2,14(13)-Dimethoxy-3,13(14)-dinitrodibenzo-18-crown-6 (IV, $C_{22}H_{26}N_2O_{12}$) (mixture of syn- and anti-isomers). Yield 6%, mp 170-175°C. IR spectrum (KBr): 2860 (C–C, 1585 (C=C), 1490 (NO_2), 1110 cm^{-1} (C–O–C). PMR spectrum (DMSO-D_6): 7.70, 7.10 (4H, s, Ph), 3.90 ppm (22H, m, CH_2O). Mass spectrum: 510 (M^+).

5,6-Dimethoxybenzofuroxan (V, $C_8H_8N_2O_4$). To 0.476 g (1 mmole) of compound VI in 200 ml of dry DMSO was added 0.324 g (6 mmole) of sodium methoxide with agitation. After 2 h the reaction mixture was diluted with water, pH 7 was reached by adding dilute hydrochloric acid, and the reaction products were extracted with chloroform. Benzofuroxan V was isolated by column chromatography on silica gel. Yield 70%, mp 150-152°C. IR spectrum (KBr): 3060 (=CH), 1620 (C=C), 1475 cm^{-1} (N–O). PMR spectrum (CD_3COCD_3): 7.08 (2H, s, =CH), 4.00 ppm (6H, s, CH_3O). Mass spectrum: 196 (M^+).

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CHIROPTICAL PROPERTIES OF THE NONPLANAR AMIDE CHROMOPHORE IN N-ACYLAZIRIDINES*

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The optically active 1-acyl-substituted (1R,2R)-2-methyl- and (1R,2S)-2-methoxycarbonylaziridines were synthesized. The nonplanarity of the amide chromophore in them and its high conformational mobility, which was caused by the rotation around the N–C(O) bond, were shown on the basis of the investigation of the CD spectra and the calculations of simple models by the MNDO method. The possible correlation of the sign of the Cotton effect of the long-wave p–π* transition with the intrinsic chirality of the chromophore was studied.

The amide rotation and the inversion of the nitrogen atom in N-acylaziridines, which are rapid in the NMR time scale, were first observed in [2]. The nonplanarity of the amide group of the N-acylaziridines was established in the solid [3] and gas [4, 5] phases. A rule on the weakening of the amide conjugation with the nitrogen atom, included in the strained three-membered ring, was formulated due to the decrease of the p-character of its unshared electron pair [3-6]; it is general for the N-acyl derivatives of aziridines [6], diaziridines [7, 8], and oxaziridines [7]. The amide conjugation with the nitrogen atom of the four-membered heterocycles is weakened less significantly [9]. The nonplanarity of the amide group is also observed in β-lactams [10], crystalline peptides [11], and the rigid bi- and tricyclic structures, which are intensively studied by chiroptical methods [10, 12, 13].

*Communication 64 in the series "Asymmetric Nitrogen," for Communication 63, see [1].

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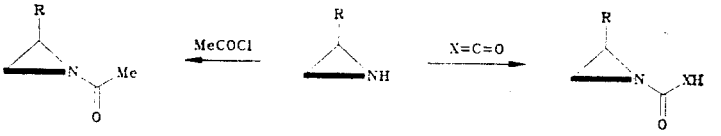
TABLE 1. CD Spectra of the N-Acyl-Substituted Aziridines (Ib,c), (IIb-e), and the Azetidine (IVb)

Compound	Solvent	T, °C	λ_{max}, nm ($[\theta]_{max}$, deg·cm²/mole)	Compound	Solvent	T, °C	λ_{max}, nm ($[\theta]_{max}$, deg·cm²/mole)
Ib	Heptane	25	247 (3460), 212 (1700)	IIc	MeOH	−42	234 (−180) 222 (80)
	MeOH	25	237 (4750), 217 sh.(2340), 195 (−18350)			−64	237 (−100), 218 (400)
	EPA*	25	241 (3110)		EPA	−54	230 (−500), 220 (−350)**
		−30	241 (4170)			−96	235 (−75), 222 (470)
		−60	240 (6320)				
		−90	240 (10280)	IId	MeOH	25	244 (−4600), 197 (7200)
Ib	Heptane	25	251 (6550), 202 (−35455)	IIe	MeOH	25	243 (3600), 198 (−19000)
	MeOH	25	243 (4630), 201 (−20938)	IVb	Heptane	25	238 (1790), 207 (−7850)
	EPA	25	249 (4870)		MeOH	25	235 (1920), 207 (−4120)
		−30	249 (5890)		EPA	−30	236 (2400)
		−60	247 (8430)			−60	236 (2690)
		−90	247 (11370)			−90	236 (3055)
IIb	Heptane	25	241 (−3900), 212 (1300), 201 (−3100)				
	MeOH	25	230 (−3300), 211 (−850)**, 200 (−4600)				

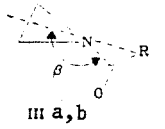
*EtOH–pentane–Et_2O, 2:5:5.
**Trough.

