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ASYMMETRIC NITROGEN.

60.* ACYLATION AS A PATHWAY TO OPTICALLY ACTIVE 1,3,3-TRISUBSTITUTED DIAZIRIDINES

G. V. Shustov, S. N. Denisenko,
M. A. Shokhen, and R. G. Kostyanovskii

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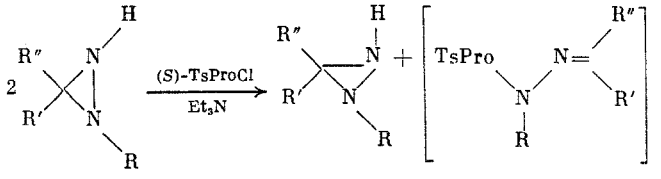
By virtue of its simplicity, the method of optical activation of 1,3,3-trialkyldiaziridines by acylation with chiral reagents [2, 3] can compete with separation through diastereomers [4, 5] or by chromatography on a chiral phase [6]. The use of (S)- or (R)-N-tosylproline chloride (TPC) as an acylating reagent makes it possible to obtain both enantiomers of diaziridines with ~40% optical purity [2, 3]. In this connection a further investigation of the possibilities of TPC for obtaining optically active diaziridines and the mechanism of its enantioselectivity seems of interest.

In the present research by means of (S)-TPC we have accomplished the kinetic separation of diaziridines (Ia-j) (Table 1), including functionally substituted comopunds (If, g, i, j) and bicyclic compounds (Ih-j). Carrying out the reaction in EtCl made it possible to obtain, in optically active form, relatively low-boiling compounds such as (Ia, d, h, i).



(Ia–j) (+)- or (–)-(Ia–j)

R = R′ = R″ = Me (a); R = Me, R′ + R″ = $(CH_2)_5$ (b); R = Me, R′(R″)C = 2,2-Ad (c); R = Bu, R′ = R″ = Me (d); R = $PhCH_2$, R′ = R″ = Me (e); R = $MeCO(CH_2)_2$, R′ = R″ = = Me (f); R = $Me_2N(CH_2)_2$, R′ = R″ = Me (g); R + R′ = $(CH_2)_3$, R″ = Me (h); R + + R′ = $(CH_2)_3$, R″ = CF_3 (i); R + R′ = $(CH_2)_3$, R″ = MeO_2C (j).

*For previous communication, see [1].

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TABLE 1. Optically Active Diaziridines

Compound	Yield,[a] %	Bp, °C (p, mm Hg), mp, °C	p,[b] %	Optical rotation		
				λ, nm	$[\alpha]_{\lambda}^{20}$, deg	solvent (C, % by volume)
(Ia)	34	37–40(200)	44	589	22.1	Benzene (3)
				365	71,3	
				589	35,4	Heptane (2)
				546	42,1	
(Ib)[c]	52	43–45(1,5)	60	589	52,8	Heptane (2)
		53–55		546	62,0	
(Ic)	93	66–68	24	589	5,5	Benzene (3)
		(cf. [14])		546	6,0	
				589	13.9	Heptane (3)
				546	16,0	
(Id)	56	40–43(10)	d	589	17.1	Benzene (1)
		(cf. [15])		546	20.4	
(Ie)[e]	74	33–36	11	589	−11,4	CCl_4 (3,5)
				436	−25.4	
(If)	52	50–51(1)	16	589	18.6	Heptane (2)
		(cf. [2])		546	21,8	
(Ig)	67	38–40(1)	7	589	−6.2	Heptane (3)
		(cf. [2])		546	−7,6	
(Ih)	50	61–62(55)	75	589	37,8	Heptane (2)
		(cf. [9])		546	45,8	
(Ii)	59	40–42(45)	d	589	−1,3	Heptane (7)
		(cf. [9])		546	−1,7	
(Ij)[f]	86	47–48(1)	35	589	21,2	MeOH (2,5)
				546	25,6	
(Ik)	68	–	d	589	20,3	Heptane (2)
				546	23,8	

[a] Based on the pure enantiomer.
[b] Optical purity.
[c] Compare with the boiling point, melting point, and $[\alpha]_D^{20}$ value in [2].
[d] Not determined.
[e] Compare with the melting point and $[\alpha]_{436}^{20}$ value in [6].
[f] Compare with the boiling point and $[\alpha]_D^{20}$ value in [7, 9].

