singlet, 1-H), 2.89-9.23 (1H, multiplet, 5-H), 4.05-4.26 (2H, multiplet, OCH₂CH₃), and 6.25 ppm (1H, doublet, 4-H). Found: C 64.2 and H 8.0%. C₁₆H₂₄O₅. Calculated: C 64.7 and H 8.7%.

<u>6,10-Dimethyl-5,6-epoxy-3-ethoxycarbonyl-9,10-dichloromethyleneundec-3-en-2-one (V)</u>. The solution of 5.6 g (0.02 mole) of compound III and 0.4 g of TEBA in 12.8 ml (0.16 mole) of chloroform is cooled to 10°C, and 24 ml of a 50% solution of NaOH together with 7 ml of methylene chloride are added with intense stirring. The mixture is kept for 3 h. It is extracted with ether and chloroform and then dried. Compound V is isolated with a yield of 3.04 g (42%); it has bp 144-147°C (1 mm) and $n_D^{2°}$ 1.5293. The UV spectrum, λ_{max} (log ε), is as follows: 207 (4.32) and 265 nm (4.30). The PMR spectrum is as follows: 1.08-1.30 (12H, multiplet, 6,10, 11-CH₃, OCH₂CH₃), 1.84-2.30 (5H, multiplet, 7,8-H, 9-H), 2.52 (3H, singlet, 1-H), 3.12 (1H, multiplet, 5-H), 4.04-4.26 (2H, multiplet, OCH₂CH₃), and 6.28-6.40 ppm (1H, multiplet, 4-H). Found: C 57.0, H 6.5, and Cl 20.0%. C_{1.7}H_{2.4}Cl₂O₄. Calculated: C 56.2, H 6.7, and Cl 19.5%.

<u>Dioxolanes VIIa-c</u>. To the mixture of 0.6 g of anhydrous ferric chloride and 15 ml of the ketone are added, with stirring, 5 g (0.021 mole) of the acetal of citral oxide VI. The mixture is heated for 5 h at 45-50°C, washed with a saturated solution of K_2CO_3 , extracted, and dried. The dioxolanes VIIa-c are isolated by distillation. The constants of the dioxolanes are presented in Table 1.

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SYNTHESIS OF THE DIASTEREOMERIC 2-ARYL-1-CYCLOHEXYL-3-(2,3-EPOXYPROPIONYL)AZIRIDINES

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substrate and reactants.

The reaction of cinnamoyloxiranes with an iodine-cyclohexylamine complex in the presence of an excess of amine led to a mixture of the four diastereomeric epoxypropionylaziridines the ratio of which depended on steric and electronic factors in the

The interaction of 2-methyl-2-cinnamoyloxiranes with iodine-methyl- or iodine-ethylamine complexes in aprotic solvents led to a mixture of the two diastereomeric trans-epoxypropionylaziridines differing in configuration at the chiral center of the epoxide ring [1]. In a continuation of the study of the influence of steric and electronic factors on the stereochemistry of the resulting epoxypropionylaziridines and with the aim of synthesizing new compounds in this series, the interaction of substituted cinnamoyloxiranes with an iodine-cyclohexylamine complex has been studied in the present work.

It has been established that in difference to the iodine-methyl- and iodine-ethylamine complexes the reaction of epoxyenes Ia-g with the iodine-cyclohexylamine complex in benzene orether led to a mixture of four or three diastereomeric 1-cyclohexyl-2-aryl-3-(2,3-epoxypro-pionyl)aziridines two of which had trans (IIa, b-VIIIa, b) and two (or one) cis configuration of the aziridine ring (IXa, b-XIIIa, b, XIVb, XVb).

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TABLE 1. Physicochemical Characteristics of trans- and cis-2-Aryl-1-cyclohexyl-3-(2,3-epoxypropionyl)aziridines IIa,b-XIIIa,b, XIVb, XVb

Compound	mp, °C	Found N,	Empirical formula	Calculated, N %	Yield, %
IIa	77-78	47			25
IIb	67-68	4.5	$C_{19}H_{25}NO_2$	4,7	21
IIIa	9899	5.0	C18H23NO2	4.9	23
IIIb	83	4,9			24
[Va	9596	4,7	$C_{19}H_{25}NO_{2}$	4,7	37
IV b	107-108	4,7			24
Va	121-122	5,0	$C_{18}H_{23}NO_2$	4,9	43
Vb	111-112	4,0			28
WIa	122-123	3,8	C ₁₈ H ₂₂ BrNO ₂	3,9	33
VI _b	119-120	3,8			23
VIIa	142-143	8,5	$C_{18}H_{22}N_2O_4$	8,5	14
VIID	130-132	8,4	C H N C		10
VIIIa	126-127	4,4	$C_{19}H_{25}NO_3$	4,4	30
VIIID		4,4		17	28
IX a	79 70	4,6	$C_{19}H_{25}NO_2$	4,7	· 0
	1079	4,7	СИМО	4.0	12
Ad Vh	02 04	4,0	$C_{18} G_{23} NO_2$	4,9	10
Y la	114-116	4,9	CHNO.	17	5
XIb	76-78	4.6	01911251102	4,7	19
XILa	99100	49	CueHanNOa	49	īš
XIID	93-94	4.8	01811231102	1,0	20
XIIIa	118119	3.7	C18H99BrNO2	3.9	14
XIIIb	108-110	3,7	-1022		20
XIVb	127128	8,4	· G18H22N2O4	8,5	38
XVb	99100	4,4	$C_{19}H_{25}NO_3$	4,4	11