On the other hand, the peptides containing aziridine-2-carboxylic acid (aziline, Azy) [14], for which the N-acylaziridines are the simplest model, are being widely investigated. The known optically active N-acylaziridines [14, 15] are unsuitable for the study of the chiroptical properties of the amide chromophore itself, since the absorption bands of the amide and the aromatic chromophores overlap in their CD spectra.

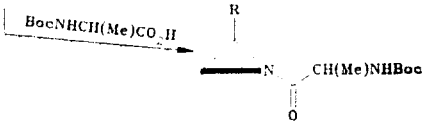
The optically active N-acylaziridines (Ib, c) and (IIb, c) were synthesized in the present work; (Ib) and (IIb) only contain the amide chromophore, and (Ic) and (IIc) simulate the aziline-containing peptides most closely.



(1*R*,2*R*)-Ib (1*R*,2*S*)-Ib (2*R*)-IIa (2*S*)-IIa (1*R*,2*R*)-Ic (1*R*,2*S*)-IIc



IIIa,b

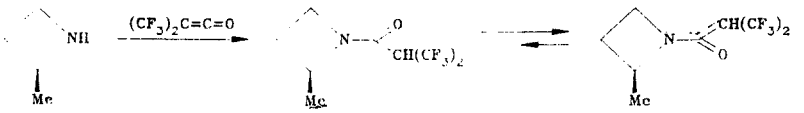


(1*R*, 2*S*, α*S*)-IId (1*R*, 2*S*, α*R*)-IIe

Ia-c, IIIb R=Me, IIa–c R=CO_2Me; IIIa R=H; Ic X=MeN, IIc X=$(CF_3)_2$C

Together with the chiroptical investigations of the compounds (Ib, c) and (IIb-e), the aziridine (Ib) and its simple analogs (IIIa, b) were calculated by the MNDO method for the clarification of features of the electronic structure and the conformational behavior of the N-acylaziridines.

Moreover, the optically active N-acylazetidine (IVb) was synthesized for the comparison with the aziridine (Ic) according to the chiroptical properties. The known planar configuration of the amide fragment in the azetidine (IVb) was confirmed by the PMR spectral data, whereby a double set of signals on account of the retarded rotation about the N–C(O) bond (the ratio of the rotamers is 1:3), which is characteristic of planar amides, is observed.



(2S)-IVa (2S)-IVb

In the CD spectra of the N-acylaziridines (Ib,c) (Table 1), the intense bands of the dichroic absorption around 250 and 200 nm are determined by the p—π* and π—π* transitions [16] correspondingly. The correctness of the assignment of the longwave band to the p—π* transition is confirmed by its hypsochromic shift when the nonpolar aprotic solvent – heptane – is substituted by methanol. The comparatively small Cotton effect observed in the spectrum of the aziridine (Ib) at 212-217 nm may be assigned either to the Rydberg p-3S [5] or to the p—π* transition with the second occupied MO, which is mainly the uncombined orbital of the O atom according to the calculations of the aziridines (Ib) and (IIIa,b) (Fig. 1). As in the case of the bi- and tricyclic amides [10, 13], the signs of the Cotton effect π—π* and π—p* transitions are opposite for the aziridines (Ib,c) (Table 1). The bathochromic shift of the band of the p—π* transition is considered to be one of the most significant phenomenological criteria for the nonplanarity of the amide chromophore [13]. Such a shift is well noted in the comparison of the maxima of the longwave Cotton effects of the N-hexafluoroisobutyryl derivatives – the nonplanar aziridine (Ic) and the planar azetidine (IVb) (Table 1). According to the indicated criterion, the N-acylaziridines (Ib,c) contain the most nonplanar of the known amide chromophores [10, 12, 13]. In fact, the experimental [5] and the calculated values of the angle of the β-slope of the N—C(O) bond relative to the plane of the aziridine ring of (Ib) and (IIIa,b) (Table 2) indicate the high pyramidal character of the N atom, whereas the N atom is significantly depressed in the majority of the other nonplanar amides; their nonplanarity is mainly guaranteed by the rotation around the N—C(O) bond.

