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OPTICALLY ACTIVE 1-ALKOXY-2,2-BIS(TRIFLUOROMETHYL)AZIRIDINES*

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1-Alkoxy-2,2-bis(trifluoromethyl)aziridines containing an ester group in the α position of the alkoxy substituent undergo nucleophilic substitution (ammonolysis and hydrolysis) with retention of the aziridine ring. The corresponding carboxylic acids, which were separated to give the antipodes with an optical purity of 95% through the diastereomeric salts with R- and S-α-phenylethylamine, were obtained.

The configuration stability of 1-hydroxy-2,2-bis(trifluoromethyl)aziridine derivatives is sufficient for their existence in the optically active form under ordinary conditions ($\Delta G^{\neq}$ = 30 kcal/mole) [2]. However, their antipodes have not yet been isolated. Attempts to obtain their enantiomerically enriched arylsulfonates by partial asymmetric destruction by the action of an optically active amine [2, 3] and also by crystallization from optically active solvents [l-methyl lactate and (−)-α-pinene] were unsuccessful. Attempts at separation through the diastereomeric carbonates, which are formed in a ratio of 1:1 and are not separated by crystallization from alcohol (the l-methyl derivatives) and chromatography on silica gel (the l-methyl lactate derivatives), also did not give the desired results [2]. This can be explained by the considerable remoteness of the asymmetric centers (four bonds). In fact, when the latter are close together (up to two bonds) as in O-[2,2-bis(trifluoromethyl)-1-aziridino]lactamides, the racemic diastereomers are separated completely by one crystallization from benzene [1].

*Communication 22 in the series "Asymmetric Unbridged Nitrogen." See [1] for Communication 21.

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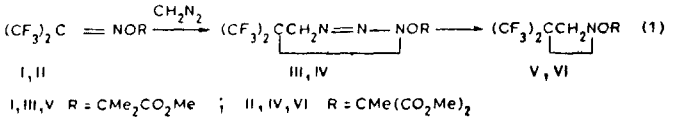
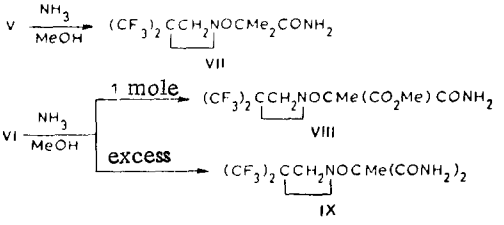
In this connection we investigated 1-alkoxy-2,2-bis(trifluoromethyl)aziridines containing an ester group in the α position of the alkoxy substituent and accomplished their separation into antipodes via the scheme developed for 1-alkoxyaziridine-2,2-dicarboxylic acid esters [4].

We have previously shown that hexafluoroacetone oxime derivatives $(CF_3)_2C{=}NOX$ (where X = $ArSO_2$, ArCO, and ROCO) readily add diazomethane to give triazolines, which undergo decomposition to give the corresponding aziridienes. Mesomerically positive substituents (X = Me_2N and MeO) prevent the reaction, since by decreasing the polarization of the C=N bond $[(CF_3)_2C{=}N{-}X \leftrightarrow (CF_3)_2C^-{-}N{=}X^+]$ they hinder nucleophilic attack of diazomethane. The introduction of electronegative substituents in the alkoxy group [X = CF_3CFHCF_2O and $(CF_3)_3CO$] again leads to a facile reaction with diazomethane [2]. It was later found that one electronegative α substituent [X = $PhCH_2O$, EtO_2CCH_2O, and $RO_2CCH(Me)O$] is sufficient for this [1].

In conformity with the material presented above, we synthesized and studied new aziridines (V and VI):

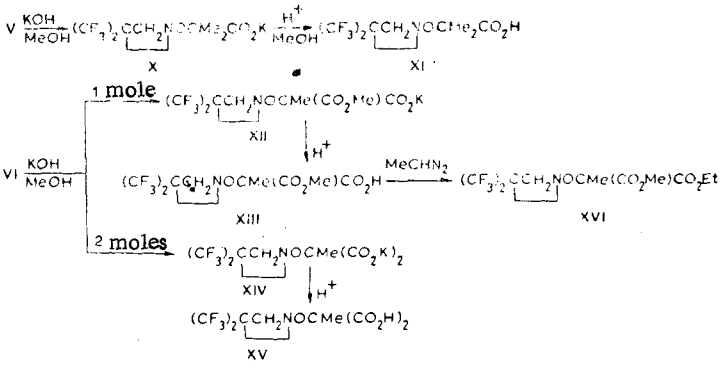


The ester groups in esters V and VI readily undergo ammonolysis:



