DIAZABICYCLOALKANES WITH NITROGEN ATOMS IN BRIDGEHEAD POSITIONS.

18*. INTRAMOLECULAR CYCLIZATION OF 1-(β-HALOETHYL)-1,2,3,4-TETRAHYDROQUINOXALINIUM SALTS IN ACIDIC MEDIA

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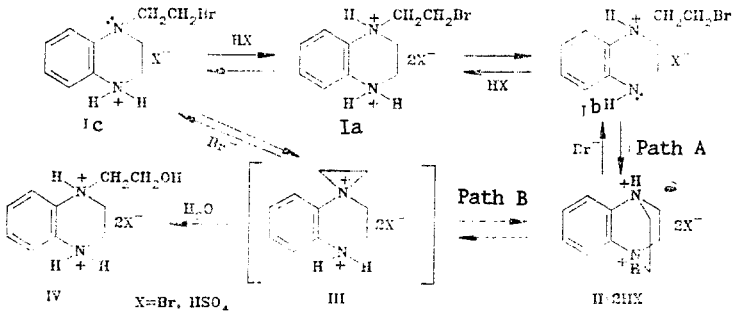
1-Methyl-1-(β-haloethyl)-1,2,3,4-tetrahydroquinoxalinium salts were synthesized and the dependence of the hydrolysis and cyclization rate constants on the acidity of the medium and presence of halide was found. It was determined that the monocations of tetrahydroquinoxalines participate in the formation of the benzo[b]-1,4-diazabicyclo[2.2.2]octene system, since blocking the free electron pair of the tertiary nitrogen atom with a methyl substituent significantly accelerates the cyclization and suppresses the hydrolytic side reaction.

Earlier, through the intramolecular cyclization of 1-(β-bromoethyl)-1,2,3,4-tetrahydroquinoxaline (I) in hydrobromic acid, we synthesized benzo[b]-1,4-diazabicyclo[2.2.2]octene (II) [2]. It was assumed that the cation Ib cyclized, out of the collection of protonated forms of the tetrahydroquinoxalines Ia-c which are found in the solution in acid–base equilibrium, and that II is formed principally through path A.



However, the presence of the free electron pair on the nitrogen atom in the base I and its monoprotonated form Ic do not exclude the formation of the aziridinium cation III since similar active intermediates occur regularly in alkylation reactions by β-haloethylamines [3, p. 21]. Related to this, the formation of II is possible also by rearrangement of the aziridinium cation III in a few equilibrium steps, i.e., path B.

The role of the free electron pair on the tertiary nitrogen atom in the cyclization should be clarified in order to choose the reaction path by comparing under identical conditions the behavior of the N-protonated and model N-methylated 1-(β-haloethyl)-1,2,3,4-tetrahydroquinoxalines. The hydrobromide 1-(β-bromoethyl)- (I·HBr) and hydrochloride 1-(β-chloroethyl)-1,2,3,4-tetrahydroquinoxaline (V) were obtained by the methods of [2, 4], and their N-methylderivatives VI and VII from the products of opening benzo[b]-1,4-diazabicyclo-[2.2.2]octene with haloformate esters [1].

*For Communication 17, see [1].

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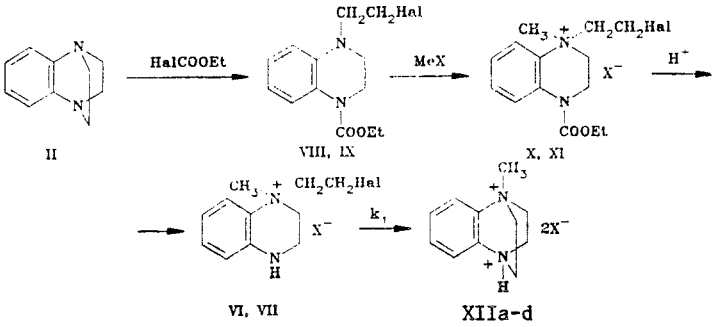


VI, VIII, X Hal=Br, X=SO_3F; VII, IX, XI Hal=Cl, X=ClO_4; XII a X=HSO_4, b X=Cl, c X=Br, d X=ClO_4

Methylation of the β-haloethyl derivatives VIII and IX was accomplished by the strong alkylating agents methylperchlorate and methylfluorosulfonate [5]. PMR, IR, and UV spectra of the quaternary ammonium salts X and XI were consistent with the structures expected.

