PYRROLOINDOLES.

8.* ELECTROPHILIC SUBSTITUTION IN THE 1H,5H-PYRROLO[2,3-f]INDOLE

AND 3H,6H-PYRROLO[3,2-e]INDOLE SERIES

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UDC 547.759.3'5.07:540.14.5:541.621.2: 541.621.2:543.422'51

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The principles of the electron density distribution in 1H,5H-pyrrolo[2,3-f]indole and 3H,6H-pyrrolo[3,2-e]indole molecules were determined on the basis of quantumchemical calculations. These results were confirmed by the results of the investigated electrophilic-substitution reactions. The reaction centers of these compounds proved to be the same positions as in indole, viz., the 3 and 7 and 1 and 8 positions, respectively. The impossibility of 1,8-disubstitution in the angular heteroring was demonstrated in the case of bulky substituents; this was explained by a steric effect.

We have previously described [1] a new synthesis of 1H,2H-pyrrolo[2,3-f]indole (I) and 3H,6H-pyrrolo[3,2-e]indole (X). In order to study the effect of the structure of pyrroloindoles on the character of the orientation of electrophilic substitution we studied some reactions of these condensed systems, specifically, the Vilsmeier and Mannich reactions, diazo coupling, and acetylation.



XVI X=CI; XVII X= NO_2

*See [1] for communication 7.

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Fig. 1. Molecular diagrams of 1H,5H-pyrrolo[2,3-f]indole (I) and 3H,6H-pyrrolo-[3,2-e]indole (X): a) overall ($\sigma + \pi$) charges; b) $\sigma - \pi$ electron densities.

To determine the primary centers of initial electrophilic attack we made quantum-chemical calculations for heterocycles I and X. The calculations were made by means of the MO CNDO (complete neglect of differential overlap) method using the program of V. G. Maslov [2] (see Fig. 1). The calculations were performed with a BÉSM-6 computer in the Institute of Applied Mathematics of Tbilisi State University.

A comparison of the results of quantum-chemical calculations for linear I and angular X molecules reveals almost no differences in the electron densities of the corresponding positions of the pyrrole rings. The chemical shifts for the latter also differ slightly, and their difference can be partially ascribed to a concentration effect (the derivatives of the I series are significantly less soluble than the derivatives of the X series). However, the difference in the shifts of the 1-H and 8-H β protons, which are virtually unaffected by the concentration effect [3] is evidently associated with the steric interaction of the β protons for isomer X. This also explains the impossibility of 1,8-disubstitution in the case of bulky substituents.

The results of the quantum-chemical calculations were confirmed by the results of the investigated electrophilic-substitution reactions.

Formulation of pyrroloindole I and X with the aid of the Vilsmeier complex [4] in a ratio of 1:3 leads to 3,7-diformy1-1H,5H-pyrrolo[2,3-f]indole (II) and 1,8-diformy1-3H,6H-pyrrolo-[3,2-e]indole (XI). 3,7-Bis(dimethylaminomethyl)-1H,5H-pyrrolo[2,3-f]indole (III) and 1,8bis(dimethylaminomethyl)-3H,6H-pyrrolo[3,2-e]indole (XII) are formed in the aminomethylation [5] of I and X at room temperature in acetonitrile with the crystalline Mannich reagent. Acetylation [6] of pyrroloindoles I and X with acetic anhydride in glacial acetic acid leads to the formation of a mixture of compounds, which was separated by column chromatography. We were able to isolate 1,5-diacety1-1H,5H-pyrrolo[2,3-f]indole (V), 1,3,5-triacety1-1H,5Hpyrrolo[2,3-f]indole (VI), 3,6-diacety1-3H,6H-pyrrolo[3,2-e]indole (XIII), 3-acety1-3H,6Hpyrrolo [3,2-e]indole (XIV), and 1,3,6-triacetyl-3H,6H-pyrrolo [3,2-e]indole (XV). The yields of monosubstituted derivatives of pyrroloindoles I and X substantially exceed the yields of the di- and triacetyl derivatives, evidently because of deactivation of the aromatic ring by electron-acceptor substituents. Diazo coupling of pyrroloindoles I and X with benzenediazonium, p-chlorobenzenediazonium, and p-nitrobenzenediazonium chlorides was carried out in aqueous dioxane solutions at a pH of 6-7 [7]. The diazonium salts and pyrroloindoles were subjected to the reactions in a ratio of 3:1. The corresponding disubstituted pyrroloindoles VII and VIII were obtained as a result of the reaction of pyrroloindole I with benzenediazonium and p-chlorobenzenediazonium chlorides. The reaction of pyrroloindole I with pnitrobenzenediazonium chloride leads only to monosubstituted pyrroloindole IX. This is evidently explained by the fact that the nitro group in IX deactivates to a significant degree the aromatic system due to the effect of conjugation. The reaction of pyrroloindole X with diazonium salts leads only to monosubstituted derivatives XVI and XVII, apparently as a consequence of steric effects. We were unable to isolate a product of diazo coupling with benzenediazonium chloride in this case because of its low stability.

