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A STUDY OF NITROGEN- AND SULFUR-CONTAINING HETEROCYCLES.

41.* SYNTHESIS AND SPATIAL STRUCTURE OF 3*a*-ALKYL-4,7-DICHLORO-1,2-DIOXOOXAZOLIDINO[3,2-f]PYRIDO[2,3-b][1,4]THIAZINES

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The structure of the products of the chlorination of oxazolidino[3,2-f]pyrido-[2,3-b][1,4]-thiazines has been studied with the aid of spectral methods. It has been shown that the chlorine atom substitutes position 4 of the tricyclic system (in the thiazine ring). It has been established on the basis of PMR and ^{13}C NMR spectra that in solution the compounds obtained exist in the form of mixtures of two diasteromers with the cis and trans orientations of the substituents at the $C_{(3a)}$ and $C_{(4)}$ carbon atoms of the tricyclic system in each case. The configurations of the diastereomers have been determined from the chemical shifts in the ^{13}C NMR spectra and from the relaxation times in the PMR spectra. It has been shown that the isomer with the transoid arrangement of the substituents on the $C_{(3a)}$ and $C_{(4)}$ atoms of the tricyclic system, which are included in a thiazine ring present in the "half-chair" conformation, is energetically the more favorable.

We have previously developed a method for the synthesis of derivatives of the tricyclic system oxazolidino[3,2-f]pyrido[2,3-b][1,4]thiazine (Ia-c) among which substances possessing antitumoral activity have been found [2, 3].

With the aim of a further search for new biologically active compounds in the 1,4-thiazine series, in the present investigation we have made an attempt to synthesize the 4-halogen derivatives (IIa-c). It has been shown that when substances (Ia-c) are heated in a mix-

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*For communication 40, see [1].

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TABLE 1. Characteristic Ions in the Mass Spectra of (IIa-c)*

Compound	M^+	$[M-Cl]^+$	$[M-Cl, -CO, -CO_2]^+$	$[M-CH_2Cl]^+$	$[M-2CO]^+$	$[M-CH_2Cl, -2CO]^+$†	COR^+
IIa	304(53)	269(2)	197(100)	255(2)	248(2)	199(30)	43(100)
IIb	318(20)	283(4)	211(95)	269(2)	262(4)	213(21)	57(100)
IIc	332(31)	297(1)	225(23)	283(3)	276(5)	227(14)	71(100)

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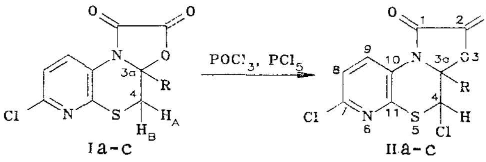
*For the chlorine-containing fragments the mass numbers and intensities of the peaks of the ions containing the ^{35}Cl isotope are given.

†In the determination of the intensities of the peaks of the ions $[M - CH_2Cl, - 2CO]^+$ the contribution to the total intensity of the intensity of the peak of the $[M - Cl, - CO, - CO_2]^+$ ion containing the ^{37}Cl isotope was taken into account.

ture of PCl_5 and $POCl_3$ at 100-105°C, the hydrogen atom in position 4 of the tricyclic system is replaced by a chlorine atom with the retention of the tricyclic system and, as a result, compounds (IIa-c) are formed in quantitative yield.



I–IIa $R=CH_3$; b $R=C_2H_5$; c $R=C_3H_7$

The structure of the substances synthesized was investigated by the methods of IR and UV spectroscopy, mass spectrometry, and PMR and ^{13}C NMR spectroscopy. The IR spectra of compounds (IIa-c) in the crystalline state and in solutions in $CHCl_3$ contained strong bands of the stretching vibrations of the carbonyl groups of an oxazolidinedione ring ($C_{(1)}=O$ 1730-1755, $C_{(2)}=O$, 1810-1830 cm^{-1}), and weaker bands at 1550-1570 cm^{-1} belonging to the $\nu C=C$ and $\nu C=N$ vibrations of the pyridine ring. Similar bands were observed in the IR spectra of the initial compounds (Ia-c) [2, 3].

The UV spectra of compounds (IIa-c) each had two absorption maxima: λ 296 and 241-240 nm (ε 8040-8080 and 11,000-11,100, respectively). Similar absorption maxima were recorded in the UV spectra of the corresponding initial compounds (Ia, b): λ 298-300 and 244-245 nm (ε 8560-9080 and 11,460-12,520, respectively).