TABLE 2. Parameters of the PMR Spectra[a] of Diastereomeric Derivatives of Diaziridines[b]

Compound	MeCHN[c]	δ, ppm			Solvent
		R	R′	R″	
(Ia)+Eu(tfc)$_3$[d]	–	2,90	1,67	1,83	$CDCl_3$
	–	2,15	1,63	1,69	
(If)+Eu(tfc)$_3$[e]	–	2,27 (Me), 3,35 m (CH_2CH_2)	1,76	1,84	CCl_4
	–	2,34 (Me), 3,35 m (CH_2CH_2)	1,69	1,69	
(IIa)	1.41, 5,22	1.75 (Me), 2,23 m (CH_2CH_2)	1,10	1,45	C_6D_6
	1.31, 5,17	1.95 (Me), 2,23 m (CH_2CH_2)	1,07	1,29	
(IIb)	1.22, 5,14	2,36	1,4–1,9 m		C_6D_6
	1.23, 5,13	2,26	1,4–1,9 m		
(IIc)	1.16, 5.11	1,05–1,87m (CH_2C), 2,40 m, 2.94 m (CH_2N)		1,18	C_6D_6
	1,16, 5.11	1,05–1,87 m (CH_2C), 2,40 m, 2.80m (CH_2N)		1,38	

[a] At 400 MHz and 60 MHz for If; the chemical shift of the indicator group is underlined.
[b] For all of the compounds the chemical shifts of the preponderant isomer are presented on the second line.
[c] Doublet and quintet, $^3J_{MeCH} = {}^3J_{CHNH} = 6.8$ Hz.
[d] Molar ratio 15:1.
[e] Molar ratio 9:1.

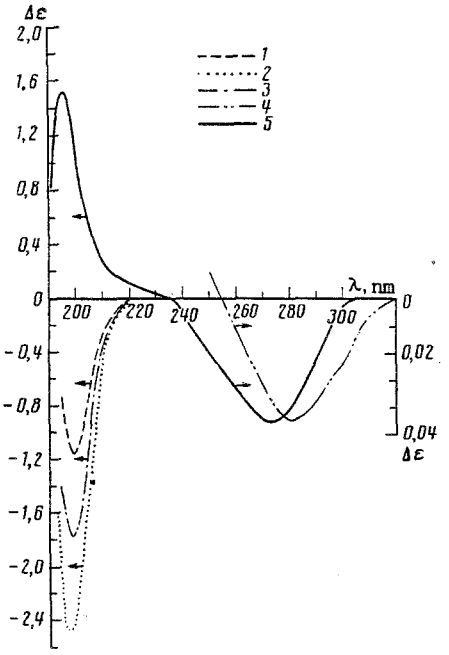


Fig. 1

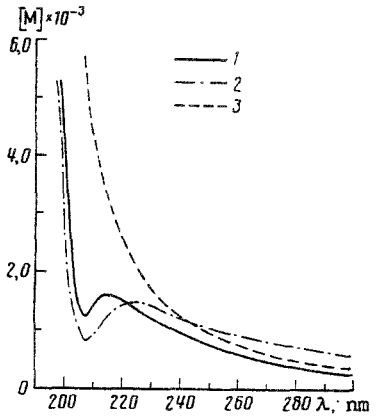
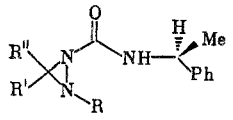