Monoamide VIII is produced in the form of a mixture of diastereomers (in a ratio of ∿ 3:2 according to the PMR spectrum, Table 1), which differ markedly with respect to their solubilities in hydrocarbons. Pure diastereomer VIIIa is isolated readily by washing a mixture of amides VIII with hexane. However, enantiomeric enrichment of diamides IX is not observed in the case of three crystallizations from l-methyl lactate.

The ester groups in esters V and VI are hydrolyzed by alcoholic alkali at 20°C. Treatment of the resulting salts with a cation-exchange resin (H^+) gives the stable acids (acid XIII remains unchanged after heating at 100°C in CCl_4 for 30 min):



Monoesters XII and XIII are produced in the form of a mixture of diastereomers; XIII is obtained as an oil that crystallizes upon cooling and contains the diastereomers in a ratio of 3:2 (according to the PMR spectrum). Predominant diastereomer XIIIa was isolated

TABLE 1. ^1H and ^{19}F NMR Spectra of Aziridines

Compound	Solvent	δ, ppm				J, Hz			δ, ppm		J, Hz
		Me	MeO	H_A	H_B	H_AH_B	B-CF_3H_A	A-CF_3H_B	A-CF_3	B-CF_3	CF_3CF_3
V	CCl_4	1,3 1,45	3,63	2,43	2,81	−3,7	2,4	1,0	−8,62	−16,38	7,5
VI	CCl_4	1,58	3,78	2,53	2,95	−4,5	3,0	1,0	−7,8	−16,3	7,5
VI	Ph_2O	1,55	3,4 3,45[a]	2,25	2,72	−4,7	2,5	1,0	—	—	—
VII	$CDCl_3$	1,42 1,45	—	2,52	2,78	−3,5	2,3	1,0	−8,83	−16,75	
VIII	CD_3OD	1,68 1,63[b]	3,68 3,73[b]	2,75	c	−3,7	2,5		−6,8 −6,96	−14,69 −14,85	7,5
VIII a	CD_3OD	1,68	3,68	2,75	c	−3,7	2,5				
IX	C_2D_5OD	1,66	—	2,75	3,38	−4,7	2,5	1,0	−7,47	−15,51	7,5
X	D_2O	1,66	—	2,95	3,25	−5,0	3,0	1,0	−9,1	−16,84	8,2
XI[d]	CCl_4	1,38 1,54	—	2,5	2,85	−4,0	2,5	1,0	−8,67	−16,38	7,5
XII	D_2O	1,94 2,0[c]	4,08 4,03[c]	3,00	3,41	−5,0	2,5	1,0	−7,97 −8,24	−16,16 −16,29	8,2
XIII	C_6H_6	1,5 1,6[b]	3,38 3,30[b]	1,99	2,53	−5,0	2,5	1,0	−7,5 −7,54	−15,17	8,0
XIII a	C_6H_6	1,5	3,38	1,99	2,53	−5,0	2,5	1,0	−7,5	−15,17	8,0
XIV	D_2O	1,84	—	3,0	3,35	−5,0	2,5	1,0	—	—	—
XV	CD_3OD	1,3	—	2,66	3,05	−5,0	2,5	1,0	−7,23	−15,05	7,5
XVI f	C_6H_6	1,55	3,30 3,24[g]	1,94	2,46	−4,5	2,3	0,5	−8,08 −8,16	−15,89 −15,97	7,05
XVIa[h]	C_6H_6	1,55	3,30	1,94	2,46	−4,5	2,3	0,5	−8,08	−15,89	7,05
XVIIa XVIIb	CD_3OD [i]	1,2	—	2,48	3,00	−4,0	2,5	1,0	−8,03	−15,95	8,5