The strong bathochromic shift of the band of the p—π* transition of the aziridines (Ib, c) permits the proposition of the significant "carbonyl" character of the amide chromophore in the N-acylaziridines. However, according to the calculation, the main contribution to the HOMO is introduced by the noncombining orbital of the N atom (Fig. 1) and not by the O atom as in the isolated C=O group. Consequently, the possible application of the rule of octants, relating the sign of the p—π* transition of the Cotton effect with the stereochemistry of the environment of the carbonyl group, to this chromophore is excluded [17].

The dependence of the p—π* transition of the Cotton effect on the temperature indicates the conformational mobility of the amide chromophore in the aziridines (Ib,c) on account of the rotation around the N—C(O) bond (Table 1; Fig. 2). A similar dependence is also observed in the case of the planar amide (IVb). However, it is less marked (Table 1), and is evidently determined by the conversion of the azetidine ring:

The barrier to the rotation about the N—C(O) bond in the N-acylaziridines is not successfully measured experimentally [6]. Therefore, we calculated the functions of the potential energy of the N-acylaziridines (Ib) and (IIIa,b) from the dihedral angle φ between the C=O bond and the bisector of the ring CNC bond angle (Table 2; Fig. 3). These functions were obtained in steps of 10° and by the optimization of the geometry at each point of calculation. The calculated geometrical parameters of the rotamer B(D) of the N-acetylaziridine (IIIb) having the greatest occupancy are close to the experimental ones [4, 5] taking into account the systematic shortening of the bonds in the MNDO method (Table 2). In all cases, the rotamers B and D have the occupancy with the maximal overlapping of the p-orbital of the N atom and the π*-orbital of the C=O group.

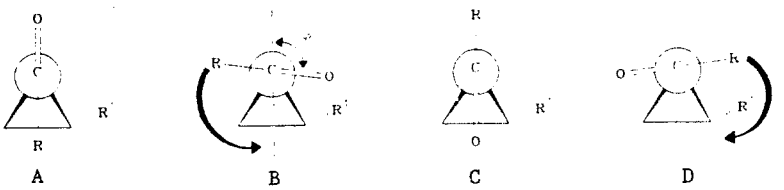


TABLE 2. Calculated Geometrical and Energy Parameters* of the N-Acylaziridines (Ib) and (IIIa,b)

Compound	Rotamer	φ°	β°	r, Å				Energy of the MOs, eV				H_f, kcal/mole	Relative energy, kcal/mole
				CO	N–C(O)	CN	CC	π* (LUMO)	P_N (HOMO)	P_O	π		
Ib	A	0	134,2	1,222	1,450	1,478	1,525	0,59	−10,28	−11,17	−12,56	−14,3	7,4
Ib	B	110	136,5	1,225	1,429	1,475	1,528	0,78	−10,44	−11,06	−13,51	−21,7	0
Ib	C	180	131,8	1,224	1,447	1,484	1,520	0,52	−10,54	−11,13	−12,60	−20,1	1,6
Ib	D	250	136,9	1,226	1,429	1,473	1,529	0,76	−10,42	−11,07	−13,47	−21,6	0,1
IIIa	A	0	128,6	1,216	1,446	1,481	1,513	0,64	−10,44	−11,51	−12,93	−0,5	5,5
IIIa	B	100	137,5	1,222	1,420	1,471	1,522	0,92	−10,49	−11,26	−14,24	−6,0	0
IIIa	C	180	132,2	1,220	1,440	1,484	1,512	0,59	−10,60	−11,36	−12,92	−3,4	2,6
IIIb	A	0	134,1	1,222	1,450	1,477	1,515	0,59	−10,26	−11,29	−12,71	−6,4	7,4
IIIb**	B	110 (118,5)	137,1 (118,0)	1,226 (1,226)	1,428 (1,447)	1,473 (1,485)	1,520 (1,485)	0,78	−10,42	−11,16	−13,05	−13,8	0
IIIb	C	180	132,0	1,224	1,447	1,483	1,512	0,52	−10,53	−11,25	−12,76	−12,1	1,6

*The torsion angle is given by φ. The angle of slope of the N–C bond with the plane of the ring is given by β. The heat of formation is given by H_f.