In the mass spectra of compounds (IIa-c), the ratio of the intensities of the isotopic peaks of the molecular ions showed the presence of two chlorine atoms in the molecules under investigation. The mass numbers of the molecular ions (IIa-c) (see Table 1) correspond to the suggested structures. The observed fragmentation corresponds to the hypothesis of the introduction of a chlorine atom into position 4 of the tricyclic system (in the thiazine ring). The suitability of the stabilization of the charge on the sulfur atom of the thiazine ring through the elimination of the chlorine atom present in the α position to the sulfur atom largely determines the fragmentation of compounds (IIa-c). The spectra show the presence of the ions $[M - Cl]^+$ and $[M - Cl, - CO, - CO_2]^+$.* The peaks of the ions $[M - CO, - CO_2]^+$, $[M - CO, - CO_2, - H]^+$ and $[M - CO, - CO_2, - R]^+$ that are characteristic for the decomposition of compounds (I) [2, 3] are absent from the spectra of compounds (IIa-c). Another feature of the mass spectra of compounds (IIa-c) is the presence in them of strong peaks of the ions OR^+ and of signals due to the elimination of the CH_2Cl group from the molecular ion (the ions $[M - CH_2Cl]^+$ and $[M - CH_2Cl, - 2\ CO]^+$). This direction of fragmentation must obviously be preceded by the rearrangement of the molecular ion, which takes place with the cleavage of $C_{(3a)}-C_{(4)}$ bond. Apparently, the observation nature of the fragmentation is due to the increasing strain of the thiazine ring in compounds (IIa-c) because of the presence of voluminous substituents (a Cl atom and alkyl group) in positions 3*a* and 4.

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*The sequence of formation of the fragments was determined in a study of the DADI spectra of compounds (IIa-c) and by the method of metastable defocusing.

ABLE 2. PMR Spectra of Compounds (I) and (II) (solvent, MSO-d_6)

Compound	Type of isomer	CS, δ, ppm				t_1, sec
		C_4H	C_8H	C_9H	Alk	
Ia	—	3,84 (H_A)* 3,49 (H_B) Δδ 0,35	7,38	8,38	1,83 (CH_3)	—
Ib	—	3,83 (H_A) 3,56 (H_B) Δδ 0,27	7,31	8,11	0,80 (CH_3) 2,00 (CH_2)	—
Ic	—	3,95 (H_A) 3,59 (H_B) Δδ 0,36	7,36	8,41	0,90 (CH_3) 1,37 (CH_2) 2,09 (CH_2)	— —
IIa	trans	6,70	7,57	8,44	2,00 (CH_3)	—
	cis	6,37	7,51	8,34	1,86 (CH_3)	—
	Δδ trans-cis	0,33	0,06	0,10		
IIb	trans	6,79	7,59	8,45	1,01 (CH_3) 2,33 (CH_2)†	2,2±0,1
	cis	6,52	7,55	8,32	0,77 (CH_3) 2,10 (CH_2)† 2,44	9,3±0,2
	Δδ trans-cis	0,27	0,04	0,13		
IIc	trans	6,78	7,59	8,43	0,92 (CH_3) 1,52 (CH_2) 2,20 (CH_2)	2,2±0,2
	cis	6,50	7,54	8,39	0,92 (CH_3) 1,21 (CH_2) 2,16 (CH_2)	6,6±0,2
	Δδ trans-cis	0,28	0,05	0,04		

*$^2J_{C_4H_AH_B}$ = 12 Hz.

†The protons of the methylene fragment in the ethyl substituent are nonequivalent and form a multiplet in the PMR spectra; as the CS for δCH_2 in the trans isomer is given the center of the multiplet, and for the cis isomer it was possible to determine the CS of each proton.

The PMR and ^{13}C NMR spectra confirm the tricyclic structure of compounds (IIa-c) (Tables 2 and 3). In the PMR spectra of these compounds the signals of the protons of a pyridine ring are observed at 8.39-8.45 ppm ($H_{(9)}$, d) and 7.51-7.59 ppm ($H_{(8)}$, d) and that of the $H_{(4)}$ methine proton at 6.37-6.79 ppm (s), together with the signals of the alkyl groups in position 3*a*. In the ^{13}C NMR spectra of compounds (IIb, c)* the signals of all the carbon atoms are close in relation to their chemical shifts (CSs) to the analogous signals of the carbon atoms in the initial compounds (Ib, c) (Table 3), with the exception of the signal of the $C_{(4)}$ carbon atom which, on passing from compounds (Ib, c) to (IIb, c), is shifted downfield by 26-33 ppm. Such a shift of the signal is in harmony with the expected influence of the substituents — the chlorine atom in position 4† — on the CSs and with the retention of the tricyclic structure in the molecule under investigation.

