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ISOMERIZATION OF PYRIDAZINO[4,5-b]INDOLES TO PYRROLO[3,4-b]INDOLES

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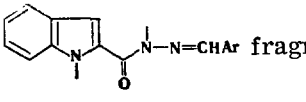
The dihydropyridazine ring undergoes contraction to a dihydropyrrole ring to give 1-phenyl-2-benzylideneaminodihydropyrrolo[3,4-b]indol-3-ones when 1-phenyldihydropyridazino[4,5-b]indol-4-ones are treated with aromatic aldehydes under acid catalysis conditions. The reaction mechanism consists in the formation of a (3-indolyl)phenylmethyl cation, which leads to opening of the pyridazine ring and subsequent development of a bond between the carbonium center and the amide nitrogen atom.

Heating 1-phenyldihydropyridazino[4,5-b]indol-4-ones (I) with aromatic aldehydes leads to the addition of 1 mole of aldehyde to 1 mole of indole compound with the loss of a molecule of water. The change in the UV spectrum (Fig. 1) on passing from starting I, which have λ_{max} 300 nm, to condensation products II, the spectra of which contain the long-wave maximum at 340 nm that is characteristic for 2-indoylhydrazones of aromatic aldehydes containing a  fragment, is significant. Compounds II are capable of undergoing slow acid hydrolysis with regeneration of the aldehyde [according to gas-liquid chromatography (GLC) data], but the second hydrolysis product cannot be isolated in pure form in this case. The increase in the frequency of the stretching vibrations of the carbonyl group from 1630 cm^{-1} in the spectrum of I to 1680 cm^{-1} in the spectra of IIa-f indicates the formation of a five-membered cyclic amide.

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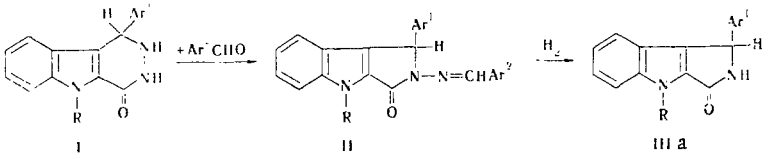
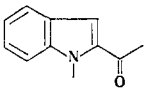
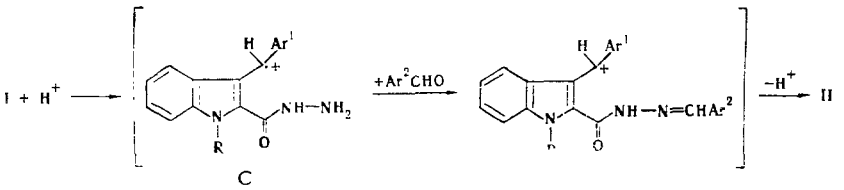
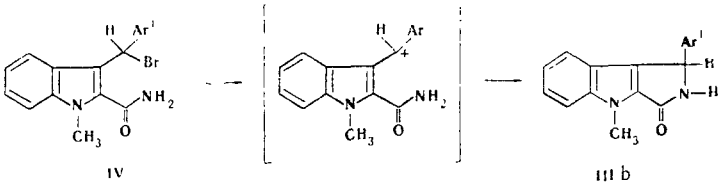


A convincing proof for the exocyclic orientation of the benzylideneamino group is provided by its cleavage when II is treated with pyrophoric nickel. The 1-phenyldihydropyrrolo[3,4-b]indol-3-one (III) formed during hydrogenolysis retains the high frequency of the stretching vibrations of the carbonyl group (1680 cm^{-1}), which reflects retention of the five-membered ring. The long-wave absorption at 340 nm vanishes in its UV spectrum, and the maximum at 300 nm characteristic for the  chromophore appears. The contraction of the six-membered pyridazine ring to a five-membered ring with migration of an amino group to the exocyclic position under the influence of aldehydes is well known for cyclic hydrazides of phthalic acid [2]. The latter react with aldehydes to give benzylidene derivatives of N-aminophthalimides. 1-Aryldihydropyridazino[4,5-b]indol-4-ones are also cyclic hydrazides, but the mechanism of contraction of the pyridazine ring in them is evidently explained by the effect of the phenyl group (in the 1 position) on the ease of cleavage of the $C_{(1)}-N$ bond. Under acid catalysis conditions, cleavage of the carbon–oxygen and carbon–halogen bonds in 1-methyl-2-carboxy-3-(α-X-benzyl)indoles (IV), where X = Cl, Br, OAc, and OAlk, leads to the formation of (3-indolyl)phenylmethyl cations [3], which have a UVspectrum with a characteristic form with a maximum at 440-460 nm.