**The experimental data are presented in brackets for the rotamer B [5].

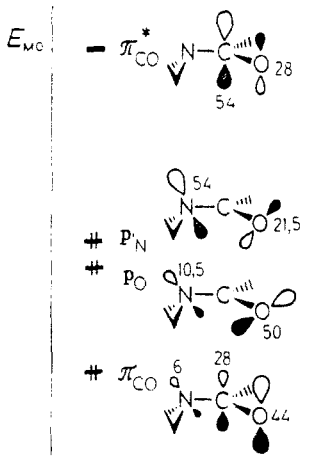


Fig. 1

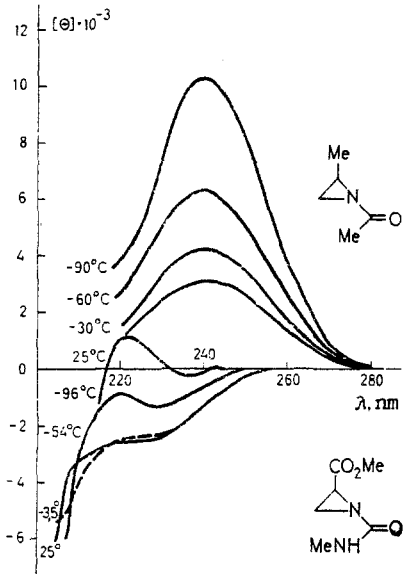


Fig. 2

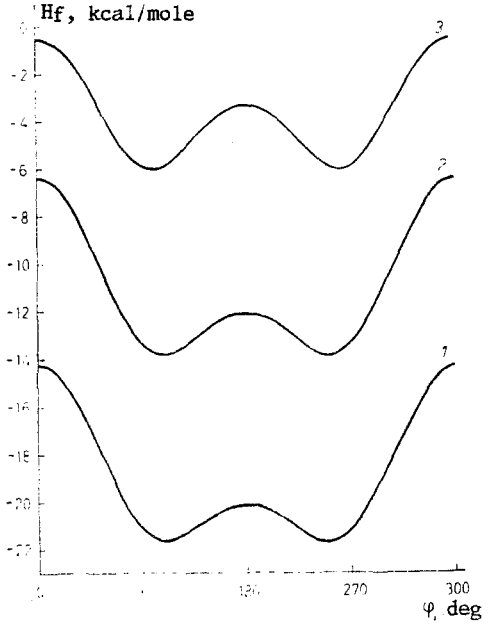


Fig. 3

Fig. 1. The MOs of N-formylaziridine (IIIa) (rotamer B) participating in the optically active transitions, and the partial occupancy of these MOs in %.

Fig. 2. The dependence of the CD spectra of the aziridines (Ib) and (IIc) on the temperature (EtOH–pentane–Et_2O, 2:5:5).

Fig. 3. Profiles of the potential energy of the rotation about the N–C(O) bond of N-acylaziridines: 1) (Ib); 2) (IIIa); 3) (IIIb).

The barriers to the rotation obtained as the difference in the energies of the restrained (B, D) and shielded (A, C) rotamers (Table 2) are of the same order as those calculated by the INDO method on the basis of the experimental geometry [5]. This indicates the ready interconversion of the rotamers B and D, which have opposite internal chirality, via the internal achiral rotamer C. In the case of the N-carbamoyl derivative (IIc), a still lower barrier to the rotation about the N_{cycl}–C(O) bond should be expected due to the weakening of the p–π conjugation by the concurrent interaction of the C=O group with the stronger donor – the MeNH group. The dependence of the longwave Cotton effect on the temperature (Table 1; Fig. 2) is observed for this compound, as in the case of (Ib,c), in the CD spectra.

The difference in the energy values of the most favorable rotamers B and D in the unsymmetrical aziridine (Ib) is close to the error in the method of calculation (Table 2). However, the high occupancy of the right-spiral rotamer D can be assumed; the positive Cotton effect of the p–π* transition and the negative Cotton effect of the π–π* transition should

be observed for it according to the data of the calculation of the rotational force of the simplest models of the nonplanar amide chromophore [18].

