cipitate developed. It was then maintained at 20°C for 16 h, after which the precipitate was removed by filtration and washed with alcohol to give 2.58 g (91.6%) of a product with mp 152-153°C (from ethanol). IR spectrum: 2640-2660 cm^{-1} (OH). Found: C 59.9; H 6.1; Cl 12.8; N 9.8%. $C_{14}H_{17}ClN_2O_2$. Calculated: C 60.0; H 6.1; Cl 12.7; N 10.0%.

B) A solution of 1.44 g (10 mmole) of m-chlorophenylhydroxylamine in 10 ml of acetone was added to a solution of 2.04 g (10 mmole) of diol II in 10 ml of water, and the mixture was allowed to stand at 20°C for 16 h. The resulting precipitate was removed by filtration and washed with acetone to give 2.5 g (88.8%) of a product with mp 152-153°C (from ethanol).

2-Methylene-3-oxoquinuclidine Benzoate (VII). A 0.45-g (3.28 mmole) sample of 2-methylene-3-oxoquinuclidine in 2 ml of water was added to a suspension of 0.4 g (3.28 mmole) of benzoic acid in 4 ml of water, and the mixture of reagents was stirred, during which a precipitate with a new structure formed. The reaction mixture was allowed to stand at 20°C for 4 h, after which the precipitate was removed by filtration and washed with water to give 0.66 g of salt VII with mp 134-136°C (dec.). Found: C 65.8; H 7.1; N 5.1%. $C_8H_{11}NO \cdot C_7H_6O_2 \cdot H_2O$. Calculated: C 65.5; H 6.9; N 5.1%. The aqueous mother liquor was evaporated, and the residue was triturated with acetone to give an additional 0.11 g of salt VII with mp 134-136°C for an overall yield of 83.6%.

2-Methylene-3-oxoquinuclidine Barbiturate (VIII). A solution of 1.37 g (10 mmole) of quinuclidine I in 10 ml of dimethylformamide (DMF) was added to a solution of 1.28 g (10 mmole) of barbituric acid in 50 ml of DMF, and the precipitate that formed immediately was removed by filtration after 1 h to give 2.6 g (98.1%) of a product with mp 277-279°C (dec., from DMF). Found: C 54.6; H 6.0; N 15.6%. $C_8H_{11}NO \cdot C_4H_4N_2O_3$. Calculated: C 54.4; H 5.7; N 15.8%.

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SYNTHESIS, STEREOCHEMISTRY, AND ISOMERIC TRANSFORMATIONS OF cis- AND trans-1,2-DIMETHYL-4-ARYL-5-AROYL-2-IMIDAZOLINES

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The corresponding trans- and cis-1,2-dimethyl-4-aryl-5-aroyl-2-imidazolines were obtained from complexes of cis- and trans-1-methyl-2-aryl-3-aroylaziridines with BF_3 by heating with acetonitrile. The reaction proceeds with inversion of the configuration of the starting 3-aroylaziridines. In the presence of bases the complexes of cis-1,2-dimethyl-4-aryl-5-aroyl-2-imidazolines readily undergo isomerization to the corresponding trans analogs. The structures of the products were established on the basis of the IR, PMR, and mass spectra and the results of elementary analysis. The configurations of the compounds were determined by means of the Overhauser nuclear effect.

Preparations based on 2-imidazolines are widely used in medicine and pharmacology [1, 2]. However, the known methods for the synthesis of 2-imidazolines [3] make it virtually