Fig. 2

Fig. 1. Circular dichroism (CD) spectra of diaziridines: 1) (+)-Ia, $\Delta\varepsilon_{198}$ −1.157; 2) (+)-Ib, $\Delta\varepsilon_{197}$ −2.475; 3) (+)-Ic, $\Delta\varepsilon_{198}$ −1.769; 4) (+)-If, $\Delta\varepsilon_{280}$ −0.045; 5) (+)-Ik, $\Delta\varepsilon_{275}$ −0.046; $\Delta\varepsilon_{196}$ 1.52 in n-heptane. The Δε values for (Ia-c, f) are scaled to 100% optical purity.

Fig. 2. Optical rotatory dispersion (ORD) spectra of diaziridines: 1) (+)-Ia, $[m]^{20}_{213}$ 1612, $[M]^{20}_{200}$ 3479; 2) (+)-Ib, $[M]^{20}_{223}$ 1466, $[M]^{20}_{200}$ 3221; 3) (+)-Ih, $[M]^{20}_{220}$ 2602, $[M]^{20}_{207}$ 5624 in n-heptane. The $[M]^{20}_{\lambda}$ values are scaled to 100% optical purity.

The optical purities of the enantiomerically enriched diaziridines were determined from the PMR spectra by integration of the most separated signals of diastereomers, derivatives of (Ic, g, h) – adducts (IIa-c) with (S)-α-phenylethyl isocyanate – by means of europium tris(3-trifluoroacetyl-d-camphorate) $Eu(tfc)_3$ for (Ia, f) (Table 2) and (Ib, e, j) with respect to the angles of optical rotation on the basis of the data in [2, 3, 6, 7].



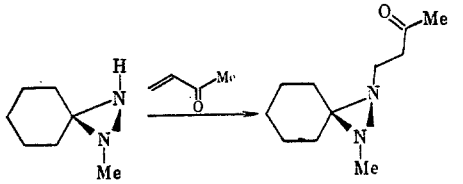
(IIa-c)

R = $Me_2N(CH_2)_2$, R′ = R″ = Me (a); R = Me, R′(R″)C = 2,2-Ad (b); R + R′ = $(CH_2)_3$, R″ = Me (c).

It must be noted that the anantioselectivity of the reaction with (S)-TPC is sensitive to the experimental conditions (the rate of addition of the solutions of TPC and Et_3N and the temperature). Thus (+)-(Ib) can be obtained with an optical purity of ~60%, but in some experiments it was only 8-9%. However, on the whole, the high optical yields of (+)-(Ia, b, h) (Table 1) are reproduced with a deviation of ±5%. An increase in the optical purity was observed for diaziridine (+)-(Ib) when it was sublimed (0°C): the angle of optical rotation of partially sublimed crystals of this compound was smaller by a factor of two than that of the starting mixture with an optical purity of 46%; the optical purity of the residue increased by 7%, i.e., to 53%.

A negative Cotton effect (CE) at 197 nm, which vanishes when heptane is replaced by MeOH, is observed in the circular dichroism (CD) spectrum of diaziridine (+)-(Ib) with a known (1R,2R) absolute configuration [3] in heptane (Fig. 1). This constitutes evidence for participation of the n electrons of the N atoms, the antibonding n_+ combination of the unshared electron pairs (UEP), in the optically active transition, as follows from a nonempirical quantum-chemical calculation [8]. Coincidence of the experimental and calculated signs of

