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ASYMMETRICAL NONBRIDGEHEAD NITROGEN XII.[1] THE ABSOLUTE CONFIGURATION OF CHIRAL DIAZIRIDINES.

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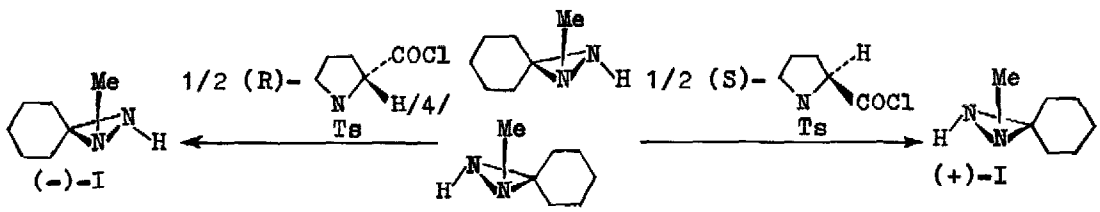
The possibility of resolution of antipodes with an asymmetric center at a nitrogen atom alone was demonstrated for the first time in the example of 1-methoxyaziridine-2,2-dicarboxylic ester.[2]

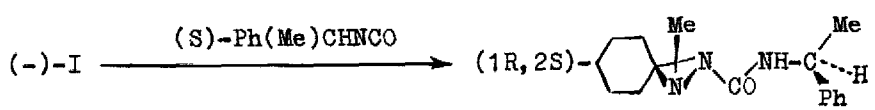
Now we report on the antipodes of diaziridine I, which were obtained by means of kinetic resolution according to the scheme described earlier[3] for (+)-I



Compound	Optical purity[a]	$[\alpha]_\lambda^{20}$ in n-C_7H_{16} (c 4.3)[b]			$\Delta\varepsilon^{c}_{max}$
	%	λ 589 nm	λ546 nm	λ365 nm	(λ 197 nm)
(-)-I	47.5	-42.2°	-84.2°	-218.0°	2.15
(+)-I	63.5	56.1°	112.4°	290.1°	-3.3

a. After the enhancement of optical purity via the adduct with chloral[3].

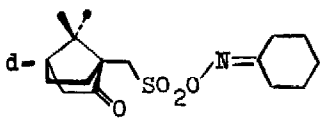
b. Perkin-Elmer 141 instrument. c. Jobin-Yvon Dichrograph III instrument. The absolute configuration of antipodes was established by X-ray analysis of the pure diastereomer II, derived from (-)-I [5]:



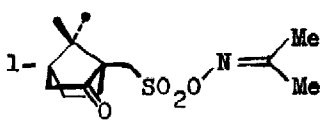
(II)[6]

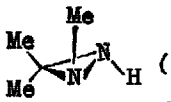
It must be noted that each of the antipodes, (+)-I and (-)-I, displays the opposite signs of the corresponding ORD and CD curves. Positive rotation and negative Cotton effect correspond to 1R,2R-configuration, negative rotation and positive Cotton effect – to 1S,2S-configuration[7].

On the basis of this correlation the absolute configuration of diaziridines (+)-I and (-)-III, obtained by asymmetric synthesis[8], must be as follows:



$\xrightarrow[CH_2Cl_2,\ -16°]{MeNH_2}$ (+)-I, $[\alpha]^{20}_{365}$ 1.1° (c 6.5 n-C_7H_{16}), optical purity ~0.2%



$\xrightarrow[0°]{MeNH_2}$  (-)-III, $[\alpha]^{20}_{546}$ -7.4°; $\Delta\varepsilon$ $2.8\cdot10^{-2}$(203nm) (c 4.1 n-C_7H_{16}), optical purity 9.9%

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4. From R-proline ($[\alpha]^{20}_D$ +86.1° (c 1.2 H_2O)[3]; m.p. 55-56°); $[\alpha]^{20}_D$ +69.1° (c 1.8 C_6H_6).

5. O.A.Dyachenko, L.O.Atovmyan, S.M.Aldoshin, A.E.Polyakov, R.G.Kostyanovsky, Chem.Commun., 1976, 50.

6. Described earlier[3], differ from 1S,2S-epimer on chemical shift MeN, $\Delta\nu$= 0.09 ppm (C_6H_6).

7. The configuration of the nitrogen atoms in diaziridines can be designated by the direction of the helix formed by the 1,2-substituents when viewed along the N-N-bond; see R.S.Cahn, C.K.Ingold, V.Prelog, Angew.Chem., 78, 413 (1966).

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