EXPERIMENTAL

The course of the reaction and the purity of the compounds were monitored by means of thin-layer chromatography (TLC) on Silufol UV-254 plates. Preparative chromatography was carried out on SiO₂ (100-250 μ m). The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The UV spectra of solutions in ethanol were recorded with a Specord UV spectrophotometer. The PMR spectra were recorded with a Varian CFT-20 spectrometer with tetramethylsilane as the internal standard; the accuracy in the measurement of the chemical shifts was ± 0.02 ppm, whereas the accuracy in the measurement of the spin—spin coupling constants was ± 0.1 Hz. The mass spectra were recorded with an MKh-1303 spectrometer with a modified system for introduction of the samples (direct introduction into the ion source) at an ionizing-electron energy of 50 eV.

<u>3,7-Diformyl-lH,5H-pyrrolo[2,3-f]indole (II).</u> A 1.11-g (15.3 mmole) sample of distilled dimethylformamide (DMF) was cooled to -5° C, 0.59 g (3.8 mmole) of freshly distilled POCl₃ was added dropwise to it, and the mixture was stirred at room temperature for 40 min. The mixture was again cooled to -5° C, and a solution of 0.2 g (1.3 mmole) of I in 2 ml of DMF was added slowly at no higher than 0°C. The mixture was then stirred at room temperature for 1.5 h, during which a yellow precipitate formed. Ice water (30 ml) was added to it, and the mixture was made alkaline with 10% aqueous NaOH solution. The precipitate was removed by filtration, washed with water until the washings were neutral, and dried to give 0.25 g (93%) of pyrroloindole II and recrystallized from ethanol to give a product that decomposed at 420°C and had R_{f} 0.16 [benzene-acetone (3:1)]. IR spectrum: 3200 (NH) and 1635 cm⁻¹ (C=0). UV spectrum, λ_{max} (log ε): 204.5 (4.13), 206 shoulder (3.95), 222 (4.39), 229.8 (4.39), 279 (4.45), 300 shoulder (4.01), and 345 nm (4.22). Found: C 67.6; H 4.4; N 12.9%; M⁺ 212. Calculated: C 67.9; H 3.8; N 13.2%; M 212.

<u>3,7-Bis (dimethylaminomethyl)-1H,5H-pyrrolo[2,3-f]indole (III)</u>. The crystalline Mannich reagent (0.4 g) was suspended in 20 ml of dry acetonitrile, a solution of 0.2 g (1.3 mmole) of I in 10 ml of dry acetonitrile was added dropwise, and the mixture was stirred at room temperature for 3 h. The solvent was decanted, the precipitate was dissolved in 30 ml of water, and the solution was alkalized to pH 11 with a 10% aqueous solution of NaOH. The precipitate was removed by filtration, washed with water, and dried to give 0.24 g (69%) of a product with mp 210-212°C (dec.) and R_f 0.55 [isopropyl alcohol-33% ammonium hydroxide (3:1)]. IR spectrum: 3100-3200 cm⁻¹ (NH). UV spectrum, λ_{max} (log ε): 202.5 (4.19), 204.5 shoulder (4.57), 220 (4.87), 238 shoulder (4.65), 305 (4.35), 330 (4.17), and 340 nm (4.17). Found: N 20.6%; M⁺ 270. Calculated: N 20.7%; M 270.

Acetylation of 1H,5H-Pyrrolo[2,3-f]indole. A 5-ml sample of distilled acetic anhydride and 0.4 ml of glacial acetic acid were added to 0.2 g (1.3 mmole) of I, the mixture was refluxed for 30 h, and the solvent was evaporated. The reaction mixture was then poured into water, and the resulting precipitate was removed by filtration, washed until the washings were neutral, and dried to give 0.25 g of product. Several spots were visible on the chromatogram of this precipitate [benzene-acetone (3:1)]. Separation of this mixture to give the individual substances was carried out with a column by means of elution with benzene-ether (10:1). The yields of the individual compounds were calculated as a function of the initial amount of the mixture applied to the column.