A feature of the PMR and ^{13}C NMR spectra of the solutions of compounds (IIa-c) is the double set of all the signals. In the initial compounds (Ia-c) no doubling was observed either in the PMR or in the ^{13}C NMR spectra for (Ib, c) (Tables 2 and 3). The reason for the double set of signals is the existence of each of the compounds (IIa-c) under investigation in solution in the form of a mixture of two diastereomers with the cis and trans orientation of the substituents at the $C_{(3a)}$ and $C_{(4)}$ thiazine carbon atoms in the tricyclic system.

In favor of this hypothesis are results on the difference in the CSs of the signals of different atoms (or groups) in ^{13}C NMR and PMR spectra. In the ^{13}C NMR spectra the CSs of the pairs of signals of the $C_{(4)}$ atom and of the atoms (or groups) directly connected with

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*The ^{13}C NMR spectra were taken for compounds (IIb) and (IIc).

†The multiplicity of the signal of the $C_{(4)}$ carbon atom in the spectra taken with incomplete decoupling of protons changed on passing from compounds (Ib, c) to (IIb, c) (t for (Ib, c), d for (IIb, c)), which again shows the presence of one hydrogen atom at the $C_{(4)}$ atom in each of the compounds (IIb and c).

TABLE 3. CSs $\delta^{13}C$ of Compounds (Ib, c) and (IIb, c) (solvent DMSO-D_6)

Compound	Type of isomer	$C_{(1)}$	$C_{(2)}$	$C_{(3a)}$	$C_{(4)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$	$C_{(11)}$	C_α*	C_β*	C_γ*
Ib	—	157,21	149,91	89,52	30,48	146,39†	120,57	134,35	126,41	146,10†	27,72	5,94	—
Ic	—	156,97	149,71	89,06	30,81	146,22†	120,39	131,50	126,33	146,04 †	36,32	14,78	13,27
IIb	trans	156,47	149,87	90,69	63,22	147,30	122,28	132,58	125,67	142,57	27,69	6,01	—
	cis	156,36	149,63	90,16	56,94	147,19	121,76	132,75	124,84	145,76	21,99	4,70	—
IIc	trans	156,38	149,75	90,28	63,22	147,26	122,21	132,51	125,63	142,46	35,93	14,79	13,36
	cis	156,25	149,53	89,82	56,92	147,12	121,72	132,64	124,87	145,54	30,31	13,75	13,03

*C_α and C_β are the carbon atoms of the ethyl substituent; C_α, C_β, and C_γ are the carbon atoms of the n-propyl substituent.
†The opposite assignment is possible.

the thiazine atoms $C_{(3a)}$ and $C_{(4)}$ of the tricyclic system have the greatest difference.* This difference is appreciably less for atoms spatially remote from the $C_{(3a)}$—$C_{(4)}$ bond (Tables 2 and 3). An analogous effect is observed in the PMR spectra where the difference in the values of the CSs of the methine protons are the greatest ($\Delta\delta C_4H \sim 0.3$ ppm), while for the protons of the pyridine ring this difference is considerably smaller. It must be stated that in the initial lactones (Ia-c) the methylene protons in position 4, which is part of the triazine ring, are nonequivalent and the difference in the CSs of these protons amounts to about 0.3 ppm, as in the cis-trans isomers of compounds (IIa-c).

The ratio of the intensities of the pairs of signals and, consequently, the amounts of the isomers in the substances investigated changed when their solutions in benzene were heated in single and repeated crystallization. In the case of compound (IIb) (R = C_2H_5), it was possible to isolate an individual isomer in this way.

During the prolonged heating of solutions of compounds (IIa, b) (T = 80°C, solvent DMSO-D_6), a change in the ratio of the intensities of the pairs of signals as compared with the spectra of the freshly prepared solutions was observed, and after 10 h a ratio of the intensities had been established in the solution which did not change on further heating. Obviously, in the freshly prepared solutions the amounts of the components were determined both by kinetic factors and by the methods used for isolating and purifying these compounds; on prolonged heating the ratios of the components in the mixtures changed, approaching equilibrium. For compounds (IIa) (R = CH_3) in the equilibrium state the trans isomer† somewhat predominated (54:46‡). For compound (IIb) (R = C_2H_5), an increase in the amount of the preferred trans isomer was observed (63:37). It was impossible to reach the thermodynamic equilibrium for compound (IIc) (R = C_3H_7), and prolonged heating led to the formation of a mixture of products among which, in addition to the trans and cis isomers, decomposition products of compound (IIc) were present. In the sample of propyl derivative investigated, the ratio of trans and cis isomers was 67:33.