[a]The signals do not merge in the case of heating, at 200°C, $\Delta\nu$ = 1.2 Hz. [b]This is the signal of the second diastereomer, the ratio is ∿ 1.5. [c]Covered by the signals of the solvent. [d]12.16 ppm (OH). [e]These are the signals of the second diastereomer, the ratio is ∿ 1.8. [f]EtO: 0.81 (CH_3) and 3.84 (CH_2), J = 7.0 Hz, EtO (for only the second diastereomer): 0.85 (Me) and 3.88 (CH_2), j = 7.0 Hz. [g]This is the signal of the second diastereomer. [h]EtO: 0.81 (CH_3) and 3.84 (CH_2), J = 7.0 Hz. [i]1.54 and 1.62 (Me—CH), 4.38 (CH—Me, J = 8.0 Hz), and 7.37 ppm (Ph, m).

TABLE 2. Activation Parameters for the Inversion of 1-Alkoxyaziridines[a]

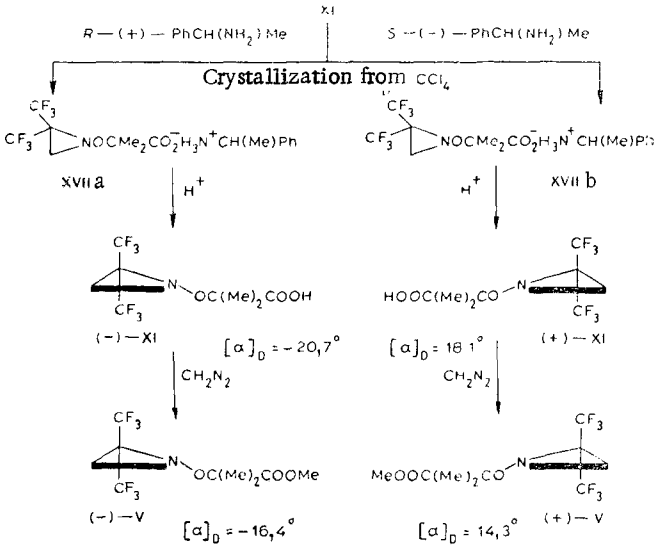
Compound	Solvent	Temp., °C	Observed group	Percentages of the diastereomers		$\vec{k}_{inv} \cdot 10^5$ ($\overleftarrow{k}_{inv} \cdot 10^{-5}$) c^{-1} (at 100°)	$\overleftarrow{\Delta G_{25}^{\neq}}$ ($\vec{\Delta G_{25}^{\neq}}$), kcal/mole	$\vec{\tau}_{1/2}$, yr (25°)
				initial	equilibrium			
(+)-V	CCl_4	100	—	—	—	3,02±0,96	29,83±0,23	10,8
VIIIa	CD_3OD	100	MeO	100/0	43/57	3,71±0,23 (2,77±0,17)	29,7±0,4 (29,9±0,6)	12,4
XVIa	C_6H_6	100	MeC	100/0	50/50	2,97±0,17	29,84±0,05	14,4

[a]From the kinetics of racemization of (+)-V on the basis of the $[\alpha]^{20}_{365}$ values and epimerization of the diastereomerically pure VIIIa and XVIa according to PMR spectroscopy. The calculations were made as in [1].

in pure form by crystallization from pentane. Esterification of monoester XIII with diazomethane gives mixed ester XVI with the same ratio of diastereomers, while diastereomerically pure ester XVIa is obtained from XIIIa in this case.

The observed stability of aziridinecarboxylic acids XI, XIII, and XV enabled us in the case of XI to realize the separation of 1-alkoxyaziridines into their antipodes through diastereomeric salts XVIIa and XVIIb with R- and S-α-phenylethylamine. The salts were crystal-

lized from CCl_4 until they had constant melting points the diastereomers did not differ with respect to their PMR spectra in [CD_3OD and $(CD_3)_2CO$]. Optically active acids (+)-XI and (−)-XI were isolated by the action of a cation-exchange resin (H^+), while optically active esters (+)-V and (−)-V were isolated by treatment with diazomethane:



The optical purity, which was found to be ∿ 95%, was determined for (−)-V by NMR spectroscopy with the application of the optically active shift reagent $Eu(tfc)_3$; the optical purity of (+)-V is consequently ∿83%. Optically active samples of (+)-V and (−)-V undergo complete racemization when they are heated (for 16 h at 100°C). According to PMR spectroscopy, the products isolated from solution after heating did not differ from the starting compounds.

