The PMR spectra of 90-110 mg/ml solutions of the compounds in deuteroacetone (with hexamethyldisiloxane as the internal standard) and in sulfuric acid (with tetramethylammonium bromide as the internal standard) were measured with a Perkin–Elmer R-12 spectrometer (60 MHz) at 40°C.

The UV spectra of V were measured with a Perkin–Elmer 402 spectrophotometer (the layer thickness was 1 cm, and the concentration was 10^{-4} mole/liter). The optical densities at the analytical wavelengths were recorded by means of a V2-23 digital voltmeter.

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SYNTHESIS AND STEREOCHEMISTRY OF 2,2,3-TRIMETHYL-5-ARYL-4-AROYLOXAZOLIDINES

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cis-2,2,3-Trimethyl-5-aryl-4-aroyloxazolidines were obtained by heating complex boron trifluoride salts of trans-1-methyl-2-aryl-3-aroylaziridines with acetone. The reaction of complex boron trifluoride salts of cis-1-methyl-2-aryl-3-aroylaziridines leads to substituted benzaldehydes and ω-N-methylaminoacetophenones.

In [1] it was demonstrated that the simplest 1H-aziridines react readily with aldehydes with expansion of the three-membered ring and the formation of oxazolidines. However, it was later [2-4] found that the products of the reaction of 1H-aziridines with carbonyl compounds are α-alkyl-N-methylolethyleneimines and β-aminoethylethyleneimine derivatives. Nevertheless, it was established in [5, 6] that 5-azoniadispiro[4.0.5.1]dodecane perchlorates react with ketones and aldehydes upon heating to give substituted oxazolidines.

In the present paper we present data on the reaction of complex salts of N-alkyl-3-aroylaziridines with acetone.

We have shown that complexes of trans-1-methyl-2-aryl-3-aroylaziridines with boron trifluoride react upon heating with excess acetone to give cis-2,2,3-trimethyl-5-aryl-4-aroyloxazolidines (VIII-XIV, Table 1) in 50-80% yields. In contrast to [7], according to the results of thin-layer chromatography (TLC) and PMR spectroscopy of the reaction mixtures, the formation of trans analogs of VIII-XIV was not observed. The relative reactivities of complexes I-VII change as a function of the electron-donor properties of the substituents in the 4 position of the aryl group in the order $CH_3 > H > Br \approx Cl$. This makes it possible to propose that the benzyl center undergoes attack by the nucleophile.

The hydrolysis of VIII in an acidic medium led to the formation of acetone, which was identified from its 2,4-dinitrophenylhydrazone, and 1-phenyl-2-N-methylamino-3-hydroxy-3-(p-bromophenyl)-1-propanone (XV). By means of retroaldol cleavage of the latter we obtained p-bromobenzaldehyde (XVI) and ω-N-methylaminoacetophenone (XVII), which confirms opening of the C–N bond of aziridine by acetone on the β-carbon atom side with respect to the carbonyl group.

In addition to absorption bands of aromatic rings (3080, 3040, 1600, and 1500 cm^{-1}), the IR spectra of VIII-XIV contain bands of stretching and deformation vibrations of C–H (2987, 2800, 1450, and 1380 cm^{-1}) and C–O (1095 cm^{-1}) bonds. The intense band of stretching vibra-

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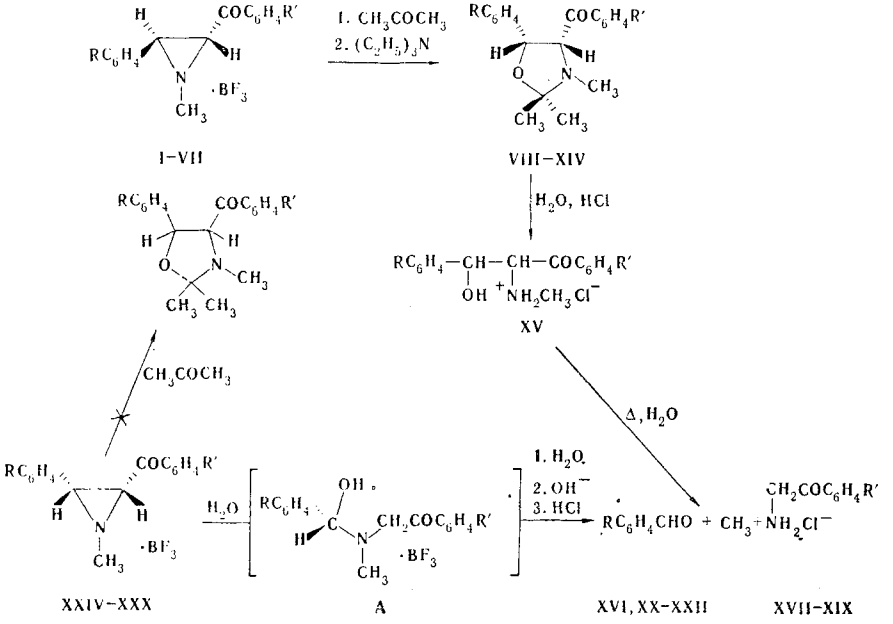
TABLE 1. cis-5-Aryl-4-aroyloxazolidines