TABLE 2. Influence of Substituent at the α -Carbon Atom of the Epoxy Ring (R³) on the Ratio of Diastereomeric 2-Phenyl-1-cyclohexyl-3-(2,3-epoxypropionyl)aziridines IIa,b-Va,b, IXa,b-XIIa,b

Com- pound	R'	R²	R,	Yield, %		^a trans	^b trans	Yield, %	
				a	b	acis	^b cis	Σа	Σb
11 1X 111 X 1V X1 !V X11	CH ₃ CH ₃ CH ₃ CH ₃ CH ₃ CH ₃ H H	CH ₃ CH ₃ H H H H H H	H H H CH ₃ CH ₃ CH ₃ CH ₃	$25 \\ 6 \\ 23 \\ 13 \\ 37 \\ 5 \\ 43 \\ 5$	21 8 24 14 24 19 28 20	4,2 1,8 7,4 8,6	2,6 1,7 1,3 1,4	31 36 42 48	29 38 43 48



The configuration of compounds IIa,b-XIIIa,b, XIVb, XVb was confirmed by data of IR and PMR spectroscopy. Stretching vibrations of C=O groups of the trans isomers IIa, b-VIIIa,b were observed in the region of 1690-1695 cm⁻¹ and of the cis isomers IXa, b-XIIIa,b, XIVb, XVb at 1710-1715 cm⁻¹ [2]. The vicinal protons of the aziridine ring of epoxypropionylaziridines IIa,b, XIIIa,b, XIVb, XVb appeared in the PMR spectra as AB spin systems. The values of the coupling constants of these protons were 2.7-3.0 Hz for the products of trans confirmation IIa, b-VIIIa,b and 6.5-7.0 Hz for diastereomers of cis configuration IXa,b-XIIIa,b, XIVb, XVb and correspond to constants for trans and cis acylaziridines known from [3].

The stereochemical relationships between the diastereomeric cis and trans aziridinylepoxyketones were established when studying the isomerization of the latter. Thus isomerization of compound Va in a methanol-DMSO mixture in the presence of sodium methylate led to the formation of the cis isomer XIIa, i.e., compounds Va and XIIa and Vb and XIIb differ in the

TABLE 3. Influence of Substituent in the Benzene Nucleus on the Ratio of trans- and cis-Aziridines Va,b-VIIIa,b, XIIa,b, XIIIa,b, XIVb, XVb

Company	Аг	Yield	trans	
Compound		trans	cis	cis
Va,b, XIIIa,b VIa,b, XIIIa,b VIIa,b, XIVb VIIIa,b, XVb	C ₆ H ₃ 4-BrC ₆ H ₄ 4-NO ₂ C ₆ H ₄ 2-CH ₃ OC ₆ H ₄	71 56 24 58	25 34 38 11	2,8 1,7 0,6 5,3

configuration of the α -carbon atom of the aziridine ring. On the basis of the difference in the chemical shifts of the gem and vic protons of the aziridine and epoxide rings [1], and also of the chemical shifts of the methyl group protons in compounds IIa,b-XIIIa,b, XIVb, XVb by analogy with compounds Va,b and XIIa,b all the synthesized aziridinyl ketones were assigned to group α or group b. The diastereomers belonging to group α differed from the diastereomers of group b in the configuration at the center of chirality of the epoxy ring while the cis and trans isomers of one group (α or b) had the opposite configuration at the α -carbon atom of the aziridine ring. Isomerization of trans aziridinylepoxyketones IIb-Vb into the cis isomers IXb-XIIb confirmed the configurational interrelation of the diastereomers.