The results of a study of the configurational stability of the 1-alkoxyaziridines obtained are presented in Table 2. A comparison with similar derivatives that contain a less bulky N-alkoxy substituent, viz., $(CF_3)_2CCH_2NOCH(Me)COX$ (X = OR, NH_2) shows that in our case the inversion barriers are increased significantly (by 0.7-1.7 kcal/mole). This completely unexpected fact (see [5]) will be investigated more thoroughly. It can be explained by the fact that in the case of sufficiently bulky substituents the inversion transition state is destabilized, since only a conformation with an eclipsed orientation of the unshared electron pairs of the N and O atoms is realized because of steric restrictions in it.

EXPERIMENTAL

The spectra were measured with JNM-C 60-HL and Tesla BS-487c spectrometers. The optical rotation was measured with a Perkin-Elmer 141 polarimeter.

Hexafluoroacetone oxime was synthesized by the method in [6] from α-hydrohexafluoroisobutyric acid and nitrosyl chloride, which was obtained from alkyl nitrites and $SiCl_4$ [7].

Hexafluoroacetone N-(2-Methoxycarbonyl-2-propoxy)imine (I). A 9.05-g (50 mmole) sample of hexafluoroacetone oxime and 9.05 g (50 mmole) of methyl α-bromoisobutyrate were added at 20°C to 7.0 g (50 mmole) of potassium carbonate in 30 ml of acetonitrile. After 2 days, the precipitate was removed by filtration, the solvent was evaporated, and the residue was distilled to give 7.14 g (70%) of imine I with bp 57°C (35 mm) and n_D^{20} 1.3518.

Hexafluoroacetone N-[1,1-Bis(methoxycarbonyl)ethoxy]imine (II). This compound was similarly obtained from hexafluoroacetone oxime and dimethyl methylbromomalonate. Workup gave a product with bp 49-50°C (2 mm) and n_D^{20} 1.3738 in 68% yield. Found: C 33.3; H 2.8; N 4.2%. $C_9H_9F_6NO_5$. Calculated: C 33.2; H 2.8; N 4.3%.

1-(2-Methoxycarbonyl-2-propoxy)-5,5-bis(trifluoromethyl)-Δ^2-1,2,3-triazoline (III). A 7.0-g sample of imine I was treated at 20°C with excess diazomethane in ether. The mixture was evaporated after 48 h to give 7.0 g (88%) of triazoline III. NMR spectra (CCl_4), δ: ^1H: 1.52 (Me), 3.65 (MeO), and 4.68 (CH_2), ^{19}F: −8.5 ppm [s, $(CF_3)_2$].

1-[1,1-Bis(methoxycarbonyl)ethoxy]-5,5-bis(trifluoromethyl)-Δ^2-1,2,3-triazoline (IV). This compound, with mp 71°C (from heptane), was similarly obtained in 71% yield. NMR spectra, δ: ^{1}H: 1.75 (Me), 3.75 (MeO), and 4.74 (CH_2), ^{19}F: −8.93 ppm [s, $(CH_3)_2$]. Found: C 32.8; H 2.8; N 11.3%. $C_{10}H_{11}F_6N_3O_5$. Calculated: C 32.7; H 3.0; N 11.4%.

1-(2-Methoxycarbonyl-2-propoxy)-2,2-bis(trifluoromethyl)aziridine (V). A solution of 6 g of triazoline III in 30 ml of CCl_4 was refluxed and subjected to UV irradiation (with a 250-W mercury lamp) for 1 h. The degree of conversion was monitored by PMR spectroscopy. Evaporation gave 4 g (55%) of aziridine V with bp 73°C (22 mm) and n_D^{20} 1.3665. Found: C 36.7, H 3.8, N 4.7%. $C_9H_{11}F_6NO_3$. Calculated: C 36.6, H 3.8, N 4.7%.

1-[1,1-Bis(methoxycarbonyl)ethoxy]-2,2-bis(trifluoromethyl) aziridine (VI). This compound, with bp 74-75°C (1 mm) and n_D^{20} 1.3852, was similarly obtained in 76% yield. Found: C 35.2; H 3.1; N 4.1%. $C_{10}H_{11}F_6NO_5$. Calculated: C 35.4; H 3.3; N 4.1%.