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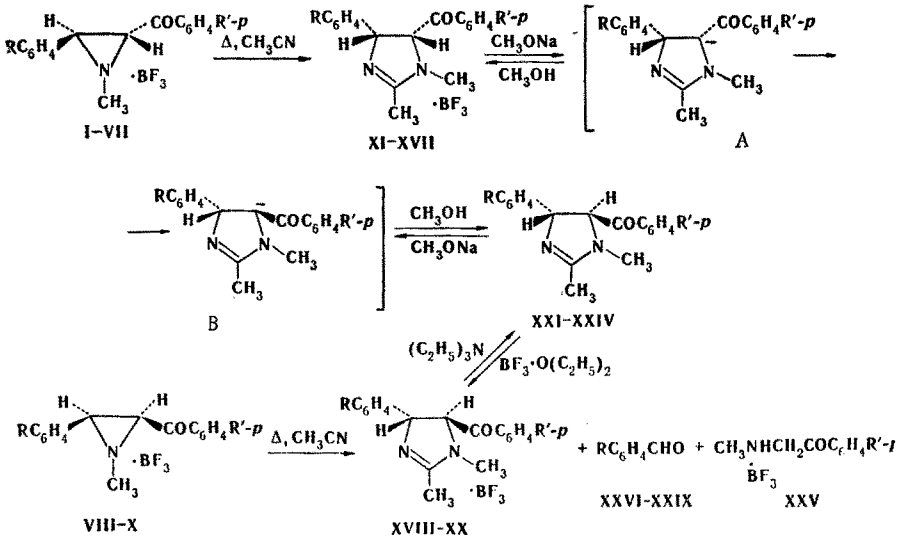
TABLE 1. 1,2-Dimethyl-4-aryl-5-aroyl-2-imidazolines (XI-XXIV)

Compound	R	R′	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
				C	H	N		C	H	N	
XI	*p*-Br	H	231	50,9	4,1	6,5	$C_{18}H_{17}BrN_2O \cdot BF_3$	50,8	4,0	6,6	78
XII	*p*-Cl	H	219	56,4	4,3	7,3	$C_{18}H_{17}ClN_2O \cdot BF_3$	56,8	4,5	7,4	74
XIII	*p*-Me	H	228	63,1	5,6	7,8	$C_{19}H_{20}N_2O \cdot BF_3$	63,3	5,5	7,8	75
XIV	H	H	189	62,6	5,4	7,9	$C_{18}H_{18}N_2O \cdot BF_3$	62,4	5,2	8,1	68
XV	*m*-NO_2	H	251	55,4	4,4	10,5	$C_{18}H_{17}N_3O_3 \cdot BF_3$	55,2	4,3	10,7	64
XVI	H	*p*-Br	189	50,6	3,9	6,8	$C_{18}H_{17}BrN_2O \cdot BF_3$	50,8	4,0	6,6	62
XVII	H	*p*-Cl	184	56,5	4,2	7,1	$C_{18}H_{17}ClN_2O \cdot BF_3$	56,8	4,5	7,4	63
XVIII	*p*-Br	H	173	50,5	3,8	6,5	$C_{18}H_{17}BrN_2O \cdot BF_3$	50,8	4,0	6,6	43
XIX	*p*-Cl	H	170	56,7	4,6	7,3	$C_{18}H_{17}ClN_2O \cdot BF_3$	56,8	4,5	7,4	41
XX	*p*-Me	H	181	63,7	5,7	7,8	$C_{19}H_{20}N_2O \cdot BF_3$	63,3	5,6	7,8	43
XXI	*p*-Br	H	118	60,4	4,5	7,6	$C_{18}H_{17}BrN_2O$	60,5	4,8	7,8	84
XXII	*p*-Cl	H	93	69,2	5,6	9,1	$C_{18}H_{17}ClN_2O$	69,1	5,4	8,9	82
XXIII	*p*-Me	H	87	78,3	7,0	9,3	$C_{19}H_{20}N_2O$	78,1	6,8	9,6	82
XXIV	H	H	—	77,5	6,6	9,9	$C_{18}H_{18}N_2O$	77,7	6,5	10,1	79

impossible to obtain compounds of this class with functional substituents such as a carbonyl group in the 5 position.

In the present research we studied the synthesis of 1,2-dimethyl-4-aryl-5-aroyl-2-imidazolines by heating the complexes of 1-methyl-2-aryl-3-aroylaziridines with boron trifluoride in acetonitrile.



I, VIII, XI, XVIII, XXI, XXVI R=*p*-Br, R′=H; II, IX, XII, XIX, XXII, XXVII R=*p*-Cl, R′=H; III, X, XIII, XX, XXIII, XXVIII R=*p*-CH_3, R′=H; IV, XIV, XXIV, XXIX R=R′=H; V, XV R=*m*-NO_2, R′=H; VI, XVI R=H; R′=*p*-Br; VII, XVII R=H, R′=*p*-Cl

We found that the complex salts of cis- and trans-1-methyl-2-aryl-3-aroylaziridines with BF_3 (I-X) react with acetonitrile upon heating in an inert atmosphere to give the salt forms of 1,2-dimethyl-4-aryl-5-aroylimidazolines (XI-XX) in 40-80% yields (Table 1).