 $\frac{1,5-\text{Diacetyl-1H,5H-pyrrolo[2,3-f]indole (IV).}{\text{The reaction produced 0.02 g (8%) of white crystals with mp 224-225 °C and R_f 0.68 [benzene-acetone (3:1)]. IR spectrum: 1700 cm⁻¹ (CO). UV spectrum, <math>\lambda_{\text{max}}$ (log ε): 204 (3.8), 256 (4.27), 286 (3.95), 293 (3.98), 298.5 (4.07), 321 (3.91), and 334 nm (4.08). Found: C 69.9; H 5.4; N 11.5%; M⁺ 240. Calculated: C 70.0; H 5.0; N 11.7%; M 240.

 $\frac{1-\text{Acetyl-1H,5H-pyrrolo[2,3-f]indole (V).}}{\text{R}_{f} 0.44 \text{ [benzene-acetone (3:1)] in the form of white crystals with mp 181-182°C. IR spectrum: 3350 (NH) and 1680 cm⁻¹ (C=O). UV spectrum, <math>\lambda_{\text{max}}$ (log ε): 206.5 (4.28), 217 (4.22), 268 (4.35), 307.7 (4.02), 322 (3.97), and 334 nm (3.99). Found: C 73.0; H 5.1; N 13.9%; M⁺ 198. Calculated: C 72.7; H 5.1; N 14.1%; M 198.

TABL	Е 1.	Chemi	cal Sh	ifts (δ	, ppm)	and S	pin-Sp	pin Coup	ling Co	ons tants	; (Ј, Н;	z) in the P	MR Spectra of	I-IX in dAcetone
Com- pound	H-1	2-H	Н-8	4-H	H-5	Н-9	H-7	Н-8	C H	CH ₂ —N	CH ₃ N	сосн	A B A	J, Hz
1	9,7 br.s	7,20 dd	6,36dd	7,46 br.s ^a	9,7br.s	7,20dd	6,36 dd	7,46 b rs a	[ļ				$J_{12} = J_{56} = J_{23} = J_{67} = 2.7;$
GIII	11,6br.s:	8,11 s	I	8,16 br.s	11,6br.s	8,115	1	8,16 br.s	9,85 s		[1	J	$J_{13} = J_{57} = 2,4$
<u>=</u> >>	9,40F.s	7,72 d 7,56 d	6,77dd 6,62dd	7,50 br.s	9,4 Dr.S	7,72d	6,77 dd 6,54 m	7,000 8,56br.s 8,61br.s	[]	3,55 s	2,18 s	2,66s 2,77 s	11	$egin{array}{llllllllllllllllllllllllllllllllllll$
VIb	 	3,64 s	ł	9,17 b r.s	1	7,83d	6,83 dd	8,51br.s		1	1	7,76 sr , 2,56 s		$J_{56}^{25} = 2,5; J_{57}^{38} = 0,1; J_{67}^{47} = 0,0; J_{57}^{25} = 2,1; J_{67}^{26} = 3,1$
	11,0br.s	8,30d 3,33 d	1	8,67 d 8,65 d	11,0 br.s 11,2 br.s	8,30d 8,33d		8,67d 8,65d		1		2,63 s 	7,31—7,89, R=H 7,89d (A); 7,82d	$J_{12} = J_{56} = 3,2; J_{14} = J_{58} = 0,8$ $J_{19} = J_{56} = 3,5; J_{14} = J_{56} = 0,7$
IX	11,2br.s	3,34 d		8,62 br.s	10,2 b r.s	7,40dd	6,52 m	7,64 br .s].	I	(B); $R = Ci$ 7,94d, (A); 8,32d (B); $R = NO_2$	$J_{12} = 3,6; J_{56} = 2,6; J_{67} = 3,3; J_{47} = 0,7; J_{AB} = 8,8; J_{57} = 2,1$
aThe the with	broad unsymm a sol	ening: etric: ution	s are al mol of th	due to ecules, e compo	the sm and a und in	all SS lso, p d e- DM	SCC of sossib SO; th	the tra ly, reta ne NH pr	insoid t irded ro roton ev	-ype th tation vidently	cough fi of the r partic	lve bonds o N-acyl gro cipates in	r coupling of ups. ^b The spece	the para protons for ctrum was recorded

Chemical Shifts (ô, ppm) and Spin-Spin Coupling Constants (SSCC) (J, Hz) in the PMR Spectra of X-XVII in de-TABLE 2.