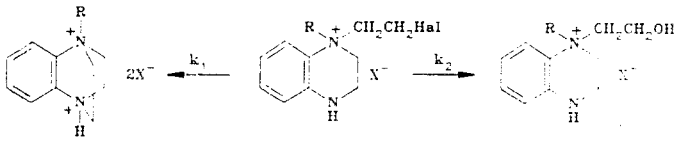
According to liquid chromatographic data, X and XI in boiling hydrobromic acid give complex mixtures due to the unstability of the products of cyclization of II·2HBr and XIIc (opening of the diazabicyclic fragment and partial demethylation due to the bromide ion). The reaction goes without complications in sulfuric acid. Heating in 12 M H_2SO_4 (H_0 ~ −6) leads to loss of acyl protection with formation of VI and VII which are in the unreactive protonated forms. Upon dilution of the sulfuric acid solutions to H_0 > −2, the cyclization occurs with formation of the 1-methylbenzo[b]-1-azonia-4-azabicyclo[2.2.2]octene (XII), synthesized earlier by methylation of II [6]. The propensity toward cyclization interferes with separation of the pure salts of VI and VII, however, impurities of X-XII, which are stable in dilute acids, do not interfere with the measurement of the cyclization reaction rate constants.

Cation exchange microcolumn chromatography was used for studying the reaction kinetics of the haloethyl derivatives I·HBr, V, and the quaternary salts VI and VII. In the cases of cyclization of VI and VII, with high rates, the most suitable method was direct photometry of the reaction mixtures since the conversion of these compounds is not accompanied by side reactions (from LC results), while there are substantial differences in the UV spectra of the starting compounds and the cyclization product XII.

The indicated features of the cyclization of the quaternary salts VI and VII (high cyclization rate and complications in concentrated hydrobromic acid) dictated the choice of sulfuric acid as the reaction medium and a temperature of 50°C. The optimal pH values, at which comparison was possible, were found by determining the dependence of the cyclization rate constants (k_1) VII → XII at 50°C on the acidity of the medium. The curve of k_1 vs. H_0 coincides well with the curve of the change in VII base concentration upon increasing the acidity of the medium (Fig. 1). The results obtained show that by increasing the degree of protonation of the quaternary salt of VII the cyclization rate sharply falls at H_0 ~ −2, and in strongly acidic media at H_0 < −5 the reaction practically does not occur. Thus, a pH value of 1-2 is most expedient for comparison, since the haloethyl derivatives I·HBr and V are practically completely found in the monoprotonated forms (pK_{a_1} of the tetrahydroquinoxaline is 4.84 [7], 4.74 [8], and 4.60 [9]) and the quantity of the unreactive diprotonated form is insignificant. It is not possible to evaluate more accurately the concentration of the diprotonated forms since the known pK_{a_2} data for the tetrahydroquinoxaline have substantial scatter (2.11 [7], 0.26 [8], and 1.17 [9]). Besides this, at pH 1-2, as was shown in separate experiments, the opening reactions of the cyclization products by nucleophilic components of the medium (H_2O, Cl^-, Br^-, and HSO_4^-) are completely absent, which somewhat simplifies comparison of the kinetic measurement results.

Under the conditions chosen (H_2SO_4, HBr, or HCl; 50°C; pH 1-2), the behavior of compounds I·HBr, V, VI, and VII were studied. Average values of the constants obtained are given in Table 1. As seen from experiments 1 and 2, cyclization could not be observed above the background of the accompanying hydrolysis, which dominates even in more acidic media (2.4 N H_2SO_4), for the haloethyl derivatives I·HBr and V. The quaternary salts VI and VII under these conditions (experiments 5 and 6) undergo cyclization with high rates, while the hydrolysis practically does not occur. Only in basic media (pH > 9) is the formation of

TABLE 1. Cyclization (k_1) and Hydrolysis (k_2) Rate Constants of the 1-(β-haloethyl)-1,2,3,4-tetrahydroquinoxalines I·HBr, V, VI, and VII in acidic media at 50°C.