An analysis of the reaction mixtures by PMR spectroscopy showed that only substituted 2-imidazolines are formed in the case of trans-aziridines (I-VII). However, in the case of cis-aziridines (VIII-X), in addition to 2-imidazolines, one observes the formation of small amounts of ω-(methylamino)acetophenones (XXV) and benzaldehydes (XXVI-XXIX), the development of which can evidently be explained by the presence of traces of water in the reaction mixture; it may be assumed that the formation of side products occurs either as a result of initial attack by a molecule of water on the C_2 atom of the aziridine ring with subsequent retroaldolization of the resulting keto amino alcohol [4] or as a result of the synchronous dissociation of the C–C bond of the aziridine ring [5] and attack by a molecule of water on the C_2 atom. In order to ascertain the pathway of the formation of the side products 1-phenyl-2-methylamino-3-hydroxy-3-(p-bromophenyl)-1-propanone hydrochloride was heated for a long time at 90°C in acetonitrile. However, in this case we did not observe the formation of ω-(methylamino)acetophenone and p-bromobenzaldehyde. These products are evidently formed via the second pathway [6].

TABLE 2. Mass Spectra of 1,2-Dimethyl-4-aryl-5-aroyl-2-imidazolines

Compound	m/e (relative intensity, %)*
XI	356 (3), 355 (7), 251 (31), 250 (27), 209 (11), 196 (10), 131 (100), 130 (16), 105 (36)
XII	312 (4), 311 (12), 207 (100), 206 (59), 164 (13), 151 (13), 131 (96), 130 (36), 105 (37)
XIII	292 (5), 291 (4), 187 (100), 186 (17), 174 (19), 145 (51), 131 (31), 130 (11), 105 (21)
XVI	356 (4), 355 (6), 252 (8), 183 (13), 173 (100), 172 (14), 132 (57), 131 (12), 117 (25)
XVII	312 (3), 311 (6), 208 (14), 173 (100), 172 (20), 139 (16), 132 (87), 131 (16), 116 (45)
XVIII	356 (3), 355 (5), 251 (72), 250 (18), 209 (9), 196 (11), 131 (100), 130 (16), 116 (45)
XIX	312 (4), 311 (5), 207 (8), 206 (100), 164 (11), 150 (31), 131 (8), 130 (13), 105 (10)

*The molecular ion of the base and the eight most characteristic peaks are presented.

TABLE 3. PMR Spectra of 1,2-Dimethyl-4-aryl-5-aroyl-2-imidazolines (XXI-XXIV) and Their Borofluorides (XI-XX)

Compound	R	R′	δ, ppm					J_{4-5}, Hz
			2-Me	1-Me	5-H	4-H	Ar—H	
XI	*p*-Br	H	2,50	3,13	6,40	5,90	7,30—7,91	12,6
XII	*p*-Cl	H	2,53	3,20	6,36	5,90	7,06—7,83	12,6
XIII	*p*-Me	H	2,53	3,20	6,36	5,90	6,90—7,70	12,4
XIV	H	H	2,47	3,13	6,37	5,90	7,07—7,80	12,6
XV	*m*-NO_2	H	2,60	3,26	6,46	6,13	7,30—7,91	12,6
XVI	H	*p*-Br	2,61	3,25	6,38	5,93	7,05—7,56	12,6
XVII	H	*p*-Cl	2,53	3,20	6,40	5,90	7,03—7,66	12,4
XVIII	*p*-Br	H	2,50	3,21	6,03	5,12	7,02—8,10	7,4
XIX	*p*-Cl	H	2,55	3,25	6,00	5,15	7,07—7,97	7,4
XX	*p*-Me	H	2,63	3,26	6,00	5,06	7,16—7,76	7,4
XXI	*p*-Br	H	1,93	2,76	4,86	4,60	7,00—7,73	7,2
XXII	*p*-Cl	H	2,03	2,83	5,03	4,67	7,13—7,76	7,2
XXIII	*p*-Me	H	1,93	2,80	4,86	4,56	7,00—7,90	7,0
XXIV	H	H	2,01	2,80	4,91	4,61	7,02—7,73	7,2

It should be noted that only one isomeric product of the opposite configuration is formed from the salts of both cis- and trans-aziridines, i.e., the reaction proceeds with a high degree of stereospecificity.