Acet	one													
Com- pound	1-H	2-H	3-H	4-H	5-H	Н-9	H-2.	H-8	CC H	CH2N	CH ₃ N	сосн	A B	J, Hz
x	6,64 m	7,21 dd	10,0 br.s	7,20 d	7,20 d	10,0br.s	7,21dd	6,64 m]	I	[I	$I_{13} = I_{68} = 2,2; I_{12} = I_{78} = 2,9;$ $I_{22} = I_{22} = 0.5; I_{12} = I_{78} = 2,9;$
		8,01s 7,05d 7,76d	12,0 br.s 9,9 br.s	7,38 s 7,11 s 8.38 d	7,38 s 7,11 s 8.38 d	12,0br.s 9,9br.s	8,01s 7,05d		10,20 s	3,84s	2,20 s	1 0960 1 000	1 [$I_{23}^{23} = I_{67}^{67} = 2,0$, $I_{14}^{14} = J_{38}^{28} = 0,0$ $I_{23}^{23} = I_{67}^{2} = 2,3$ $I_{19}^{23} = I_{79}^{23} = 3,8$: $I_{14}^{23} = I_{66}^{26} = 0,6$
XIV	6,89 dd	7,65d		8,24 dd	7,36 dd	10,1b r.s	7,30dd	6,70 m		1	1	2,67 s	1	$J_{12}^{12} = 3,4; \ J_{14}^{13} = 0,3; \ J_{45}^{10} = 9,1; \ J_{58}^{10} = 0,5; \ J_{67} = 2,2; \ J_{68} = 2,1;$
XV	1	8,68 s	1	8,24 d	8,36 dd	1	7,79 d	7,61 dd		1	1	2,66 st 2,78 st	1	$J_{45} = 2.9$ $J_{45} = 8.6; J_{58} = 0.8; J_{78} = 3.8$
IVX		7,50 đ	10,8 br.s	7,22 d	7,45 dd	10,3br.s	7,28dd	6,77 m	l	I	l	c,022	7,80 d (A); 7,49 d (B);	$J_{23} = 3,3; J_{45} = 8,9; J_{68} = 0,7; J_{67} = 2,4; J_{68} = 2,1; J_{AB} = 8,7;$
XVII	1	7,63 d	11,4 br.s	7,24 d	7,50 dd	10,4br.s.	7,28dd .	6,81 m		[[ļ	$R=CI7,96 d (A);8,35 d (B);R=NO_2$	$I_{78} = 2,6$ $I_{22} = 3,2; I_{45} = 8,6; I_{58} = 0,9;$ $I_{67} = 2,6; I_{68} = 2,0; I_{78} = 2,9;$ $I_{AB} = 8,9$
				•		-	-		-			-		

*The spectrum was obtained from a solution in d.-DMSO; the NH proton evidently participates in exchange.

<u>1,3,5-Triacetyl-1H,5H-pyrrolo[2,3-f]indole (VI)</u>. The reaction produced 0.1 g (4%) of white crystals with mp 260-261°C and R_f 0.59 [benzene-acetone (3:1)]. IR spectrum: 1721, 1700, and 1665 cm⁻¹ (C=0). UV spectrum, λ_{max} : 204, 243.5, 252, 277, 287 shoulder, 322, and 335 nm. Found: C 68.3; H 5.5; N 9.7%; M⁺ 282. C₁₆H₁₄N₂O₃. Calculated; C 68.1; H 5.0; N 9.9%; M 282.

3,7-Diphenylazo-1H,5H-pyrrolo[2,3-f]indole (VII). A solution of 3.9 mmole of benzenediazonium chloride was added dropwise at -5° C to a solution of 0.2 g (1.3 mmole) of I in 15 ml of dioxane and 10 ml of water while maintaining the solution at pH 6-7 by the addition of sodium acetate, and the mixture was then stirred for 3 h. The resulting precipitate was removed by filtration to give 0.4 g (87%) of a substance, which was chromatographed with a column by elution with benzene-ether (5:1). The light-brown crystals had a decomposition temperature of 305-307°C and R_f 0.53 [benzene-ether (3:1)]. IR spectrum: 3200 cm⁻¹ (NH) and 1410 cm⁻¹ (N=N). UV spectrum, λ_{max} (log ε): 204 (4.41), 241 (4.37), 306 (4.51), and 236 nm (4.64). Found: N 23.0%; M⁺ 364. C₂₂H₁₆N₆. Calculated: N 23.1%; M 364.