Experiment	Starting compound	R	Hal	Reaction medium composition, pH 1-2	$k \cdot 10^5$ sec^{-1}*	
					k_1	k_2
1	I·HBr	H	Br	0,03 N. H_2SO_4	<0.1	4,4
2	V	H	Cl	0,03 N. H_2SO_4	<0,01	0,45
3	I·HBr	H	Br	2 N. LiBr, 0,01 N. HBr	0,28	0,16
4	V	H	Cl	2 N. LiCl, 0,01 N. HCl	$<10^{-4}$	0,027
5	VI	CH_3	Br	0,03 N. H_2SO_4	260**	<0,1
6	VII	CH_3	Cl	0,03 N. H_2SO_4	13**	<0,01

*Constants were calculated assuming first-order, and for hydrolysis, pseudo-first-order reactions; error is not more than ±10%. The values of relatively small constants are limited by the sensitivity of the method (see Experimental).
**Measured photometrically, hydrolysis products were not observed chromatographically.

hydrolysis products observed by LC. Two parallel reactions, cyclization and hydrolysis, are proposed based on the differences in behavior of compounds I·HBr, V and VI, and VII which should proceed by different mechanisms. The hydrolysis reaction of compounds I·HBr and V under equilibrium conditions have an S_N1 mechanism with participation of the intermediate aziridinium cation III, while the cyclization goes by an intramolecular S_N2 mechanism. This proposal was confirmed by studying the effect of added lithium halide on the reaction of I·HBr and V (experiments 3 and 4). A sharp decrease in hydrolysis rate was observed due to the effect explained by the mass action law and characteristic for reactions occurring by an S_N1 mechanism, and a small increase in the cyclization rate related to the change in ionic strength, an effect characteristic for an S_N2 mechanism (compare experiments 1 and 3). Consequently, the cyclization of I·HBr and V in acidic media more probably should occur as the monocation Ib through an intramolecular S_N2 mechanism, i.e., path A. The monocation Ib, in contrast to the model compounds VI and VII, is not fixed and is in equilibrium with the monocation Ic and base I, which are able to form the highly reactive spiroaziridinium cation III. The geometry of the latter is such that it quickly reacts only with external nucleophiles (H_2O and Br^-) and practically does not undergo intramolecular cyclization at the amino group. The success of using concentrated hydrobromic acid for the cyclocondensation reaction of aromatic haloethylamines, in particular, for synthesis of benzo[b]-1,4-diazabicyclo[2.2.2]octene [2], apparently is explained by its rather high acidity and high concentration of bromide ion. This simultaneously facilitates protection of the bases from intermolecular reactions due to protonation and suppression of hydrolysis due to shifting the equilibrium Ic ↔ III + Br^- to the left.

It can be expected that the monocation Ib and the model compound VI under identical conditions will undergo cyclization with high rate. Direct comparison of the observed cyclization constants is unreliable since for I·HBr the observed constant k_1 requires adjustment for the fraction of the reactive form Ib in the acid–base equilibrium Ib ↔ Ic. Lowering the basicity of aromatic amines upon introduction of β-haloethyl groups by 1.2-1.4 pKa units [10] should lead to a concentration ratio of compounds Ib and Ic equal approximately to 1:20, i.e., to a lowering of the concentration of the reactive form Ib and consequently to a lowering of the observed cyclization constant by ~20 times. Since k_1 for I·HBr and VI differ by more than 2600 times (experiments 1 and 5), it can be seen that in the model compounds, with the methyl substituent which is more voluminous than the proton, the intramolecular cyclization is substantially accelerated probably due to the spatial proximity of the reactive centers.

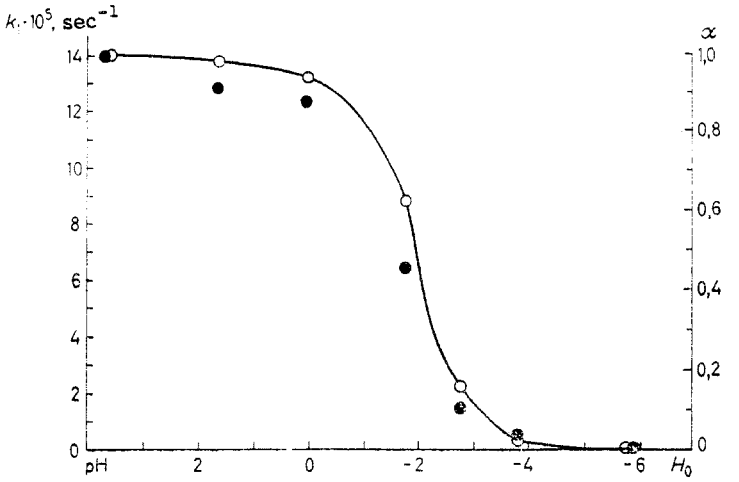


Fig. 1. Plot of the apparent cyclization rate constants, VII → XII, k_1 (•), and the fraction of base VII, α, (o), in the acid–base equilibrium VII + HX ↔ VII·HX vs. the acidity of the medium at 50°C.