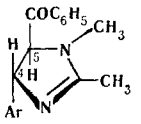
The relative reactivities of the aziridine salts I-X with respect to acetonitrile are proportional to the electron-donor properties of the para substituents of the 2-aryl residue and change in the order Me > H > Cl ≈ Br > m-NO_2. This makes it possible to assume that the nucleophilic attack by acetonitrile is directed at the C_2 atom of the aziridine ring.

Peaks of low intensity of the imidazoline bases, viz., $[M]^{+\cdot}$ and $[M-1]^{+\cdot}$, are observed in the mass spectra of 2-imidazoline salts XI-XIII and XVI-XIX. The $[M-1]^{+\cdot}$ ion is evidently associated with splitting out of an H atom from the 5 position of the imidazoline ring. The $[M-105]^+$ ($[M-183]^+$ and $[M-139]^+$ for XVI and XVII, respectively) peaks, which correspond to splitting out of ArCO· from $[M]^{+\cdot}$, have high intensities. The presence of $[M-147]^+$ and $[M-162]^+$ peaks ($[M-225]^+$ and $[M-240]^+$ and $[M-181]^+$ and $[M-196]^+$ for XVI and XVII, respectively) indicates that the structure of the 2-imidazolines (XI-XX) corresponds to that presented in the scheme. The masses of the ions presented above would be 15 m/e units greater for the products of attack by acetonitrile at the C_5 atom of the aziridine ring (Table 2).

Bands of a carbonyl group (1680 cm^{-1}), of the C=N bond of the imidazoline ring (1620 cm^{-1}), and of the stretching and deformation vibrations of the aromatic rings (3065, 3020, and 1600 cm^{-1}) are observed in the IR spectra of XI-XX.

Singlets of MeN protons (3.13-3.26 ppm) and doublets of 2-Me (2.47-2.63 ppm) and of the 5-H (6.00-6.46 ppm) and 4-H (5.06-6.13 ppm) methylidyne protons with vicinal constants

TABLE 4. Overhauser Nuclear Effects (ONE) for trans-1,2-Dimethyl-4-(p-chlorophenyl)-5-benzoyl-2-imidazoline (XXII)

Compound	Irradiated group	Observed proton	ONE, %
	1-Me (2,83 ppm)	5-H	0
	1-Me (2,83 ppm)	4-H	0
	o-H(Ar)* (7,13 ppm)	4-H	29
	o-H(Ar) (7,13 ppm)	5-H	26

*The symbol o-H(Ar) designates the ortho protons of the p-chlorophenyl substituent.

12.4-12.6 Hz for XI-XVII and 7.4 Hz for XVIII-XX, as well as a multiplet of aromatic protons (6.9-7.9 ppm), are observed in the PMR spectra of all of the 2-imidazoline salts (XI-XX; Table 3). The 5-H and 4-H signals were assigned on the basis of an experiment involving deuterium exchange. It should be noted that the doublet of the 4-H protons is split additionally (J = 1 Hz) and that the same splitting is also observed for the signals of the protons of the 2-Me group (J = 1 Hz); this is explained by their long-range spin–spin coupling through the double bond and thus confirms its presence. On the basis of the vicinal constants for XI-XVII (J = 12.4-12.6 Hz) a cis configuration is proposed for them, while a trans configuration is proposed for XVIII-XX (J = 7.4 Hz) [7, 8]. This was confirmed by an experiment utilizing the Overhauser nuclear effect (ONE) for the 2-imidazoline base (XXII, J = 7.2 Hz). A significant increase in the intensities of the signals of both the 5-H (5.03 ppm) and 4-H (4.67 ppm) protons was observed when the ortho protons of the aryl residue (7.13 ppm) were irradiated (Table 4). These results confirm the trans configuration of XXII and are in good agreement with the ONE data [8]. In the case of the cis isomer the effect should have been observed only for the 4-H proton.

An increase in the intensity of the 4-H and 5-H signals was not observed when the Me–N protons were irradiated. This fact indicates that the MeN group in trans-2-imidazolines is preferably found in the syn conformation with respect to the carbonyl group, as in the case of 1-alkyl-3-aroylaziridines [9]. A comparison of the PMR spectra of XXII in CCl_4 and C_6H_6 showed that the differences in the chemical shifts ($\delta_{CCl_4} - \delta_{C_6H_6}$) of the methylidyne protons are −0.21 and +0.19 ppm for 5-H and 4-H, respectively, and this additionally confirms [10] the trans configuration of XXII.