The positive Cotton effect of the p—π* transition should also be expected for the N-acylaziridines (IIb,c) on the basis of the rule of the spirality of the nonplanar amide chromophore [13, 18]. However, the CD spectra of (IIb,c) show a negative Cotton effect in the region of 240 nm (Fig. 2; Table 1); this may be caused either by the increase in the stability of the left-spiral rotamer B [in contrast to the aziridine (Ib)] or by the anomalous contribution of the MeO_2C group to the Cotton effect [19]. It is also impossible to exclude completely the possible superposition of the dichroic absorption bands associated with transitions in the MeO_2C group [20]. However, the aziridine (IIb) has a value of the longwave Cotton effect which is close to that of (Ib), which is 1-2 orders of magnitude higher than in the case of the N-acyl-α-aminoacid esters [20]. It can be seen that the comparatively high amplitude of the Cotton effect of the p—π* transition in the N-acyl-aziridines is associated with the induced intrinsic chirality of the amide chromophore. This is observed especially clearly in the comparison of the values of longwave Cotton effects of the aziridine (Ic) and the azetidine (IVb), which contain the identical chromophore. In the first case, the chromophore is nonplanar and, consequently, intrinsically chiral; in the second case, it is planar and achiral.

A significant asymmetric perturbation of the nonplanar amide chromophore by the alanine residue is observed for the dipeptides (IId,e) (Table 1); the signs of both Cotton effects (the longwave and the shortwave) are the same as in the case of the α-aminoacid esters of the corresponding configuration [20], but the CD spectra do not mirror each other. The last effect is evidently caused by the influence of chiral center at $C_{(2)}$ of the aziridine ring on the relative occupancy of the rotamers B and D. This influence is thereby the same as in the case of the aziridines (IIb,c) judging from the decrease in the intensity of the longwave band of the dichroic absorption and the increase of the shortwave band for the (1R,2S, αR)-dipeptide (IIe) by comparison with (1R,2S,αS)-(IId).

Therefore, the high pyramidality of the N atom and the free rotation about the N—C(O) bond in the optically active N-acylaziridines determine the strong bathochromic shift and the dependence of the intensity of the dichroic absorption band, due to the p—π* transition, on the temperature. The presence of the MeO_2C functional group in the α-position of the substituent at the N atom leads to the inversion of the sign of the Cotton effect of this transition. The signs of the Cotton effects of the p—π* and π—π* transitions in the dipeptides of the type Me—Azy—Ala—Boc are mainly determined by the configuration of the alanine fragment.

EXPERIMENTAL

The CD spectra were measured on the JASCO J-500A (with the DP-500N processor) and Jobin—Ivon Dichrograph III instruments. The angles of optical rotation were measured on the Perkin—Elmer 141 and Polamat A polarimeters. The PMR spectra were measured on the Bruker WM-400 and Bruker WH-90/DS spectrometers relative to TMS. The data of the elemental analysis of the compounds (IIe,d) for C, H, and N correspond with the calculated data.

(1R,2R)-1-Acetyl-2-methylaziridine (Ib). To the solution of 0.38 g (6.7 mmoles) of the aziridine (IIa) [21] and 0.67 g (6.9 mmoles) of Et_3N in 5 ml of absolute hexane is added, dropwise with cooling (—5°C) and stirring, the solution of 0.52 g (6.4 mmoles) of acetyl chloride in 5 ml of absolute hexane. After maintaining the mixture for 12 h at 10°C, the residue is filtered off; the filtrate is concentrated in vacuo, and the residue is distilled. The yield of 0.3 g (45%) of (1R,2R)-N-acetylaziridine (Ib) is obtained; it has the bp 48°C (20 mm of Hg stem) and the $[\alpha]_D^{20}$ −54.7° (c = 1; MeOH). According to the data of [22], bp 47.5-48°C (20 mm of Hg stem). The PMR spectrum (400 MHz, $CDCl_3$) is as follows: 1.3 ppm (3H, d, ^3J = 5.5 Hz, Me), 1.92 ppm (1H, d, $^3J_{AC}$ = 3.5 Hz, H_C), 2.12 ppm (3H, s, MeCO), 2.31 ppm (1H, d, $^3J_{AB}$ = 6.0 Hz, H_B), and 2.48 ppm (1H, m, H_A).

