proceeds ambiguously, and the structures of the final products depend on substituent R in the 3 position of the starting diketones. Thus, as in the case of ammonium acetate, 2,4,6-triphenyl-3-chloropyridine (IIc) is formed in the reaction of Ic with ammonia. Under the same conditions, unsubstituted diketone Ia gives 2-benzoyl-5-phenylpyrrole (IIIa) in 80% yield, whereas in the case of 3-methyl-1,5-diphenyl-2,4-dichloropentanedione (Ib) we obtained a mixture of the corresponding β-chloropyridine IIb and 2-benzoyl-3-methyl-5-phenylpyrrole (IIIb). The formation of pyrrole derivatives IIIa,b can be represented by the scheme

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