Compound	mp, °C	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
VIII	135	60,9	5,5	3,6	$C_{19}H_{20}BrNO_2$	61,0	5,4	3,7	80
IX	122	69,0	6,3	4,2	$C_{19}H_{20}ClNO_2$	69,2	6,1	4,2	75
X	109	67,5	6,1	8,0	$C_{19}H_{20}N_2O_4$	67,2	5,9	8,2	60
XI	97	77,1	7,3	4,7	$C_{19}H_{21}NO_2$	77,3	7,2	4,7	55
XII	113	77,4	7,5	4,2	$C_{20}H_{23}NO_2$	77,6	7,4	4,5	65
XIII	120	69,0	6,8	4,2	$C_{19}H_{20}ClNO_2$	69,2	6,1	4,2	60
XIV	133	60,8	5,3	4,0	$C_{19}H_{20}BrNO_2$	61,0	5,4	3,7	75



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

tions of a CO group is split (1707, 1680 cm^{-1}), which can be explained by the presence of two conformers due to rotation of the COPh group.

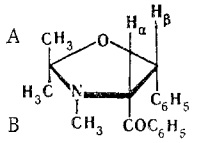
Signals of protons of three methyl groups — one attached to the nitrogen atom (2.31-2.37 ppm) and two attached to the carbon atom in the 2 position (1.20-1.36 and 1.47-1.58 ppm) — are observed in the PMR spectra of oxazolidines VIII-XIV. Signals of methylidyne protons appear in the form of doublets (H_α 5.37-5.67 ppm, $H\beta$ 4.58-4.93 ppm, J = 8.9-9.1 Hz). The doublet at 5.37-5.67 ppm was assigned to H_α on the basis of data on deuterium exchange. The high value of the spin—spin coupling constant (SSCC) of the methylidyne protons makes it possible to propose [7] a cis configuration for oxazolidines VII-XIV; this is confirmed by data on the Overhauser nuclear effect (ONE) [8] for VIII (Table 2).

The lower values of the effect for H_α can evidently be explained by the greater length of the C—N bond as compared with the C—O bond of the five-membered ring [9].

We also studied the dependence of the chemical shifts of the protons of the oxazolidine ring on solvents: The difference in the chemical shifts of the H_α and $H\beta$ protons of VIII in CCl_4 and benzene is 25 Hz for H_α and 22 Hz for $H\beta$, which is characteristic for cis-substituted acyl derivatives of cyclic systems [10].

One might have expected that complexes of cis-1-methyl-2-aryl-3-aroylaziridines with boron trifluoride would react similarly with acetone to give oxazolidines. However, we found that the products of this reaction are ω-N-methylaminoacetophenones XVII-XIX and benzaldehydes XVI and XX-XXIII, i.e., cis-aziridines XXIV-XXX do not react with acetone but rather with the

TABLE 2. Overhauser Nuclear Effect (ONE) for 2,2,3-Trimethyl-5-(p-bromophenyl)-4-benzoyloxazolidine



Irradiated CH_3 group	Observed proton	ONE, %
A	H_α	6
A	H_β	11,5
B	H_α	0
B	H_β	2,5

water that is present in trace amounts in the reagents and is also formed primarily as a result of crotonic condensation in the presence of boron trifluoride at elevated temperatures. An experiment carried out with the thoroughly dried complex of boron trifluoride and cis-aziridine XXV showed that the chemical mechanism remained essentially unchanged. The reaction products were ω-N-methylaminoacetophenone, p-chlorobenzaldehyde, and, in contrast to the preceding experiments, p-chlorobenzalacetone, the formation of which is explained by condensation of p-chlorobenzaldehyde and acetone with splitting out of water. The latter fact indicates that catalytic amounts of water are, in principle, necessary for the complete conversion of cis-aziridines to decomposition products XVII-XIX, XVI, and XX-XXIII.