1-(2-Carbamoyl-2-propoxy)-2,2-bis(trifluoromethyl)aziridine (VII). A mixture of 0.15 g (0.5 mmole) of aziridine V and 0.17 g (10 mmole) of ammonia in 2 ml of absolute methanol containing a catalytic amount of sodium methoxide was maintained at 20°C in a sealed ampul for 2 days. Evaporation yielded 0.12 g (84%) of aziridine VII with mp 111°C (from hexane). Found: C 34.2; H 3.7; N 10.2%. $C_8H_{10}F_6N_2O_2$. Calculated: C 34.4; H 3.6; N 10.0%.

1-(C-Carbamoyl-1-methoxycarbonylethoxy)-2,2-bis(trifluoromethyl)aziridine (VIII and VIIIa). A mixture of 3.4 g (0.01 mole) of aziridine VI and 0.17 g (0.01 mole) of ammonia in 5 ml of absolute methanol containing a catalytic amount of sodium methoxide was maintained at 20°C in a sealed ampul for 2 days. Evaporation yielded 1.7 g (52%) of aziridine VIII with mp 110-130°C, according to the PMR spectra, the product was a mixture of diastereomers in a ratio of 3:2. Pure diastereomer VIIIa (in 30% yield), with mp 128-130°C, remained after washing with hexane. Found: N 8.8%. $C_9H_{10}F_6N_2O_4$. Calculated: N 8.6%.

1-(1,1-Dicarbamoylethoxy)-2,2-bis(trifluoromethyl)aziridine (IX). This compound, with mp 175-177°C (from ethanol), was obtained in 70% yield by a method similar to that used to obtain VII. Found: C 31.3; H 3.1; N 13.6%. $C_8H_9F_6N_3O_3$. Calculated: C31.1; H 2.9; N 13.6%.

1-(2-Carboxy-2-propoxy)-2,2-bis(trifluoromethyl)aziridine (XI). A mixture of 4.2 g (14 mmole) of aziridine V and 0.9 g (16 mmole) of KOH in 40 ml of absolute methanol was maintained at 20°C for 2 days. Evaporation of the mixture yielded 3.8 g (80%) of hygroscopic potassium salt X, which, after azeotropic drying with benzene, began to carbonize at 230°C. A solution of 3.8 g of salt X in 30 ml of methanol was treated with 8 g of Dowex 50W × 12 ion-exchange resin in the H^+ form and stirred for 2 h. After 12 h, the resin was removed by filtration and washed with ether. The filtrate was evaporated to give 1.7 g (53%) of acid XI with mp 66°C (from hexane). Found: C 34.0; H 3.6; N 5.1%. $C_8H_9F_6NO_3$. Calculated. C 34.2; H 3.2; N 5.0%.

1-(1-Carboxy-1-methoxycarbonylethoxy)-2,2-bis(trifluoromethyl)aziridine (XIII). This compound was obtained in the same way as acid XI [the intermediate potassium salt XII was isolated in 84% yield, the ratio of diastereomers was ∿ 9:5 (according to the PMR spectrum of a solution in D_2O)] in 85% yield as an oil that crystallized in the condenser. According to PMR spectroscopy, the ratio of diastereomers was 3:2. Four recrystallizations from pentane gave pure aziridine XIIIa, with mp 68°, in 60% yield. Found: C 33.2; H 2.7; N 4.2%. $C_9H_9F_6NO_5$. Calculated. C 33.2; H 2.8; N 4.3%.

1-(1,1-Dicarboxyethoxy)-2,2-bis(trifluoromethyl)aziridine (XV). This compound, with mp 116°C (from CCl_4–ethyl acetate), was obtained in 54% yield by a method similar to that used to obtain acid XI (intermediate salt XIV was obtained in 78% yield by a method similar to that used to obtain salt X and carbonized at 235°C).

1-(1-Methoxycarbonyl-1-ethoxycarbonylethoxy)-2,2-bis(trifluoromethyl)aziridine (XVI and XVIa). A 100-mg sample of monoester XIII (the ratio of diastereomers was ∿ 6:5) was treated at 15°C with a small excess of diazoethane, and the mixture was evaporated after 15 min. The residue was distilled to give ester XVI in quantitative yield. The ratio of diastereomers in the mixture, which had bp 80°C (1 mm), was ∿ 6:5. Diasteromerically pure ester XVIa was isolated in the case of similar treatment of acid XIIIa.