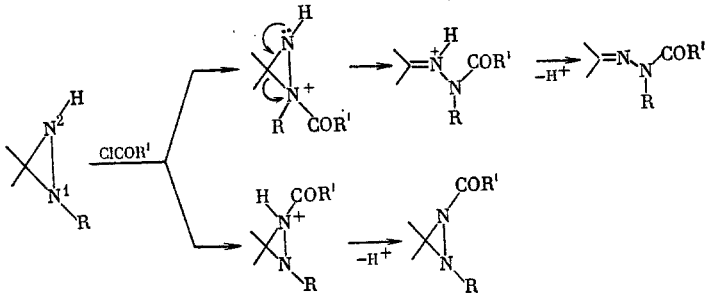
the rotational force of the first transition ($n_+ \rightarrow \sigma^*_{NN}$, 3p) is also observed. Like (+)-(Ib), diaziridines (+)-(Ia, c) have a negative CE (Fig. 1) and, consequently, a (1R, 2R) configuration of the N atoms. The destabilizing interaction of the UEP of the N atoms decreases with inclusion of one of the N atoms in the bridgehead of a bicyclic system in (+)-(Ih) and (−)-(Ii); this leads to a decrease in the energy of the highest occupied MO of n_+ [9] and, correspondingly, to a shift of the $n_+ - \sigma^*_{NN}$ transition to the short-wave region. A Cotton effect (CE) is therefore not observed in the CD spectra of bicyclic diaziridines (Ih, i) in the region up to 190 nm. However, the optical rotatory dispersion (ORD) spectra of bicyclic (+)-(Ih) and monocyclic diaziridines (1R, 2R)-(+)-(Ia, b) are characterized by a marked increase in the positive molecular rotation near 200 nm (Fig. 2); this is evidently due to a Rydberg $n_+ - 3s$ transition, the maximum of the band of which lies in the vacuum UV region [8]. Proceeding from this, a (1R, 5R, 6R) absolute configuration of bicyclic (+)-(Ih) may be assumed. The same configuration of the N atoms of bicyclic diaziridine (1R, 5S, 6R)-(+)-(Ij) was established by x-ray diffraction analysis. The absolute configuration of the 1-(3'-ketobutyl) derivative (1R, 2R)-(+)-(If) was assigned on the basis of coincidence of the signs of the CE at 280 nm ($n - \pi^*$ transition of the C=O group) in the CD spectra of this compound and diaziridine (1R, 2R)-(+)-(Ik), which was obtained via the following scheme:



(1R,2R)-(-)-(Ib) (1R,2R)-(-)-(Ik)

Thus (S)-TPC reacts at a high rate with the (1S, 2S) enantiomers of diaziridines (Ia-c, f, h, j). This conclusion is also evidently valid for other diaziridines (Id, e), excluding derivatives (Ig, i), in which the relative energies of the diastereomeric transition states may change substantially because of the presence of a functional group.

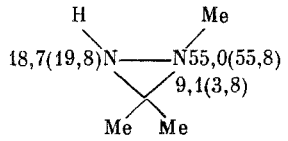
Proceeding from a knowledge of the absolute configuration of the more reactive enantiomer one can construct a stereochemical model of the transition state in conformity with the rules of steric control [10]. However, N-alkyldiaziridines can undergo attack by an acylating reagent at both the N^1 atom and the N^2 atom with the formation of, respectively, the N-acylhydrazone or the N-acyldiaziridine:



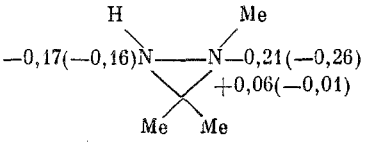
The ascertain the regioselectivity of acylation we studied the model reaction of diaziridine (Ia) with acetyl chloride. It was found from the PMR spectra of the reaction mixture that acetone N-acetyl-N-methylhydrazone (IIIa) – the product of diaziridine–hydrazone rearrangement – and the corresponding N-acetyldiaziridine (IV) are formed in a ratio of 4:1, which does not change in the course of 48 h at 20°C in CD_2Cl_2 and when $Et_3\overset{+}{N}HCl^-$ is added. On the basis of this we excluded the possibility of a diaziridine–hydrazone rearrangement under the reaction conditions, and the hydrazone/diaziridine ratio can therefore be assumed to be kinetic. Thus the attack of the acylating reagent, like that of electrophilic acetylenes [11], is realized primarily at the alkylated N^1 atom, which is more nucleophilic. The latter is confirmed by calculations of diaziridine (Ia) by the MNDO method starting from the reasonable geometry of the diaziridine ring [12], as well as with optimization of it.*