A consideration of molecular models of compounds (IIa-c) showed a smaller steric hindrance of the trans isomer than of the cis isomer, for which, even in the case of the methyl derivative (IIa) there is steric repulsion between the CH_3 and Cl groups. With an increase in the volume of the alkyl substituent, this steric hindrance becomes greater, and therefore the shift of the equilibrium in the direction of the preferred isomer that was observed for compounds (IIb, c) indirectly showed the trans configuration of these isomers. The correctness of this assignment of the configurations of the isomers was confirmed by an analysis of the ^{13}C NMR spectra.

It is known that the steric hindrance of a carbon atom leads to an upfield shift of its signal in the ^{13}C NMR spectra [6]. In particular, the signal of a carbon atom present in the γ-position in the gauche orientation relative to the substituent shifts upfield (the "γ-gauche

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*The CSs of the $C_{(3a)}$ carbon atom differ little in the cis and trans isomers ($\Delta\delta \approx 0.5$ ppm), which is natural for a quaternary carbon atom [5].
†We call the trans isomer that which the 4-Cl and 3a-Alk substituents have the trans orientation.
‡The accuracy of the determination of the amounts of the isomers was 3%.

effect" [7]). In the chlorine derivatives (IIa-c) under consideration, the $C_{(3a)}$ atom in the cis isomer is such a carbon atom. Consequently, the upfield shift ($\Delta\delta \approx 5.7$ ppm) of the signals of the C_α atom observed in the ^{13}C NMR spectra of compounds (IIb, c) in the energetically less favorable isomer with respect to the corresponding signal both of the preferred isomer and of the unsubstituted derivative (Ib) shows the cis configuration of the minor isomer (in agreement with the above-mentioned assignment of the configuration of the isomers). In its turn, the appreciable upfield shift of the signal of the $C_{(4)}$ atom ($\Delta\delta \approx 3.7$ ppm) in the same isomer relative to the corresponding signal in the trans isomer confirms the existence of powerful steric interactions between the substituents at the carbon atoms of $C_{(3a)}$—$C_{(4)}$ bond similar to that which has been observed in the cis-trans isomers of decalin [5].

Among the parameters of the PMR spectra of the diastereomers of (II) that we studied, the most stereospecific and unambiguously interpretable proved to be the spin-lattice relaxation time t_1 of the $H_{(4)}$ proton. For the chlorine derivative (IIb) the values of t_1 of this proton were, respectively, 2.2 ± 0.1 sec (signal with δ6.79 ppm, trans isomer) and 9.3 ± 0.2 sec (signal with δ 6.52 ppm, cis isomer). The values of t_1 obtained were in complete harmony with the assignment of the configurations of the isomers made above, since in the trans isomer the ethyl substituent is spatially close to the 4-H methine proton and causes the rapid relaxation of the latter. Similar relationships are observed between the t_1 values of the $H_{(4)}$ proton in the isomers of (IIc) ($R = C_3H_7$):

$$t_1 = 2.2 \pm 0.2 \text{ sec (signal with } \delta \text{ 6.78 ppm, trans isomer)},$$
$$t_1 = 6.6 \pm 0.2 \text{ sec (signal with } \delta \text{ 6.50 ppm, cis isomer)}.$$

An attempt was made to measure the nuclear Overhauser effect (NOE) in compound (IIb). However, because of the considerable nonequivalence of the protons of the CH_2 group of the ethyl substituent it proved impossible to cause the saturation of the signals of these protons simultaneously. Precisely for this reason, the value of the NOE in compound (IIb) proved to be nonstereospecific (the NOE for the methine proton at the $C_{(4)}$ atom in the trans isomer was 6.2%, and in the cis isomer 4%).