The ratio of the diastereomeric aziridinylepoxyketones in the iodine-alkylamine-complexcinnamoyloxirane reaction fetermined from the PMR spectra of the reaction mixtures, are shown in Tables 1-3. From these data and also from the results of [1] it follows that the amount of the resulting diastereomers and their ratio depend on the size of the alkyl group of the amine, the presence of a substituent at the a-carbon atom of the epoxy ring, and the character of the substituent on the benzene ring. The observed ratio of products may be explained by considering the structure of the transition complex and by using the data on the reaction mechanism from [4]. In accordance with the mechanism of formation of 2-acylaziridines the stereochemistry of the final product is determined by the iodination stage of the intermediate aminoenol with subsequent stereospecific cyclization. The aminoenol may be found as a cyclic chelate complex the iodination of which leads in the end to the trans-aziridine while iodination of the nonchelated form of the aminoenol proceeds nonselectively. It follows from Table 2 that since the overall yields of the resulting trans- and cis-isomers a and b are approximately equal in the majority of cases $(a_{trans} + a_{cis} = b_{trans} + b_{cis})$ then addition of amines to the cinnamoyloxirane proceeds nonselectively. This means that the stereochemistry of the reaction products is determined at ths stage of iodination of the intermediate diastereomeric aminoenols a and b and participation in the reaction of the chelated forms of the diastereomeric aminoenols, as might have been expected, must increase the stereoselectivity of the reaction.

Evidently, in the case of the iodine-methyl- and iodine-ethylamine complexes, a high degree of chelate formation of the diastereomeric aminoenols takes place, the attack of which from the unhindered side led to trans-aziridinylepoxyketones in [1]. An increase in the dimensions of the alkyl group in the case of the iodine-cyclohexylamine complex hinders the formation of the cyclic chelate structure which leads to a mixture of trans- and cis-isomers IIa,b-XIIIa,b, XIVb, XVb.

The observed selectivity of the formation of diastereomers IVa-VIIIa in relation to diastereomers IVb-VIIIb is probably linked with the influence of the substituent at the α -carbon atom of the epoxide ring, which is particularly graphically illustrated by the stereoselectivity of formation of trans isomers in relation to cis isomers between the diastereomeric pairs $(a_{\text{trans}}/a_{\text{cis}}, b_{\text{trans}}/b_{\text{cis}})$ for compounds IIa,b-Va,b, IXa,b-XIIa,b. In the absence of a substituent at the α -carbon atom of the oxirane ring the stereoselectivity of formation of trans-aziridinylepoxyketones IIa and IIb, and IIIa and IIIb is close. On the other hand, the diastereomeric aminoenol α of compounds IVa and Va is iodinated highly selectively almost exclusively in the chelate form while iodination of aminoenols b occurs nonselectively, and is probably linked with steric hindrance created by the α -methyl group in attack of the intermediate aminoenol by the iodinating agent [1].

The character of the substituent in the benzene ring of the initial epoxyenone Id-g influences appreciably the ratio of transaziridinylepoxyketones Va,b-VIIIa,b and cis isomers XIIa,b-XVb. It is evident from Table 3 that the introduction of an electron donating substituent favors the formation of trans-aziridinylepoxyketones VIIIa,b. This may be linked with the change in basicity of the amino group nitrogen in the intermediate diastereomeric aminoenones. Electron accepting substituents reduce the nitrogen basicity so that nonchelated conformations begin to play a guiding role.

Therefore a combination of steric and electronic factors in the substrate and reactant determine the amount and the ratio of diastereomeric epoxypropionylaziridines obtained in the reaction of epoxyenone-iodine-alkylamine complex.

EXPERIMENTAL

IR spectra of substances in CCl₄ of concentration 10^{-1} mole/liter (layer thickness 0.01 cm) were taken on a Specord 75-IR spectrophotometer. PMR spectra sere measured on a Varian HA-100D-15 spectrometer in benzene and CCl₄, internal standard was HMDS.

<u>2-Aryl-1-cyclohexyl-3-(2,3-epoxypropionyl)aziridines IIa,b-XIIIa,b, XIVb, XVb.</u> Cyclohexylamine (150 mmoles) was added dropwise slowly to a solution of cinnamoyloxirane Ia-g (50 mmoles) and iodine (50 mmoles) in ether. The precipitated solid was filtered off, the ether partially evaporated, the residue filtered through a layer of silica gel, hexane added, and the mixture of diastereomeric epoxypropionylaziridines IIa,b-XIIIa,b, XIVb, XVb isolated. Samples of compounds intended for analytical purposes were prepared by the chromatographic resolution of the mixture of diastereomers on silica gel, eluent was a linear gradient of petroleum ether-ether 1:1. The cis,trans-isomers (IIa,b-XIIIa,b, XIVb, XVb were separated by crystallization from alcohols.

Isomerization of 2-Phenyl-1-cyclohexyl-3-(2,3-epoxypropionyl)aziridines IIb-IVb, Va,b. trans-Epoxypropionylaziridine IIb-IVb, Va,b (1 mmole) was dissolved in a mixture of methanol-DMSO and potassium hydroxide (0.3 mmole) in methanol (10 ml) was added. The course of the isomerization was followed by TLC. AFter 5-24 h the reaction mixture was diluted with water and extracted with benzene. The benzene was evaporated off and the PMR spectrum of the reaction mixture was drawn. Signals of protons of the cis isomers IXb-XIb, XIIa,b were separated in the spectrum and were analyzed.

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