*The starting and optimized (in parentheses) parameters of (Ia) (bond lengths in angstroms and bond angles in degrees) were as follows: N^1N^2 1.482 (1.399), N^1C^3 1.445 (1.496), N^1C^{Me} 1.470 (1.475), N^2C^3 1.451 (1.484), N^2H 0.90 (1.008), $N^2N^1C^{Me}$ 110 (118.2), $C^3N^1C^{Me}$ 117.1 (125.7), N^1N^2H 109 (111.1), C^3N^2H 113 (114.8).

cording to these calculations, the highest occupied MO is localized primarily on the N^1 atom, which also has the highest negative charge (the values obtained after optimization of the geometry are presented in parentheses):

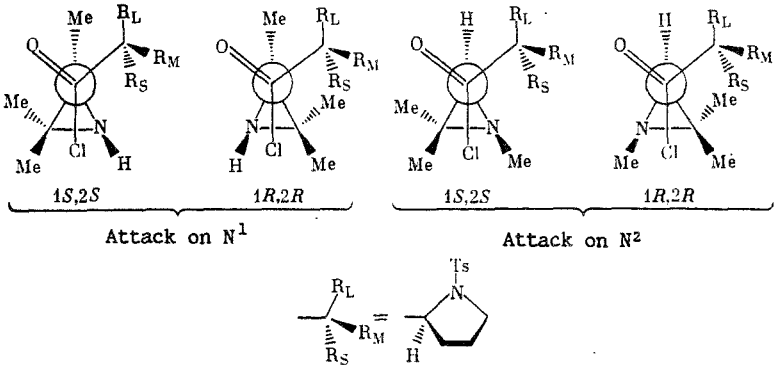


Partial population of the HOMO (%)



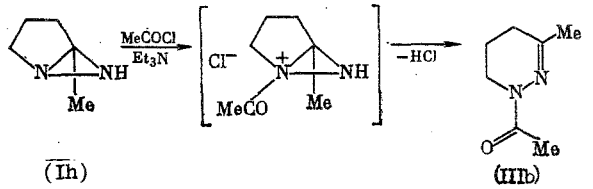
Charges on the atoms

Consequently, both orbital and charge control ensure preferred attack by the electrophile on the N^1 atom. The observed enantioselectivity of the reaction of N-alkyldiaziridines with (S)-TPC is also better explained under the assumption of greater nucleophilicity of the N^1 atom. In fact, a substantial difference in the steric interactions with the (1S, 2S) and (1R, 2R) enantiomers of (Ia) is noted when the reagent* approaches the N^1 atom from the side on which the UEP is located:



In the first case the NH group of the diaziridine draws close to the pyrrolidine ring, while in the second case the bulky Me group attached to the C^3 atom draws close to the pyrrolidine ring. In conformity with this, as demonstrated experimentally, the (1S, 2S) enantiomer reacts with (S)-TPC faster than the (1R, 2R) enantiomer. In the case of attack by (S)-TPC on the N^2 atom close steric interactions are realized for both enantiomers within the framework of the same model: the Me—N group draws close to the pyrrolidine ring in the case of the (1S, 2S)-diaziridine, while the MeC group draws close to the pyrrolidine ring in the case of the (1R, 2R)-diaziridine.

In the case of bicyclic diaziridine (Ih) attack by the acylating reagent is realized only at the N^1 atom: only the corresponding hydrazone (IIIb) is formed in the model reaction with acetyl chloride:



It should be noted that of all of the diaziridines (Ia-j) investigated, precisely (Ih) was obtained with the greatest optical purity (Table 1); this corresponds to the above-examined model with great steric control in the case of attack by the chiral acylating reagent at the alkylated N^1 atom of the diaziridine ring.