Salt of Acid XI with R-(+)- -Phenylethylamine (XVIIa). A 0.44-g (3.6 mmole) sample of R-(+)-α-phenylethylamine [$[\alpha]_D^{17}$ = 41.0° (pure liquid)] was added to a solution of 1.02 g (3.6 mmole) of acid XI in 30 ml of absolute ether. After 24 h, salt XVIIa was removed by filtration to give 1.0 g (68%) of a product with mp 130-132°C. Six recrystallizations from

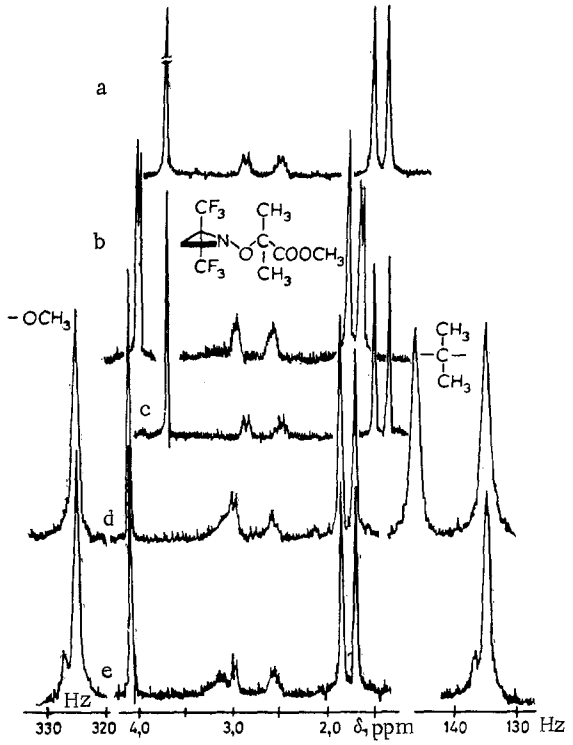


Fig. 1. PMR spectra (80 MHz, CCl_4, relative to hexamethyldisiloxane): a) racemate V; b) racemate V with added Eu(tfc)$_3$ (shift reagent: V ratio 0.1); c) (−)-V; d) the same with added Eu(tfc)$_3$ [shift reagent:(−)-V ratio = 0.25]; e) the same with added 20% racemate V [shift reagent: (±)-V = 0.21]. The signals of the shift reagent are visible in spectra b, d, and e along with the signals of the principal component.

CCl_4 gave 180 mg (18%) of salt XVIIa with mp 141-144°C. The salt (XVIIb) of acid XI with S-(−)-α-phenylethylamine ($[\alpha]_D^{20}$ = −39.25° (pure liquid)) was similar obtained in 79% yield and had mp 132-134°C; six recrystallizations from CCl_4 gave a product with mp 140-142°C in 6% yield.

The NMR spectra of salts XVIIa and XVIIb were identical.

Isolation of Optically Active Acid (−)-XI. A solution of 0.17 g of salt XVIIa (mp 141-144°C) in 10 ml of methanol was treated with 1.5 g of Dowex 50 × 12 resin in the H^+ form. After 12 h, the resin was removed by filtration, and the filtrate was evaporated to give 110 mg (93%) of an acid with mp 58-73°C. Three recrystallizations from hexane gave 30 mg (27%) of acid (−)-XI with mp 74-76°C, $[\alpha]_D$ = −20.7°, $[\alpha]_{546}$ = −25.3°, $[\alpha]_{365}$ = −69.2°, $[\alpha]_{312}$ = −112.6° (c 1.3, MeOH), λ_{max} 217 nm, and Δε 0.4.

Optically Active Acid (+)-XI. This compound was isolated similarly and had mp 73.5-76°, $[\alpha]_D$ = 18.1°, $[\alpha]_{546}$ = 24.2°, $[\alpha]_{365}$= 66.3°, and $[\alpha]_{312}$ = 109.4° (c 0.56; MeOH).

