16. H. Ogura and S. Sugimoto, Org. Mass Spectrom., 3, 1341 (1970).
17. E. K. Field and S. Megerson, Adv. Phys. Org. Chem., 6, 1 (1968).
18. I. I. Eitingon, M. M. Krasukhina, S. M. Kavun, N. P. Strel'nikova, and V. K. Butyugin, Kauchuk i Rezina, Nos. 8, 9 (1965).
19. H. Brebs, Angew. Chem., 65, 293 (1953).
20. B. A. Dogadkin, O. N. Belyatskaya, A. V. Dobrosmyslova, and M. S. Fel'dshtein, Vysokomol. Soedin., 1, 876 (1959).

CONFIGURATION OF 2-SUBSTITUTED 1-AMINOETHYLENEIMINES

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The trans configuration of 2-phenyl- and 2-methyl-1-aminoethyleneimine was proved by means of their PMR spectra in the presence of tris(dipivaloylmethanato)europium.

The establishment of the configurations of 2-substituted 1-aminoethyleneimines directly from the chemical shifts of the protons of the three-membered ring in the PMR spectra requires prior knowledge of the effect in these compounds of the anisotropy of the adjacent groups, the magnitude of which can currently be evaluated only extremely approximately. In order to establish the spatial orientation of the amino group, we used tris(dipivaloylmethanato)europium [$Eu(DPM)_3$], inasmuch as one may expect that complexing will occur only at one nitrogen atom at low concentrations of this paramagnetic-shift reagent. This assumption is confirmed experimentally: Up to $C_{Eu(DPM)_3}/C_{substance} \leq 0.3$-0.4, deviation from the linear dependence of the chemical shift (τ) on $C_{Eu(DPM)_3}/C_{substance}$ is not observed.

The results obtained after mathematical treatment of the linear dependences of the $\tau = A - BD$ type, where $D = C_{Eu(DPM)_3}/C_{I\text{-}III}$, are presented in Table 1.

*Deceased.

TABLE 1. Coefficients of the Calculated Linear Dependences and Their Mean-Square Error and Correlation Coefficients

Compound	τ*	A	B	r	s
1-Aminoethyleneimine (I)	H_{cis}	8,56	52,87	0,99	0,36
	H_{trans}	8,12	50,94	0,99	0,29
	H_2	5,71	91,52	0,99	0,57
2-Phenyl-1-aminoethyleneimine (II)	H_2	7,70	21,38	0,99	0,18
	†$H_{3\,cis}$	8,52	16,73	0,99	0,17
	H_{trans}	8,35	21,58	0,99	0,17
2-Methyl-1-aminoethyleneimine (III)	H_2	8,48	51,60	0,99	0,12
	†$H_{3\,cis}$	8,47	16,71	0,99	0,03
	$H_{3\,trans}$	8,65	35,30	0,99	0,02
	CH_3	8,88	21,29	0,99	0,06

*$\tau = A - B\,[C_{Eu(DPM)_3}/C_{I\text{-}III}]$.
†With respect to the substituent in the 2 position.

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Inasmuch as the signal from the NH_2 protons has the greatest paramagnetic shift in the spectrum of aziridine I, it can be asserted that complexing with $Eu(DPM)_3$ occurs at the primary amino group.

The large paramagnetic shifts of the absorption signals from the protons in the 2 and 3-trans positions as compared with those for the 3-cis positions in aziridines II and III constitute unambiguous proof of the trans configuration of the larger.

EXPERIMENTAL

The PMR spectra of CCl_4 solutions of the compounds (0.5 M) were obtained with a Perkin-Elmer R 12A spectrometer (60 MHz) with tetramethylsilane as the internal standard. The chemical shifts were measured with an accuracy of ±0.5% of the scanning range.

Compounds I-II and III were obtained by the methods in [1-3], respectively. Their purity was verified by means of gas–liquid chromatography.

LITERATURE CITED

1. S. A. Giller, A. V. Eremeev, M. Yu. Lidak, and V. A. Pestunovich, Khim. Geterotsikl. Soedin., 815 (1968).
2. D. Felix, J. Schreiber, K. Piers, U. Horn, and A. Eschenmoser, Helv. Chim. Acta, 51, 1461 (1968).
3. S. A. Giller, A. V. Eremeev, M. Yu. Lidak, V. A. Pestunovich, É. É. Liepin'sh, and I. Ya. Kalvin'sh, Khim. Geterotsikl. Soedin., 45 (1971).

CHEMISTRY OF INDOLE

XLIII.* NEW SYNTHESIS OF BENZ(AMINOMETHYL)INDOLES

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Indolines are amidomethylated in the 6 position in acidic media. N-Acetylation changes the orientation to give the 5-substituted isomers. Dehydrogenation of the reaction products and subsequent hydrolysis make it possible to obtain 5- or 6-aminomethylindoles.

Wooley and Shaw [2] have reported that some 5-aminomethyldimethylindoles have antiserotonin activity. However, these models must be synthesized by a roundabout method (for example, see [3, 4]), inasmuch as the pyrrole ring undergoes amidomethylation in the reaction of indole with N-methylolamides in alkaline media [5], whereas indole and 3-alkylindoles are polymerized in acidic media. We therefore used the indoline–indole method based on electrophilic substitution reactions in the benzene ring of indoline or its acyl derivatives and subsequent dehydrogenation. This method makes it possible to selectively obtain 5- or 6-substituted indoles. It was found that the reaction of both indoline and 1-acetylindolines with methylol derivatives of acetamide or chloroacetamide does not give good results (they form mixtures of substances that are difficult to separate and are, in part, easily hydrolyzed).

However, indoline (Ia) can be amidomethylated with N-methylolphthalimide in concentrated sulfuric acid at room temperature to give 6-phthalimidomethylindoline (IIa), from which, after removal of the phthalyl

*See [1] for communication XLII.

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