A comparison of the signals of the $C_{(11)}$ carbon atom in the two isomeric forms of the chlorine derivatives (IIb, c) and in the initial lactones (Ib, c) enabled the following relationships to be established: $\delta C_{(11)}$ cis-II < $\delta C_{(11)}$ trans-(II) ($\Delta\delta$ 3.2 ppm), $\delta C_{(11)}$ cis-(II) $\approx$ $\delta C_{(11)}$ I — the reverse of the relationships observed for the $C_{(3a)}$ atoms. Since the $C_{(11)}$ carbon atom, like $C_{(3a)}$, is present in the γ position to the substituent (the chlorine atom), the upfield shift of the signal of the $C_{(11)}$ atom in the trans isomers of (IIb, c) can be considered as a manifestation of the "γ-gauche effect" and indicates the existence of the thiazine ring in a conformation in which the $C_{(11)}$ and Cl atoms in the trans isomer are present in the gauche orientation relative to one another.*

An analysis of molecular models shows that in the tricyclic system under consideration only two conformations of the thiazine ring are possible, in one of which the $C_{(3a)}$ and $C_{(4)}$ carbon atoms are located on the same side of the plane of the pyridine ring ("boat" type of conformation) while in the other they are on opposite sides of the plane ("half-chair" type of conformation).† The existence of a steric interaction between the chlorine and $C_{(3a)}$ carbon atoms (of the gauche or cis type) is determined by the configuration of the compound but not by the conformation of the thiazine ring: this interaction takes place in the cis isomer and is absent in the trans isomer. Conversely, an interaction of the gauche type between the Cl and $C_{(11)}$ carbon atoms depends both on the configuration and on the conformation. Such an interaction is possible in the cis isomer for a conformation of the "boat" type and in the trans isomer for a conformation of the "half-chair" type. The presence in the ^{13}C NMR spectrum of an upfield shift of the signal of the $C_{(11)}$ atom in the trans isomer shows that it is in fact the "half-chair" conformation that is preferred for the thiazine ring.

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*It is known that the "γ-trans effect" is extremely slight, especially for a chlorine atom as substituent [7].

†Although a conformation of the "boat" type appears energetically less favorable because of the loss of conjugation of the oxazolidine ring with the pyridine ring and the existence of strong steric interactions of the eclipsed substituents at the $C_{(3a)}$—$C_{(4)}$ bond, this conformation is known as the preferred one for a number of condensed tricyclic systems containing the thiazine ring [8].

The conclusions drawn on the basis of ^{13}C NMR results concerning the conformation of the thiazine ring for compounds (II) can also be extended to the initial lactones (I) by using information on the CSs in the PMR spectra. According to Table 2, the observed differences in the CSs of the 4-H proton in the cis and trans isomers of compounds (IIa-c) practically coincide with the differences in the chemical shifts of the nonequivalent $C_{(4)}H_{(A)}H_{(B)}$ protons in the initial lactons (Ia-c).* This gives grounds for considering that the influence of a chlorine atom as substituent on the chemical shift of the 4-H proton in the cis and trans isomers of chlorine derivatives (II) is, basically, exhausted by the electronic effects and does not affect either the geometry or the conformational equilibrium of the tricyclic systems under consideration. Since on the basis of the ^{13}C NMR spectra it was shown that in the trans isomers of the chlorine derivatives (II) the thiazine ring was present in the "half-chair" conformation, it is obvious that this conformation is also preferred for the thiazine ring in the initial lactones (I).

These conclusions correspond to literature information relative to the preferred "half-chair" conformation for a thiazine ring condensed with an aromatic ring or containing a double bond.

Thus, according to the results obtained, each of the 4-chlorine-substituted 3*a*-(alkyl)-7-chloro-1,2-dioxooxazolidino[3,2-f]pyrido[2,3-b]thiazines exists in solution in the form of a mixture of diastereomers, the energetically more favorable isomer being that with the trans arrangement of the chlorine atom at the $C_{(4)}$ atom and the alkyl substituent at the $C_{(3a)}$ atom. The ratio of the isomeric forms depends on the volume of the alkyl substituent. The preferred conformation of the thiophene ring in all the compounds studied is the "half-chair" conformation.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were taken on XL-100 and XL-200 (Varian) spectrometers with TMS as internal standard. To perform the experiments on the determination of the relaxation time t_1 and the measurement of the NOE in the samples investigated, the oxygen was eliminated by the passage of gaseous helium through the solution. IR spectra were taken in paraffin oil and in chloroform on a Perkin-Elmer 599 instrument, and UV spectra (in ethanol) on a Perkin-Elmer 575 spectrophotometer, and electron-impact mass spectra and DADI spectra were obtained on a Variant MAT-112 mass spectrometer with the direct introduction of the sample into the ion source at an energy of the ionizing electrons of 70 eV and a temperature of the ionization chamber of 180°C.