EXPERIMENTAL

The angles of optical rotation were measured with a Polamat A polarimeter. The circular dichroism (CD) and optical rotatory dispersion (ORD) spectra were obtained with JASCO J-500A (with a DP-500N processor) and JASCO J-20A spectropolarimeters, respectively. The NMR spectra were obtained with Bruker WM-400 (^{1}H, 400.13 MHz), Bruker WP-80SY (^{13}C, 20.15 MHz), and Jeol JNM-C-60HL (^{1}H, 60 MHz) spectrometers.

*A conformation with eclipsing of the C=O and C—N bonds, which is characteristic for amino acids and their derivatives [13], is assumed for (S)-TPC.

Kinetic Enantiomeric Enrichment of Diaziridines (General Method). A solution of 1.44 g (5 mmoles) of (S)-TPC [2] in 10 ml of absolute CH_2Cl_2 was added dropwise with stirring and cooling (−70°C) to a solution of 10 mmole of the diaziridine in 15 ml of absolute CH_2Cl_2, after which a solution of 0.71 g (7 mmoles) of Et_3N in 5 ml of absolute CH_2Cl_2 was added, and the mixture was maintained for 5 days at −70°C to −30°C. The temperature was then raised slowly to 20°C, the precipitate was removed by filtration, the filtrate was evaporated in vacuo, and the products were extracted with absolute ether. The ether solution was diluted with an equal volume of pentane, separated from the resinous precipitate, and evaporated in vacuo. The optically active diaziridine obtained was purified by distillation or sublimation in vacuo.

The enrichment of the low-boiling diaziridines (Ia, d, h, i) was carried out by the same method in EtCl; the solutions of (S)-TPC and Et_3N were added after they were cooled to 0°C. The solvent was removed at 20°C, and the diaziridine was recondensed from the residue at 20°C (0.5 mm) into a cooled (−78°C) trap and purified by distillation. The products of kinetic enantiomeric enrichment of (Ia-j) (Table 1) were identical to the racemic compounds with respect to their boiling and melting points and PMR spectra. Diaziridines (Ia-g) underwent complete racemization* without decomposition when they were heated in sealed ampuls in benzene (for 12 h at 100°C).

1-(3'-Ketobutyl)-2-methyl-3,3-pentamethylenediaziridine [(+)-(Ik)]. A solution of 0.26 g (2.1 mmoles) of (+)-(Ib) (optical purity 60%) and 0.21 g (3 mmoles) of freshly distilled methyl vinyl ketone in 10 ml of absolute MeOH was maintained for 10 days at 20°C, after which the solvent was evaporated in vacuo, and the product was extracted from the residue with absolute ether. After removal of the ether, the residue (0.38 g) was chromatographed on silica gel [L40/100 μ, elution with hexane–ether (80:20)] to give 0.28 g of (+)-(Ik) in the form of a colorless oil (Table 1). Found: C 67.21; H 10.04%. $C_{11}H_{20}N_2O$. Calculated: C 67.30; H 10.27%. PMR spectrum (60 MHz, CCl_4, δ, ppm): 1.48 br. s [$(CH_2)_5$], 2.00 (MeCO), 2.25 (MeN), 2.44 m [$(CH_2)_2$].