<u>3,7-Bis(p-chlorophenylazo)-1H,5H-pyrrolo[2,3-f]indole (VIII).</u> This compound was obtained by the reaction of 0.2 g (1.3 mmole) of I with a solution of 3.9 mmole of p-chlorobenzenediazonium chloride. Workup of the reaction mixture gave 0.53 g (95%) of a crude substance, which was purified with a column [elution with benzene-ether (5:1)] to give light-brown crystals with a decomposition temperature of 310-315°C and R_f 0.5 [benzene-ether (3:1)]. IR spectrum: 3215 (NH) and 1420 cm⁻¹ (N = N). UV spectrum, λ_{max} (log ε): 204.5 (4.59), 227 (4.61), 246.9 shoulder (4.45), 309 (4.67), and 239 nm (4.78). Found: N 19.6%; M⁺ 433. C₂₂H₁₄Cl₂N₆. Calculated: N 19.4%; M 433.

<u>3-(p-Nitrophenylazo)-1H,5H-pyrrolo[2,3-f]indole (IX)</u>. This compound was obtained by the reaction of 0.2 g (1.3 mmole) of I with a solution of 3.9 mmole of p-nitrobenzenediazonium chloride by a procedure similar to that used to obtain VII. Workup gave 0.25 g (64%) of crude product, which was purified with a column [elution with benzene-ether (5:1)] to give dark-red crystals with a decomposition temperature of 285-290°C and R_f 0.46 [benzene-ether (2:1)]. IR spectrum: 3415, 3380 (NH); 1400 cm⁻¹ (N=N). UV spectrum, λ_{max} (log ε): 205 (4.46), 239 (4.37), 294 (4.25), 328 (4.31), and 250 nm (4.39). Found: N 22.9%; M⁺ 305. C_{16H11}N₅O₂. Calculated: N 23.0%; M 305.

 $\frac{1,8-\text{Diformy1-3H,6H-pyrrolo[3,2-e]indole (XI).}{X \text{ by a procedure similar to that used toprepare II. Recrystallization from ethanol gave a product with a decomposition temperature of 286°C and R_f 0.11 [benzene-acetone (1:1)]. IR spectrum: 3200-3300 (NH) and 1645 cm⁻¹ (C=0). UV spectrum, <math>\lambda_{\text{max}}$ (log ε): 216 (4.57), 274 (4.55), and 325 (3.95). Found: C 68.1; H 4.4; N 12.7%; M⁺ 212. C₁₂H₈N₂O₂. Calculated: C 67.9; H 3.8; N 13.2%; M 212.

 $\frac{1,8-\text{Bis}(\text{dimethylaminomethyl})-3\text{H},6\text{H-pyrrolo}[3,2-e]\text{indole (XII)}.$ This compound, with mp 163-164°C and R_f 0.47 [isopropyl alcohol-33% ammonium hydroxide (3:1)], was obtained in 74% yield by a procedure similar to that used to prepare III. IR spectrum: 3330 cm⁻¹ (NH). UV spectrum, λ_{max} (log ε): 205 shoulder (4.01), 223 (4.44), 240 shoulder (4.07), 278 shoulder (3.83), 289 (4.03), and 303 nm (4.07). Found: N 20.2%; M⁺ 270. C₁₆H₂₂N₄. Calculated: N 20.7%; M 270.

Acetylation of 3H,6H-pyrrolo[3,2-e]indole. The acetylation of 0.2 g of X was carried out as in the case of I to give 0.23 g of a mixture of acylation products. Several spots were visible on the chromatogram [benzene-acetone (3:1)]. Separation of this mixture into individual compounds was carried out with a column by elution with benzene-acetone (5:1). The yields were calculated in the same way as the yields of the products of acetylation of I.