The characteristics of the compounds synthesized are given in Tables 1-3.

3*a*-(Alkyl)-4,7-dichloro-1,2-dioxooxazolidino[3,2-f]pyrido[2,3-b][1,4]thiazines (IIa-c). A suspension of 3.5 mole of a 3*a*-(alkyl)-7-chloro-1,2-dioxooxazolidiono[3,2-f]pyrido[2,3-b]-[1,4]thiazine (Ia-c), 32.7 mmole of $POCl_3$, and 14.3 mmole of PCl_5 was heated at 100-105° for 20 h. Then the reaction mixture was poured onto ice. The precipitate that separated out was filtered off, washed with water, dried, and recrystallized from benzene. This gave compounds (IIa-c). (IIa), mp 216-218°C. Found, %: C 39.3, H 2.1, Cl 23.1, N 9.2, S 10.5. $C_{10}H_6Cl_2N_2O_3S$. Calculated, %: C 39.5, H 2.0, Cl 23.0, N 9.2, S 10.5. Yield 98.3%. (IIb), mp 192-194°C. Found, %: C 41.4, H 2.6, Cl 22.3, N 8.7, S 10.0. $C_{11}H_8Cl_2N_2O_3S$. Calculated, %: C 41.4, H 2.5, Cl 22.2, N 8.8, S 10.0. Yield 90%. (IIc), mp 213-215°C. Found, %: C 43.3, H 3.1, Cl 21.6, N 8.4, S 9.3. $C_{12}H_{10}Cl_2N_2O_3S$. Calculated, %: C 43.2, H 3.0, Cl 21.8, N 8.4, S 9.6. Yield 93.5%.

The individuality of the compounds was confirmed by chromatography on Silufol UV-254 plates in the benzene—ethyl acetate (1:1) system. A single spot was detected for each of the substances obtained, with R_f 0.87 for (IIa) and R_f 0.9 for (IIb and c).

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*In the determination of the sign of $\Delta\delta$ for the initial lactone (Ia-c) it was assumed that, as in the chlorine derivatives (IIa-c), the signal in the weaker field corresponded to the proton in the cis position with respect to the alkyl substituent.

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INTERACTION OF 5-AMINO-2,3-TRIMETHYL-3H-INDOLE WITH p-NITROBENZALDEHYDE

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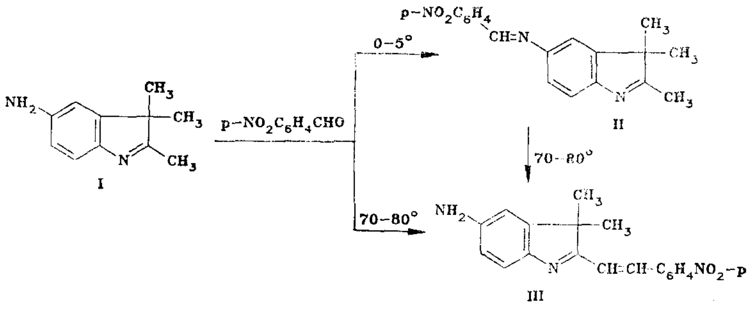
The reaction of 5-amino-2,3,3-trimethyl-3H-indole with p-nitrobenzaldehyde may take place in two directions, depending on the temperature: with the formation of a Schiff's base or of the corresponding styryl compound.

It is known that the reaction of primary amines with aldehydes leads to the formation of Schiff's bases. When 3,3-dibenzyl-2-methyl-3H-indole was heated with benzaldehyde, the corresponding styryl compound was obtained in low yield [1]. We have studied the reaction of p-nitrobenzaldehyde with 5-amino-2,3,3-trimethyl-3H-indole (I) the molecule of which has two reaction centers — the methyl group in position 2 and the amino group. It was found that the reaction took place ambiguously, and its direction depended strongly on the temperature.



The azomethine (II) was formed on the mixing of equimolar amounts of the initial compounds in ethanol at 0-5°C. Heating the initial reactants in boiling ethanol led to 5-amino-3,3-dimethyl-2-p-nitrostyryl-3H-indole (III). Chromatographic monitoring of the latter reaction showed that it took place through the stage of the formation of the azomethine (II), and the styryl compound (III) was the result of thermal rearrangement. This was also confirmed by the fact that heating the azomethine (II) in ethanol led to its conversion into compound (III).

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