Acetylation of 1,3,3-Trimethyldiaziridine (Ia). A solution of 0.39 g (5 mmoles) of acetyl chloride in 5 ml of absolute CH_2Cl_2 was added with stirring and cooling (−70°C) to a solution of 0.35 g (4.1 mmoles) of (Ia) and 0.51 g (5 mmoles) of Et_3N in 10 ml of absolute CH_2Cl_2, and the mixture was maintained for 10 h at 0°C. The precipitate was separated, the solvent was evaporated in vacuo, and the products were extracted from the residue with absolute ether. Removal of the ether gave 0.45 g (85%) of a mixture of acetone N-acetyl-N-methylhydrazone (IIIa) and 1-acetyl-2,3,3-trimethyldiaziridine (IV). PMR spectrum (60 MHz, CD_2Cl_2, δ, ppm): IIIa: 1.81 br. s (Me_2C), 1.98 (MeCO), 2.90 (MeN); IV: 1.31 and 1.18 (Me_2C), 1.98 (MeCO), 2.43 (MeN). The (IIIa)/(IV) ratio (4:1) was determined from the integral intensities of the signals of the MeN groups; the amount of (IV) coincided with the amount found as a result of iodometric titration of the mixture treated with 15% aqueous KOH solution. With respect to its PMR spectrum, N-acetylhydrazone (IIIa) was identical to a genuine sample obtained from acetone N-methylhydrazone and acetyl chloride in the presence of Et_3N, which was obtained in 72% yield and had bp 58-60°C (1 mm).

Acetylation of 5-Methyl-1,6-diazabicyclo[3.1.0]hexane (Ih). The acetylation was carried out via the preceding method. A 0.49-g sample of (Ih) gave 0.61 g (87%) of 1-acetyl-3-methyl-1,2-diaza-2-cyclohexene (IIIb), which did not contain the isomeric N-acetyldiaziridine. Vacuum distillation gave 0.55 g (79%) of (IIIb) with bp 45-46°C (1 mm). Found: C 60.20; H 8.54; N 19.71%. $C_7H_{12}N_2O$. Calculated: C 59.98; H 8.63; N 19.98%. NMR spectra ($CDCl_3$, δ, ppm): ^1H (400 MHz): 1.79 quintet (CCH_2C, ^3J = 5.8 Hz), 1.92 (MeC=N), 2.12 t (CH_2C=N), 2.24 (MeCO), 3.66 t (CH_2N); ^{13}C (partial decoupling of ^1H): 17.5 t (C^5), 24.7 t (C^4), 26.6 q (MeC=N), 27.3 q (MeCO), 38.2 t (C^6), 150.0 (C^3), 170.5 (C=O).

CONCLUSIONS

1. The acylation of 1,3,3-trisubstituted diaziridines with acyl chlorides is realized primarily at the substituted N^1 atom and is accompanied by diaziridine–hydrazone rearrangement.

2. Acylation with a 0.5-mole amount of (S)-N-tosylproline chloride is an effective method for the optical activation of 1,3,3-trialkyldiaziridines and can be used to determine the absolute configurations of these compounds.

*The results of our investigation of the kinetics of racemization will be published.

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ASYMMETRIC NITROGEN.

61.* INVERSION TOPOMERIZATION OF DIAZIRIDINES

G. V. Shustov, A. Yu. Shibaev,
Yu. V. Puzanov, and R. G. Kostyanovskii

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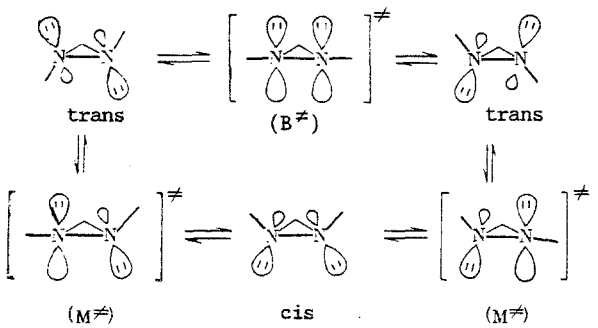
The topomerization of simple hydrazines includes processes involving the inversion of the N atoms and rotation about the N–N bond that are close in energy and, consequently, difficult to distinguish [2]. Only the first process is possible in diaziridines, and they are therefore a convenient model for a study of the mechanism of the topomerization of compounds with two bonded inverting atoms. According to the results of x-ray diffraction analysis (see [3] and the literature cited therein), PMR spectroscopy [4], electron diffraction

Scheme 1



*For previous communication, see [1].

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