Thus the reaction of 1-alkyl-3-aroylaziridine borofluorides (I-X) with acetonitrile is accompanied by inversion of the configuration and leads to cis-2-imidazolines in the case of trans-aziridines and to the trans isomers in the case of cis-aziridines.

The salt forms of cis-2-imidazolines (XI-XIV) upon alkalization give the trans-isomer bases (XXI-XXIV). Signals of methyl protons at 1.83-2.83 ppm and of the 5-H (4.86-5.03 ppm) and 4-H (4.56-4.67 ppm) methylidyne protons are observed in the PMR spectra of bases XXI-XXIV with vicinal constant J = 7.0-7.2 Hz. As in the case of the salt forms of 2-imidazolines, the signals of the 4-H and 2-Me protons are additionally split (^5J = 1 Hz) as a result of their long-range coupling through the double bond of the imidazoline ring.

An experiment involving deuterium exchange of XXII demonstrated the rather high proton lability of the hydrogen atom in the 5 position. It is therefore likely that cis-trans isomerization in basic media proceeds, as in the case of 1-alkyl-3-aroylaziridines [11], through detachment of the 5-H proton from the cis isomer under the influence of the base and the formation of carbanion A, which, because of steric hindrance, undergoes isomerization to B, and the latter then adds a proton and is converted to a trans-2-imidazoline. It should be noted that, judging from the PMR spectra, the formation of cis-2-imidazoline bases is not observed in this transformation.

An analysis of the structure of the imidazolines by means of Dreiding models demonstrated that the cis isomers are more sterically hindered than the trans analogs because of the proximity of the bulky aromatic groups. However, the effect of repulsion of the MeN and carbonyl groups is small, since they are oriented at a significant angle, inasmuch as the C_5 atom deviates from the plane of the imidazoline ring. On the basis of this it

may be assumed that the trans-2-imidazolines are thermodynamically more stable than the cis isomers. This conclusion is in good agreement with the greater thermodynamic stability of trans-2,2-dimethyl-4-aryl-5-aroyldioxolanes [4] as compared with the cis isomers.

EXPERIMENTAL

The course of the reactions and the individuality of the compounds obtained were monitored by thin-layer chromatography (TLC) on Silufol plates [ether–hexane (1:1)]. The PMR spectra of 10% solutions of XI-XVII in a mixture of $(CD_3)_2CO$ with $(CD_3)_2SO$ (2:1) and of XVIII-XXIV in $(CD_3)_2CO$ were recorded with a BS-467 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The IR spectra of KBr pellets of the compounds were recorded with an IR-75 spectrometer. The mass spectra of XI-XIII and XVI-XIX were obtained with a Varian MAT-311 spectrometer at an ionizing voltage of 70 eV and an injection-system temperature of 155°C.

The benzaldehydes were identified from the melting points of their 2,4-dinitrophenylhydrazones, while ω-(methylamino)acetophenone borofluoride was first converted to the known hydrochloride [13].

The trans-1-methyl-2-aryl-3-aroylaziridines were obtained by the reaction of chalcones with an iodine-amine complex by the method in [12].

cis-1-Methyl-2-aryl-3-aroylaziridines. A 0.1-mole sample of trans-1-methyl-2-aryl-3-aroylaziridine was dissolved in a mixture of 200-300 ml of acetone with 20-50 ml of methanol, 0.01 mole of a 15% aqueous solution of triethylbenzylammonium hydroxide was added, and the mixture was allowed to stand overnight. The solvents were removed by distillation at reduced pressure, and the residue was dissolved in ether. The ether solution was washed with water and dried with potassium carbonate, the ether was evaporated, and the residue was recrystallized from hexane–isopropyl alcohol. The products were obtained in 70–85% yields.

cis- and trans-1-Methyl-2-aryl-3-aroylaziridine Borofluorides (I-X). A 0.1-mole sample of the aziridine was dissolved in the minimum amount of methanol, and the solution was cooled to 0°C and treated with 0.1 mole of boron trifluoride etherate. The mixture was then diluted with a threefold amount of ether, and the precipitated crystals were removed by filtration and air dried. The products were obtained in 90–95% yields.