 $\begin{array}{c} \underline{3,6-\text{Diacetyl-3H,6H-pyrrolo[3,2-e]indole~(XIII).}}_{R_{f}~0.61~[benzene-acetone~(3:1)],~was~obtained~as~white~crystals.} IR~spectrum:~1710~cm^{-1}~(C=0).~UV~spectrum,~\lambda_{max}~(\log~\varepsilon):~205.8~(4.38),~218~sh~(4.06),~223~(4.01),~270~(4.43),~298.5~(4.36),~312~(4.20),~and~333~nm~(3.81). Found:~C~70.4;~H~5.4;~N~11.8\%;~M^+~240.~C_{14}H_{12}N_{2}O_{2}.~Calculated:~C~70.0;~H~5.0;~N~11.7\%;~M~240.\\ \end{array}$

 $\frac{3-\text{Acetyl-3H,6H-pyrrolo[3,2-e]indole (XIV).}}{(Crystals with mp 188-189°C and R_f 0.48 [benzene-ether (3:1)]. IR spectrum: 3385 (N) and 1695 cm⁻¹ (C=0). UV spectrum, <math>\lambda_{\text{max}}$ (log ε): 206 (4.54), 217 shoulder (4.49), 260 (4.39), 268 (4.38), and 317.5 shoulder (4.27). Found: C 72.8; H 5.0; N 13.7%; M⁺ 198. C₁₂H₁₀N₂O. Calculated: C 72.7; H 5.1; N 14.1%; M 198.

1,3,6-Triacety1-3H,6H-pyrrolo[3,2-e]indole (XV). The reaction produced 0.005 g (2%) of

yellow crystals with R_f 0.53 [benzene-acetone (3:1)] and mp 250-251°C. IR spectrum: 1720, 1700, 1670 cm⁻¹ (C=0). UV spectrum, λ_{max} (log ε): 206 (4.45), 232 (4.40), 253 (4.52), 289.8 (4.26), and 314 nm (4.30). Found: C 67.6; H 5.4; N 9.5%; M⁺ 282. C₁₆H₁₄N₂O₃. Calculated: C 68.1; H 5.0; N 9.9%; M 282.

<u>l-(p-Chlorophenylazo)-3H,6H-pyrrolo[3,2-e]indole (XVI)</u>. This compound was obtained by the reaction of 0.2 g (1.3 mmole) of X with a solution of 3.9 mmole of p-chlorobenzenediazonium chloride by a procedure similar to that used to obtain XII. Workup of the reaction mixture gave 0.29 g (78%) of crude product. The compound was purified with a column (elution with benzene) to give red crystals with mp 183-184°C and R_f 0.58 (benzene). IR spectrum: 3460, 3400 (NH); 1400 cm⁻¹ (N=N). UV spectrum, λ_{max} (log ε): 207.5 (4.49), 270 (4.03, 322 (3.95), and 242 nm (4.53). Found: N 18.9%; M⁺ 294.5. C₁₆H₁₁ClN₄. Calculated: N 19.0%; M 294.5.

 $\frac{1-(p-Nitrophenylazo)-3H,6H-pyrrolo[3,2-e]indole (XVII).}{Preaction of 0.2 g (1.3 mmole) of X with a solution of 3.9 mmole of p-nitrobenzenediazoni$ um chloride by a procedure similar to that used to obtain VII. Workup of the reaction mixturegave 0.35 g (89%) of a crude product, which was purified with a column [elution with benzene ether (6:1)] to give a product with mp 285-286°C and R_f [benzene ether (3:1)]. IR spec $trum: 3445, 3385 (NH); 1400 cm⁻¹ (N=N). UV spectrum, <math>\lambda_{max}$ (log ε): 208 (4.49), 268 (3.96), 339 (3.96), 204.5 (3.96), and 253 nm (4.54). Found: N 22.6%; M⁺ 305. C₁₆H₁₁N₅O₂. Calculated: N 23.0%; M 305.

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SYNTHESIS OF BIS (DIETHYLAMINOETHYL)

1,2-DIMETHYL-8-OXOINDENO[2,1-b]PYRROLE-3,5-DICARBOXYLATE

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An 8-oxoindeno[2,1-b] derivative, viz., the heteroanalog of the antivirus preparation thilorone, was synthesized from 6-ethoxycarbony1-1,2-naphthoquinone through a series of intermediate steps.

The antivirus preparations thilorone [1] and fluorenal [2] have been found in the fluorenone series. One of them, viz., fluorenal, has found application in medical practice.

In this connection, we have realized the synthesis of the previously unknown bis(diethylaminoethyl) 1,2-dimethyl-8-oxoindeno[2,1-b]pyrrole-3,5-dicarboxylate (X), viz., the heteroanalog of the antiviral preparation thilorone, from 6-ethoxycarbonyl-1,2-naphthoquinone (I) via the scheme:

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