(1R,2R)-1-Hexafluoroisobutyryl-2-methylaziridine (Ic). To the solution of 1.6 g (9.0 mmoles) of bis(trifluoromethyl)ketene in 10 ml of absolute ether is added, dropwise with cooling (—70°C) and stirring, the solution of 0.2 g (3.5 mmoles) of the aziridine (Ia) in 5 ml of absolute ether. After maintaining the mixture for 2 h at 20°C, the solvent is evaporated in vacuo, and the residue is distilled. The yield of 0.48 g (59%) of the N-acyl-aziridine (Ic) is obtained; it has bp 56-58°C (12 mm of Hg stem) and the $[\alpha]_D^{20}$ −35.6° (c = 1.8, heptane). According to the data of [22, 23], the bp is 35°C (2 mm of Hg stem), and the $[M]_D^{20}$ is −1820 (c = 1, nonane). The PMR spectrum (400 MHz, $CDCl_3$) is as follows: 1.38 ppm

(3H, d, ^3J = 5.4 Hz, Me), 2.15 ppm (1H, d, $^3J_{AC}$ = 3.9 Hz, H_C), 2.60 ppm (1H, d, $^3J_{AB}$ = 5.7 Hz, H_B), 2.78 ppm (1H, m, H_A), and 3.99 ppm (1H, septet, $^3J_{HF}$ = 7.6 Hz, α-H).

(1R,2S)-1-Acetyl-2-carbomethoxyaziridine (IIb). To the solution of 0.2 g (2 mmoles) of the aziridine (IIa) [24] and 0.2 g (2 mmoles) of Et_3N in 15 ml of absolute $CHCl_3$ is added, with cooling (−10°C) and stirring, the solution of 0.16 g (2 mmoles) of acetyl chloride in 5 ml of absolute $CHCl_3$. The reaction mixture is maintained for 1 h at −10°C prior to washing it with water, drying it with Na_2SO_4, and evaporation in vacuo. The yield of 0.23 g (80%) of the N-acetylaziridine (IIb) is obtained; it has the $[\alpha]_D^{20}$ −25.6 (c = 0.96, EtOH). The PMR spectrum (90 MHz, $CDCl_3$) is as follows: 2.16 ppm (3H, s, MeCO), 2.52 ppm (1H, dd, $^3J_{AB}$ = 5.6 Hz, $^2J_{BC}$ = 1.6 Hz, H_B), 2.58 ppm (1H, dd, $^3J_{AC}$ = 3.4 Hz, Hc), 3.17 ppm (1H, dd, H_A), and 3.80 ppm (3H, s, MeO).

(1R,2S)-1-Methylcarbamoyl-2-methoxycarbonylaziridine (IIc). The solution of 0.2 g (2 mmoles) of the aziridine (IIa) and 0.14 g (2.5 mmoles) of methyl isocyanate in 10 ml of absolute $CHCl_3$ is maintained for 2 h at 20°C prior to the concentration in vacuo. The yield of 0.28 g (86%) of the aziridine (IIc) is obtained; it has the $[\alpha]_D^{20}$ −105.1° (c = 1.4, EtOH). The PMR spectrum (90 MHz, $CDCl_3$) is as follows: 2.36 ppm (1H, dd, $^3J_{AC}$ = 3.6 Hz, $^2J_{BC}$ = 1.4 Hz, HC), 2.52 ppm (1H, dd, $^3J_{AB}$ = 6.9 Hz), 2.82 ppm (3H, d, ^3J = 4.8 Hz, MeN), 3.10 ppm (1H, dd, H_A), 3.77 ppm (3H, s, MeO), and 5.67 ppm (1H, broad s, NH).