cis-1,2-Dimethyl-4-aryl-5-aroyl-2-imidazoline Borofluorides (XI-XVII, Table 1). A 0.01-mole sample of trans-1-methyl-2-aryl-3-aroylaziridine borofluoride (I-VII) was placed in an ampul and dissolved in 10 ml (0.2 mole) of dry acetonitrile, and the contents of the ampul were purged with argon (nitrogen). The ampul was then sealed and heated at 100°C for 2-8 h, after which it was opened, and the contents were transferred to a flask and diluted with ether. The precipitated crystals were removed by filtration, washed on the filter with ether, and air dried.

trans-1,2-Dimethyl-4-aryl-5-aroyl-2-imidazoline Borofluorides (XVIII-XX, Table 1). A 0.01-mole sample of thoroughly dried (in a Fischer pistol) cis-1-methyl-2-aryl-3-aroylaziridine borofluoride (VIII-X) was placed in an ampul, 10 ml (0.2 mole) of dry acetonitrile was added, and the contents of the ampul were purged with argon (nitrogen). The ampul was sealed and heated at 100°C for 10-15 h, after which it was opened, and the contents were transferred to a flask and diluted with ether. The precipitated crystals were removed by filtration, the ether solution was evaporated, the residue was dissolved in methanol, and the benzaldehydes were identified in the form of their 2,4-dinitrophenylhydrazones. The insoluble ω-(methylamino)acetophenone borofluoride was removed by filtration, washed with ether, and air dried. The chloroform solution was diluted with ether, and the precipitated crystals of the 2-imidazoline were separated, washed with ether, and air dried.

trans-1,2-Dimethyl-4-aryl-5-aroyl-2-imidazolines (XXI-XXIV, Table 1). A) Ether (30 ml) was added to 10 mmole of trans-1,2-dimethyl-4-aryl-5-aroylimidazoline borofluoride (XVIII-XX), 1.8 ml (15 mmole) of triethylamine was added, and the solution was filtered. The ether was evaporated, and the residue was crystallized from toluene–hexane. Compound XXIV was isolated in the form of a viscous slightly yellowish oil.

B) A solution of 15 mmole of sodium methoxide was added to a solution of 10 mmole of cis-1,2-dimethyl-4-aryl-5-aroyl-2-imidazoline borofluoride (XI-XIV), after which the methanol was evaporated, and the residue was dissolved in ether. The solution was filtered, the ether was evaporated, and the contents of the flask were crystallized from toluene–hexane. Compound XXIV was isolated in the form of a viscous yellowish oil.

Reaction of 1-Phenyl-2-methylamino-3-hydroxy-3-(p-bromophenyl)propan-1-one Hydrochloride with Acetonitrile. A 2.7-g (10 mmole) sample of the amino hydroxy ketone and 10 ml (200 mmole) of dry acetonitrile were placed in an ampul, the contents were purged with argon, and the ampul was sealed and heated at 100°C for 15 h. It was then opened, and the hydrochloride was precipitated with ether and removed by filtration. p-Bromobenzaldehyde was not detected in the solution by TLC.

Deuteration of trans-1,2-Dimethyl-4-(p-bromophenyl)-5-benzoyl-2-imidazoline (XXII). A 0.1-g sample of imidazoline XXII and 0.03 g of sodium methoxide were placed in an ampul and dissolved in 1 ml of deuteromethanol. After 10 min, the degree of conversion was 90%. The deuterium exchange was monitored from the PMR spectra.

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PYRIMIDINES.

73.* SYNTHESIS OF ACETYLPYRIMIDINES

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UDC 547.853.1:542.957.2

It is shown that the use of benzene as the solvent in the preparation of 2- and 4-acetylpyrimidines from cyanopyrimidines via the Grignard reaction makes this reaction a practical method for the preparation of pyrimidinyl ketones. Preparatively convenient methods for the preparation of 4-acetylpyrimidine from 4-ethylpyrimidine through the α-oximino derivative and 5-acetylpyrimidine from 4,6-dichloro derivatives of pyrimidine are proposed.

Up until now, little study has been devoted to ketones of the pyrimidine series, which are not very easy to obtain. They are primarily obtained via the Grignard reaction from cyanopyrimidines or by homolytic acylation [2]. Although a related series, viz., acetylpyrimidines, has been described in the literature, experimental data are not available in all cases; in addition, the syntheses are multistep processes and give the products in low

*See [1] for communication 72.

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