The results obtained agree with [11], the authors of which showed that 1-methyl-1-(β-chloroethyl)piperazinium chloride, in contrast to 1-(β-chloroethyl)piperazine, cyclizes smoothly into the quaternary salt of 1,4-diazabicyclo[2.2.2]octene. The ease of cyclization of similar piperazinium salts is related to the stabilization of the conformation in which the β-chloroethyl group and the free electron pair of the second nitrogen atom of the heterocycle are close [12].

In conclusion, the preference of using β-bromo- in comparison to β-chloroethyl derivatives of tetrahydroquinoxaline in cyclization reactions should be noted. The observed increase in reaction rate by 20 times (experiment 5 and 6) lies within the usual values for change of alkylating ability for a series of alkylbromides and -chlorides [13].

EXPERIMENTAL

IR spectra were recorded on a UR-20 spectrometer. PMR spectra were taken on a Bruker HX-90 spectrometer with an internal standard of HMDS. Mass spectra were recorded on a MS-902 instrument (peaks with I_{rel} > 10% are given). UV spectra and photometric data were obtained on a Specord M-40 spectrometer. Analysis of the reaction mixtures used TLC on Silufol UV-254 plates with chloroform–ethanol, 20:1 (system A); and t-butanol–methylethylketone–formic acid–water, 8:6:3:3 (system B). Quantitative analysis of the reaction mixture compositions was done by ion-exchange chromatography on Aminex A-7 cation-exchange resin of 9 ± 2 μm particle size. The diameter of the microcolumn was 2 mm, height 50 mm. Eluents: 2 ml linear gradient 0.5-1.0 N $LiClO_4$ in 0.1 N AcOH–AcOLi buffer (pH 4.6) in 50% ethanol (system C); and 1.5 N $HClO_4$ in 30% methanol at 65°C (system D). Flow rate was 0.05 ml/min. The eluate was continuously analyzed by UV at 210 and 250 nm on a Milichrom chromatograph. Mathematical treatment of the chromatograms was done using the Chrom system (developed at NIBC SB AN USSR) by comparison of the peak areas at the analytical wavelengths of 210 and 250 nm accounting for calibration obtained for a blank mixture of the compounds. The reaction rate constants and statistical treatment calculations were done using the program RATCO, developed at IC SB AN USSR, based on analytical solution of a system of differential equations [14].

Benzo[b]-1,4-diazabicyclo[2.2.2]octene (II), 1-(β-bromoethyl)-1,2,3,4-tetrahydroquinozaline hydrobromide (I·HBr), and 1-(β-oxyethyl)-1,2,3,4-tetrahydroquinoxaline (IV) were obtained according to [2], the column retention times were 22, 12, and 5 min, respectively (system D). 1-(β-Chloroethyl)-1,2,3,4-tetrahydroquinoxaline hydrochloride (V) was obtained according to [4], retention time 9 min (system D). 1-Methylbenzo[b]-1-azonia-4-azabicyclo-[2.2.2]octene perchlorate (XIId) was obtained according to [6], column retention time 22 min (system C) and 19 min (system D). These compounds were used as blanks before analysis of reaction mixtures. Analytically pure samples of I·HBr and V were used for studying the cyclization reaction. Elemental analyses for C, H, Hal, and N corresponded to those calculated.

1-(β-Bromoethyl)-4-ethoxycarbonyl-1,2,3,4-tetrahydroquinoxaline (VIII, $C_{13}H_{17}BrN_2O_2$). To a solution of 0.57 g (3 mmole) bromophosgene (bp 62-63°C) [15] in 5 ml absolute acetonitrile with stirring and cooling to −41°C (acetonitrile–liquid nitrogen) was added dropwise over 30 min a solution of 0.18 ml (3 mmole) ethanol and 0.52 ml (3 mmole) diisopropylethylamine in 5 ml absolute acetonitrile, then a solution of 0.48 g (3 mmole) II in 15 ml absolute acetonitrile was quickly added. Cooling was stopped and the mixture was stirred for 2 h more. The heterogeneous reaction mass was evaporated, the residue treated with petroleum ether (4 × 5 ml), the extract obtained was filtered and evaporated. The brown oil was purified by preparative TLC on silica gel with system A. The band with R_f 0.6-0.7 and absorbing in the UV was collected. The product was eluted from adsorbent with 30 ml of a chloroform–methanol mixture, 5:1, and the solvent was removed in vacuum. Yield 0.3 g (33%) of yellow oil, darkening with time. R_f 0.72 (system A). IR spectrum ($CHCl_3$): 1050, 1340 (C–N), 1520, 1610 (C=C), 1700 (C=O), 2870, 3000-3050 cm^{-1} (C–H). UV spectrum (in methanol), λ_{max} (log ε): 227 (4.47), 268 (4.09), 313 nm (3.53). PMR spectrum ($CDCl_3$): 7.6-6.4 (4H, m, arom. protons), 4.2 (2H, q, OCH_2), 3.8-3.3 (8H, m, $4CH_2$), 1.2 ppm (3H, t, CH_3). Mass spectrum, m/z (%): 314 (22), 312 (20) M^+, 233 (10), 220 (14), 219 (100) $[M - CH_2Br]^+$, 191 (44), 160 (20), 159 (63), 147 (76), 146 (16), 145 (29), 133 (29), 132 (48), 131 (92), 119 (26), 118 (29), 117 (18), 106 (14), 105 (12), 104 (42).