The Methyl Ester of Boc-S-alanyl-S-Aziline (IId) ($C_{12}H_{20}N_2O_5$). To the solution of 0.2 g (2 mmoles) of the aziridine (IIa) and 0.38 g (2 mmoles) of Boc-S-alanine in 20 ml of absolute $CHCl_3$ is added, with cooling (0°C), the solution of 0.45 g (2.2 mmoles) of dicyclohexylcarbodiimide in 5 ml of absolute $CHCl_3$. The mixture is held for 10 h at 0°C; the residue is filtered off. The filtrate is washed with a 0.1 N solution of $NaHCO_3$, a 0.1 M solution of citric acid, and water prior to the drying with Na_2SO_4. After removal of the solvent, the yield of 0.44 g (87%) of the dipeptide (IId) is obtained; it has the $[\alpha]_D^{20}$ −29.7 (c = 0.7, EtOH). The PMR spectrum (90 MHz, $CDCl_3$) is as follows: 1.42 ppm (9H, s, Me_3C), 1.47 ppm (3H, d, MeC), 2.62 ppm (1H, dd, $^3J_{AC}$ = 3.2 Hz, $^2J_{BC}$ = 1.7 Hz, H_C), 2.72 ppm (1H, dd, $^3J_{AB}$ = 5.4 Hz, H_B), 3.24 ppm (1H, dd, H_A), 3.78 ppm (3H, s, MeO), 4.29 ppm (1H, q, ^3J = 7.0 Hz, α-H), and 5.22 ppm (1H, broad s, NH).

The Methyl Ester of Boc-R-alanyl-S-aziline (IIe) ($C_{12}H_{20}N_2O_5$). This is obtained by the preceding method from Boc-R-alanine; yield 84%; the $[\alpha]_D^{20}$ is −64.8° (c = 0.1; EtOH). The PMR spectrum (90 MHz, $CDCl_3$) is as follows: 1.40 ppm (9H, s, Me_3C), 1.50 ppm (3H, d, MeC), 2.57 ppm (1H, dd, $^3J_{AC}$ = 3.0 Hz, $^2J_{BC}$ = 0.8 Hz, H_C), 2.63 ppm (1H, dd, $^3J_{AB}$ = 6.1 Hz, H_B), 3.3 ppm (1H, dd, H_A), 3.79 ppm (3H, s, MeO), 4.31 ppm (1H, m, ^3J = 6.9 Hz, α-H), and 4.8 ppm (1H, broad s, NH).

(2S)-1-Hexafluoroisobutyryl-2-methylazetidine (IVb). This is obtained according to the method of the synthesis of the aziridine (Ic) from the azetidine (IVa) [21] with the yield of 57%; it has mp 107-108°C (from hexane) and $[\alpha]_D^{20}$ +45.7° (c = 1; MeOH). According to the data of [22], mp 66-68°C. PMR spectrum (400 MHz, $CDCl_3$) is as follows: the predominant rotamer −1.51 ppm (3H, d, ^3J = 6.3 Hz, MeC), 1.91 ppm (1H, m, ^2J = 11.6, $^3J_{2a3e}$ = 6.0 Hz, 3-H_e), 2.50 ppm (1H, m, $^3J_{3a4a}$ = 9.5, $^3J_{3a4e}$ = 6.0 Hz, 3-H_a), 3.69 ppm (1H, sept., $^3J_{HF}$ = 7.1 Hz, α-H), 4.21 ppm (2H, m, ^2J = 8.3 Hz, 4-H), and 4.58 ppm (1H, m, 2-H), and the minor rotamer −1.55 ppm (3H, d, ^3J = 6.3 Hz, MeC), 1.94 ppm (1H, m, ^2J = 11.6 Hz, 3-H_e), 2.57 ppm (1H, m, $^3J_{2a3a}$ = 8.7 Hz, $^3J_{3a4a}$ = 8.4 Hz, $^3J_{3a4e}$ = 5.7 Hz, 3-H_a), 3.66 ppm (1H, sept., $^3J_{HF}$ = 7.1 Hz, α-H), 4.10 ppm (2H, t, 4-H), and 4.60 ppm (1H, m, 2-H).

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PYRROLES FROM KETOXIMES AND ACETYLENE.

38.* NEW REPRESENTATIVES OF TRIFLUOROACETYLPYRROLES. SYNTHESIS AND TRANSFORMATIONS

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A series of previously unknown trifluoroacetyl derivatives of pyrroles were obtained with high yields by the reaction of pyrroles, including N-vinyl-substituted pyrroles, with trifluoroacetic anhydride in the presence of pyridine at room temperature. The solvent and the substituents at the α and β positions of the pyrrole ring do not affect the direction of electrophilic substitution.

It is known [2-12] that the trifluoroacetylation of compounds of the pyrrole series leads to α- or β-substitution products, depending on the structure and on the reaction conditions. While continuing an investigation into this reaction in the series of substituted pyrroles we attempted to determine the effects of substituents in the pyrrole ring and the effect of the medium on the direction of attack by the trifluoroacetyl cation and on the yield of the final products.

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