A comparative analysis of the structures on the basis of Dreiding models showed that the approach to the benzyl center of the ring from the rear is shielded to a greater extent in the complexes of cis-aziridines as compared with the trans isomers, since both phenyl rings are almost parallel to the bisector of the angle that passes through the nitrogen atom and the middle of the C—C bond of the three-membered ring, and, as a consequence of this, only the sufficiently small water molecules, in contrast to acetone molecules, can reach the reaction center. The formation of benzaldehydes and aminoacetophenones can be explained in two ways: either by the addition of water with subsequent dealdolization of amino hydroxy ketone XV or by a more or less synchronous approaching of the benzyl center of aziridine by a water molecule and dissociation of the ring C—C bond, which is observed at 60°C [11]. However, asynchronicity of dissociation of the C—C bond and the addition of water as a consequence of a decrease in the steric factors should lead to products of 1,3-dipolar addition of acetone to the cis-aziridine, which, in fact, we did not observe. Prolonged heating of hydroxy amino ketone salt XV in acetone at 100°C does not lead to decomposition products, although decomposition of this type does occur in excess water, although, to be sure, rather slowly. However, in the case of the reaction of cis-N-alkyl-3-aroylaziridines with acetone one observes the formation of benzaldehyde by means of TLC in the first 30 min, i.e., the addition of water to cis-aziridines probably proceeds via a second pathway, viz., through intermediate A.

p-Chlorobenzaldehyde was identified from its PMR spectrum and melting point [12]. The benzaldehydes were identified from the melting points of the 2,4-dinitrophenylhydrazones, while the boron trifluoride complexes with ω-N-methylaminoacetophenones were identified from the melting points of the hydrochlorides [13] or by means of the products of alternative synthesis.

EXPERIMENTAL

The course of the reactions and the individuality of the compounds obtained were monitored by TLC on Silufol plates (elution with ether—hexane). The PMR spectra of 10% solutions of the compounds in CCl_4 were recorded with a BS-467 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The IR spectra of 0.1 M solutions in CCl_4 were recorded with an IR-75 spectrometer.

cis-1-Methyl-2-aryl-3-aroylaziridines. A 15% aqueous solution of triethylbenzylammonium hydroxide containing 0.01 mole of base was added to a solution of 0.1 mole of trans-1-methyl-

TABLE 3. PMR Spectra of cis-2,2,3-Trimethyl-5-aryl-4-aroyloxazolidines

Compound	δ, ppm					J, Hz
	2-CH_3	N—CH_3	H_β	H_α	H_{Ar}	
VIII	1,30, 1,58	2,36	4,58	5,42	6,78—7,60	8,9
IX	1,32, 1,51	2,37	4,82	5,48	7,01—7,70	8,9
X	1,36, 1,55	2,37	4,93	5,67	7,36—7,91	9,1
XI	1,30, 1,58	2,36	4,58	4,58	6,78—7,60	8,9
XII	1,20, 1,47	2,33	4,78	5,36	6,77—7,67	9,1
XIII	1,31, 1,48	2,33	4,77	5,51	6,98—7,72	8,9
XIV	1,28, 1,48	2,31	4,64	5,42	6,94—7,61	9,0

2-aryl-3-aroylaziridine [14] in a mixture of 200-300 ml of acetone with 10-15% methanol, 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 a mixture of hexane with isopropyl alcohol. The compounds were obtained in 70-85% yields.

Complexes of cis- and trans-1-Methyl-2-aryl-3-aroylaziridines with BF_3 (I-VII, XXIV-XXX). A 0.1-mole sample of BF_3 etherate was added to a solution of 0.1 mole of the aziridine in the minimum amount of methanol at 0°C, and the mixture was diluted with a threefold amount of ether. The precipitated crystals were removed by filtration and air dried. The compounds were obtained in 90-95% yields.

cis-2,2,3-Trimethyl-4-aroyl-5-aryloxazolidines (VIII-XIV, Tables 1 and 3). A solution of 0.01 mole of the complex of trans-1-methyl-2-aryl-3-aroylaziridine with BF_3 was dissolved in a 20-fold amount of acetone, and the mixture was purged with argon and heated in a sealed ampul at 90°C for 1-6 h. The ampul was opened, and the solution was transferred to a flask and made alkaline with 0.015 mole of triethylamine. The mixture was evaporated to dryness, and the residue was diluted to 50 ml with ether. The ether solution was passed through a layer of silica gel on a Schott filter and allowed to stand in a refrigerator. The precipitated crystals were removed by filtration, washed with a small amount of cold ether, and air dried. The compounds were obtained in 50-80% yields.