1-Methyl-1-(β-bromoethyl)-4-ethoxycarbonyl-1,2,3,4-tetrahydroquinoxalinium Fluorosulfonate (X, $C_{14}H_{20}BrFN_2O_5S$). To a solution of 0.23 g (0.7 mmole) VIII in 1 ml absolute benzene were added in four 0.05 ml portions over 30 min (2.8 mmole total) methylfluorosulfonate. One h after the beginning of the addition a dark oil separated which after 3-5 h at 20°C crystallized. The benzene solution was decanted, the crystals were quickly washed with absolute ethanol (3 × 0.5 ml), and dried in vacuum. Yield 0.15 g (52%) light crystals, deliquescing in air, mp 97-105°C (dec.), R_f 0.47 (system B), retention time on the column 9 min (system D). IR spectrum (KBr): 720 (C–Br), 770 (C–H), 1050 (C–N), 1080 (S=O), 1240 (C–O), 1280 (S=O), 1335 (C–N), 1375 (C–H), 1505, 1610 (C=C), 1720 (C=O), 2900-3050 cm^{-1} (C–H). UV spectrum (in ethanol), λ_{max} (log ε): 208 (4.32), 241 (4.16), 279 nm (3.13). PMR spectrum (D_2O): 8.0-7.2 (4H, m, arom. protons), 4.4-3.9 (8H, m, $4CH_2$), 3.7-3.5 (5H, m, CH_2, CH_3N^+), 1.3 ppm (3H, t, CH_3).

1-Methyl-1-(β-chloroethyl)-4-ethoxycarbonyl-1,2,3,4-tetrahydroquinoxalinium Perchlorate (XI, $C_{14}H_{20}Cl_2N_2O_6$). To a solution of 3.5 g (29 mmole) IX [1] in 50 ml absolute benzene were added 5.1 ml (82 mmole) methyl iodide and 108 ml (20 mmole) 0.19 N silver perchlorate in benzene. The mixture was stirred, kept for 1 day in the dark and extracted with water (6 × 5 ml). The combined aqueous extracts were decolorized with activated carbon and evaporated in vacuum. Yield 0.75 g (38%); colorless crystals with mp 143-144.5°C, R_f 0.4 (system B), retention time on the column 19 min (system C). IR spectrum (KBr): 770 (C–H), 1100 (ClO_4^-), 1250 (C–O), 1340 (C–N), 1470 (CH_2), 1500, 1610 (C=C), 1730 (C=O), 2900, 2980-3050 cm^{-1} (C–H). UV spectrum (in ethanol), λ_{max} (log ε): 208 (4.36), 240 (4.19), 278 nm (3.34). PMR spectrum (D_2O): 8.0-7.3 (4H, m, arom. protons), 4.3-4.2 (6H, m, $3CH_2$), 4.0 (2H, m, CH_2), 3.8 (2H, t, CH_2Cl), 3.7 (3H, s, CH_3N^+), 1.3 ppm (3H, t, CH_3).