Optically Active Ester (−)-V. A 30-mg sample of acid (−)-XI (mp 74-76°C) was treated with excess diazomethane in ether, and the solvent was removed *in vacuo* (30 mm) after 30 min to give 29.4 mg (88%) of ester (−)-V with $[\alpha]_D$ = −16.4°, $[\alpha]_{546}$ = − 19.3°, $[\alpha]_{365}$ = − 52.6°, and $[\alpha]_{312}$ = − 82.2° (c 2.39, MeOH).

Optically Active Ester (+)-V. This compound was similarly obtained in 82% yield and had $[\alpha]_D$ = 14.3°, $[\alpha]_{546}$ = 17.1°, $[\alpha]_{365}$ = 48.5° (c 1.1; MeOH), λ_{max} 217 nm, and Δε 0.16.

Deterimination of Optically Active Ester (−)-V. A solution of 9 mg of optically active Eu(tfc)$_3$ shift reagent was added to 30 mg of ester V in 0.33 g of CCl_4 (the shift reagent:V ratio was 0.1). A weak-field shift of the signals (25 Hz for MeO and 23 Hz for Me_2C) and splitting of the MeO signal (1:1) and strong-field Me signal (1:1) were observed in the PMR spectrum (Fig. Ib).

A 14-mg sample of Eu(tfc)$_3$ [shift reagent:(−)-V ratio = 0.25] was added to a solution of 18 mg of ester (−)-V in CCl_4 [the PMR spectrum was in complete agreement with the PMR spectrum of the racemate (Fig. 1c)]. A weak-field shift of the signals (32 Hz for MeO and 29 Hz for Me) was observed, but the signals were not split. Thus the optical purity of ester (−)-V was no less than 95% (Fig. 1d). A 3.4-mg (20%) sample of racemate V was added to this sample for monitoring; signals of a second isomer in a ratio of ~1:10 appeared in the spectrum in this case (Fig. 1e).

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BISINDOLES.

6.* SYNTHESIS AND INVESTIGATION OF SOME PROPERTIES OF 2-FORMYL-, 3-FORMYL-, AND 3,8-DIFORMYL-1H,6H-INDOLO[7,6-g]INDOLES

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The formylation of 1H,6H-indolo[7,6-g]indole under the conditions of the Vilsmeier reaction at a molar ratio of the indoloindole and the Vilsmeier complex of 1:1 has made it possible to raise the yield of 3-formyl-1H,6H-indolo[7,6-g]indole to 43% and to also isolate 2-formyl-1H,6H-indolo[7,6-g]indole. The 1H,6H-indolo[7,6-g]indole molecule was subjected to quantum-chemical calculation by the CNDO (complete neglect of differential overlap) MO method. The formylindoloindoles were condensed with aniline, thiosemicarbazide, nitromethane, nitroethane, and hydroxylamine. The configurations of the isomeric dioximes of 3,8-diformyl-1H,6H-indole[7,6-g]indole were established by PMR spectroscopy.

In the present research we investigated the chemical properties of our previously obtained [2] 3-formyl (I, obtained in 2% yield) and 3,8-diformyl-1H,6H-indolo[7,6-g]indoles (II) under the conditions of the Vilsmeier reaction. To raise the yield of aldehyde I we carried out the formylation at a molar ratio of 1H,6H-indolo[7,6-g]indole (III) [3, 4] and the Vilsmeier complex of 1:1 at 55-60°C. Aldehyde I was obtained in 43% yield. Under these conditions we were also able to isolate 2-formyl-1H,6H-indolo[7,6-g]indole (IV) (the spectral data are presented in Table 2), the formation of which was previously not observed [2]. The 2 position of indoloindole III is also reactive in the case of acetylation with acetic anhydride in acetic acid [2]. To explain the results of the experimental studies we carried out the quantum-chemical calculation of the indoloindole molecule III by the CNDO (complete neglect of differential overlap) MO method [5] (see the diagram presented below). The formation of 2-substituted compounds along with 3-substituted compounds in the acylation of I can be explained by the presence of sufficiently high π-electron density in the 2 position of indoloindole molecule III. The absence of products of formylation in the naphthalene part of the molecule (in the 5 or 10 position) is probably associated with more pronounced steric hindrance (because of the large volume of the Vilsmeier complex) in the case of formylation

*See [1] Communication 5.

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