Hydrolysis of cis-2,2,3-Trimethyl-4-benzoyl-5-(p-bromophenyl)oxazolidine (VIII). A mixture of 0.01 mole of the oxazolidine, 15 ml of water, and 0.05 mole of hydrochloric acid was shaken and allowed to stand overnight. The precipitated crystals were removed by filtration, washed with water, recrystallized from methanol, and air dried. The yield of ketone XV, with bp 188°C, was 88%. Intense peaks of fragments from cleavage at the C_α—C_β bond with m/e 148 and 186 were observed in the mass spectrum. Found: C 51.8; H 4.4; N 3.6%. $C_{16}H_{17}BrClNO_2$. Calculated: C 52.1; H 4.6; N 3.8%.

A) The filtrate and wash waters were transferred to a round-bottom flask, and the acetone was removed by steam distillation into an adapter containing a saturated solution of 2,4-dinitrophenylhydrazine in 2 N hydrochloric acid. The precipitated hydrazone was removed by filtration, washed successively with 2 N hydrochloric acid and water to pH 7, and dried to constant weight at 90°C. The hydrazone, with mp 127°C (from methanol) (mp 128°C [15]), was obtained in 90% yield.

B) Water (30 ml) was added to the crystals, and the mixture was refluxed for 4 h. It was then extracted with ether, and the ether extract was evaporated. The p-bromobenzaldehyde was identified in the form of the 2,4-dinitrophenylhydrazone. The aqueous solution was concentrated at reduced pressure, and the precipitated ω-N-methylaminoacetophenone was recrystallized from alcohol to give a product with mp 219°C [13].

Reaction of the Complexes of cis-1-Methyl-2-aryl-3-aroylaziridines with BF_3 (XXIV-XXX) with Acetone. A solution of 0.01 mole of the complex in a 20-fold amount of acetone was purged with argon, sealed in an ampul, and heated at 90-95°C for 15-20 h. The ampul was opened, the acetone was removed, and the residue was dissolved in chloroform. The insoluble crystals were removed by filtration, washed with chloroform, and air dried to give the following complexes of ω-N-methylaminoacetophenones with BF_3: XVII (in 85% yield, mp 133°C.

Found: C 49.8; H 4.9; N 6.4%. $C_9H_{11}NO \cdot BF_3$. Calculated: C 50.0; H 5.1; N 6.4%), XVIII (in 87% yield, mp 137°C. Found: C 42.7; H 3.9; N 5.7%. $C_9H_{10}ClNO \cdot BF_3$. Calculated: C 42.9; H 4.0; N 5.5%), and XIX (in 91% yield, mp 143°C. Found: C 36.6; H 3.5; N 4.6%. $C_9H_{10}BrNO \cdot BF_3$. Calculated: C 36.5; H 3.41 N 4.7%).

The chloroform solution was evaporated, the residue was dissolved in alcohol, and the corresponding benzaldehydes were identified in the form of the 2,4-dinitrophenylhydrazones.

ω-N-Methylaminoacetophenones (XVII-XIX). Methylamine was passed with stirring into a solution of 0.05 mole of ω-bromoacetophenone in 100 ml of absolute ether for 30 min, after which stirring was continued for another hour. The precipitated crystals were removed by filtration, the filtrate was evaporated, and the residue was dissolved in alcohol—ether (1:1). A 0.06-mole sample of boron trichloride etherate was then added dropwise, the solution was diluted with ether, and the precipitated crystals were removed by filtration and air dried. The compounds were obtained in 60% yields.

Deuteration of cis-2,2,3-Trimethyl-4-aroyl-5-aryloxazolidines. A solution of 0.1 g of the oxazolidine and 0.03 g of sodium methoxide in 0.1 ml of deuteromethanol was allowed to stand in an ampul at room temperature. After 6 h, 90% exchange had occurred. Deuterium exchange was monitored by PMR spectroscopy.

Reaction of 1-Phenyl-2-N-methylamino-3-hydroxy-3-(p-bromophenyl)-1-propanone (XV) with Acetone. A solution of 0.01 mole of amino hydroxy ketone hydrochloride XV in a 20-fold amount of acetone was purged with acetone, sealed in an ampul, and heated at 100°C for 20 h. The ampul was opened, and the precipitated amino hydroxy ketone hydrochloride was removed by filtration. Analysis by TLC showed that the solution did not contain p-bromobenzaldehyde.

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