1-Methylbenzo[b]-1-azonia-4-azabicyclo[2.2.2]octene Chloride Hydrochloride (XIIb, $C_{11}H_{15}ClN_2 \cdot HCl$). A solution of 0.1 g (0.26 mmole) urethane XI was hydrolyzed with heating at 127°C in 1 ml 12 M H_2SO_4 in an evacuated ampul for 45 min. The cooled mixture was poured into 11 ml water, held for 8 h at 50°C, diluted to 100 ml with water, and passed through a column with 1 g KRS-2p cation-exchange resin in the H^+ form. The resin was washed with water to pH 7, then with 10 ml ethanol. The reaction product eluted in 70 ml 6 N HCl in 50% ethanol and the solution was evaporated in vacuum. Yield 0.06 g (93%) of colorless crystals, mp 144-147°C. The product was identical to a sample obtained from 1-methylbenzo[b]-1-azonia-1-azabicyclo[2.2.2]octene iodide [6] from cation exchange under the conditions described above. R_f 0.3 (system B), retention time on the column 22 min (system C), 19 min (system D). IR spectrum (KBr): 1480, 1490 (C=C), 2000-2550 (N^+–H), 3000 cm^{-1} (C–H). UV spectrum (in ethanol), λ_{max} (log ε): 206 (3.78), 256 (2.90), 265 nm (2.70). PMR spectrum (D_2O): 7.9-7.6 (4H, m, arom. protons), 4.3-3.2 (8H, m, $4CH_2$), 3.8 ppm (3H, s, CH_3).

Method of Measurement of Cyclization and Hydrolysis Constants of I·HBr, V, and VII in Acidic Media Using Cation-Exchange Microcolumn Chromatography. A solution of VII for study of the cyclization kinetics was obtained by heating at 127°C a solution of 37 mM urethane XI in 12 M H_2SO_4 for 30 min. The cooled mixture was poured onto ice and diluted 100 times with water. The solution was passed over a column with 1 g KRS-2p cation-exchange resin in the H^+ form, the resin was washed with water to pH 7, and the hydrolysis product

was eluted with 20 ml 6 N HCl in 50% ethanol. The eluate was evaporated and the crystalline residue, consisting of VII (>80% by LC), XI, and XIIb (20%), was dried in vacuum. UV spectrum of VII, recorded in the chromatographic peak (Milichrom chromatograph, 2 N HCl in 50% aqueous ethanol), λ_{max}: 210, 250, and 300 nm (shoulder), was similar to the UV spectrum of 1-(β-bromoethyl)-1,2,3,4-tetrahydroquinoxaline [2]; retention time on the column was 28 min (system C). For study of the reaction kinetics, a 5 mM solution (0.02-0.03 ml) of I·HBr, V, or VII in the above acidic medium was sealed in microampuls and held for some time in a thermostat. During the reaction, the ampul were opened, the reaction mixture diluted 10 times with 50% ethanol for analysis with system C (VII) and with 1.5 N $HClO_4$ in 30% methanol for system D (I·HBr and V). The composition of 0.05 ml of the mixture was analyzed on a cation-exchange column with 2 mm diameter and 60 mm length. The H_0 acidity was from H_2SO_4 at various concentrations accounting for temperature dependence [7], and pH was from buffer solutions: 0.01 M $Na_2C_2O_4$ (pH 1.68) and $Na_2C_4H_4O_6$ (pH 3.68).

The reaction rate constants calculated from the chromatographic data are given in Fig. 1 and Table 1.

Method of Studying Reaction Kinetics of VI and VII in Acidic Medium Using Photometry. Solutions of VI and VII for study of cyclization reaction kinetics were obtained by heating at 127°C 37 mM solutions of urethanes X or XI in 12 M H_2SO_4 for 30 min. After cooling, 0.015 ml of the solution of VI or VII were poured into 10 ml water, thermostated at 50°C. The concentration decrease of VI or VII was observed by the decrease in optical density at 250 nm. After completion of the reaction, the mixture was analyzed on a cation-exchange microcolumn for identification of the reaction products. The retention times of VI, X, and XII are 16, 8, and 19 min (system D), respectively. The cyclization reaction rate constants calculated based on photometric data are given in Table 1.

Method of Photometric Evaluation of the Fraction of Base VII (α) in Acid–Base Equilibrium: $B + H^+ \leftrightarrow BH^+$. A solution of VII in a buffer system or H_2SO_4 with given acidity was passed through the microcuvette of the photometer on the Milichrom chromatograph and the spectral ratio $R = D_{300}/D_{270}$ was measured accounting for background absorption. The fraction was calculated based on a linear combination of the contributions to the spectral ratio of the base (r_B) and protonated form (R_{BH+}) to the value of the measured spectral ratio R at intermediate acidity values: $R = \alpha R_B + (1 - \alpha)R_{BH+}$. Thus, $R_{BH+} = 0.39$ ($H_0 = -5.9$) relative to the density of the protonated VII ($\alpha = 0$), and $R_B = 2.58$ (pH = 3.68) relative to 100% of the base VII ($\alpha = 1$).

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