The stability of the (3-indolyl)phenylmethyl cations increases as the electron-donor properties of the substituents in the phenyl ring increase. The latter circumstance explains the ease of ring contraction on passing from I to II for derivatives with electron-acceptor substituents (I, Ar = p-$C_6H_4OCH_3$, o-C_6H_4Cl, C_6H_5) and the unsuccessful attempt to realize this sort of transformation for derivatives containing electron-acceptor substituents (I, Ar = o-, p-$C_6H_4NO_2$). The scheme of the contraction of the dihydropyridazine ring to a dihydropyrrole ring includes the following steps: protonation, ring opening to give carbonium ion C, reaction of the hydrazide group with the aldehyde, and formation of a five-membered ring by nucleophilic attack by the amide nitrogen atom on the carbonium center. The effect of acid catalysis on the reaction rate is followed by the use of bases and the hydrochlorides of I. In the first case the reaction in refluxing amyl alcohol is complete in 3-4 h, whereas in the second case it is complete in 5-15 min. The UV spectrum of 1-phenyl-5-methyldihydropyridazino[4,5-b]indol-4-one (Fig. 1, curve 4), recorded in 80% sulfuric acid, the form and position of the λ_{max} (462 nm) of which are close to those in the UV spectrum of 1-methyl-2-carboxy(3-indolyl)phenylmethyl cation (Fig. 1), served as a direct proof of the development of carbonium ion C. Experiments on the synthesis of 1-aryldihydropyrrolo[3,4-b]indol-3-ones (III) from amides and anilides of 1-methyl-3-(α-chlorobenzyl)indol-2-carboxylic acid (IV) [4] served as proof for the last step of the above scheme – nucleophilic attack on the carbonium center by the amide nitrogen atom:



EXPERIMENTAL

The UV spectra of $0.1-0.5 \cdot 10^{-4}$ M ethanol solutions of the compounds were recorded with an SF-16 spectrophotometer. The IR spectra of mineral oil suspensions of the compounds were recorded with A UR-20 spectrometer.

1-Phenyl-2-benzylidenedihydropyrrolo[3,4-b]indol-3-one (IIa). A mixture of 3 g (0.01 mole) of 1-phenyldihydropyridazino[4,5-b]indol-4-one hydrochloride [5] and 1 g (0.01 mole) of benzaldehyde in 25 ml of amyl

TABLE 1. 1-Phenyl-2-benzylideneaminodihydropyrrolo[3,4-b]-indol-3-ones (II)

Compound	Ar¹	Ar²	R	mp, °C	Empirical formula	Found, %				Calculated, %				Yield, %
						C	H	N	halogen	C	H	N	halogen	
IIa	H	H	H	290	$C_{25}H_{17}N_3O$	78,6	4,9	11,9	—	78,6	4,8	12,0	—	54
IIb	*p*-OCH_3	*p*-OCH_3	H	271	$C_{25}H_{21}N_3O_3$	72,9	5,0	10,1	—	73,0	5,1	10,2	—	63
IIc	*p*-OCH_3	*o*-Cl	H	265	$C_{24}H_{18}ClN_3O_2$	69,2	4,3	10,1	8,6	69,3	4,3	10,1	8,5	65
IId	*p*-OCH_3	H	H	260	$C_{24}H_{19}N_3O_2$	75,7	5,0	10,9	—	75,6	5,0	11,0	—	58
IIe	*p*-OCH_3	*o*-Cl	CH_3	190	$C_{25}H_{20}ClN_3O_2$	69,9	4,7	9,8	8,2	69,8	4,6	9,8	8,3	68
IIf	*o*-Cl	*o*-Cl	H	273	$C_{23}H_{15}Cl_2N_3O$	63,2	3,8	9,4	16,2	63,0	3,9	9,6	16,2	82

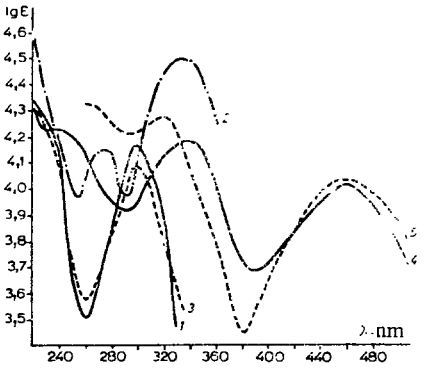


Fig. 1. UV spectra: 1) 1-phenyldihydropyridazino[4,5-b]indol-4-one [5]; 2) 1-phenyl-2-benzylideneaminodihydropyrrolo[3,4-b]-indol-3-one [6]; 3) 1-phenyldihydropyrrolo[3,4-b]indol-3-one in alcohol [4]; 4) 1-phenyl-4-methyldihydropyridazino[4,5-b]indol-4-one in 80% H_2SO_4 [5]; 5) the 1-methyl-2-carboxy(3-indolyl)phenylmethyl cation in 80% H_2SO_4 [3].

alcohol was refluxed until a precipitate began to form (15 min). The precipitate was crystallized from dioxane to give 1.54 g (54%) of IIa. Compounds IIb-f were similarly obtained from the corresponding dihydropyridazinoindoles I and aromatic aldehydes (see Table 1).

1-Phenyldihydropyrrolo[3,4-b]indol-3-one (IIIa). A mixture of 1 g (0.003 mole) of IIa and 10 g of Raney nickel in 200 ml of dioxane was refluxed with vigorous stirring in a stream of nitrogen for 3 h, after which the catalyst was removed by filtration, and the filtrate was vacuum evaporated to dryness. Crystallization of the dry residue from ethanol gave 0.60 g (75%) of IIIa with mp 238°. Found: C 77.5; H 4.9; N 11.1%; M (by the Rast method) 230. $C_{16}H_{12}N_2O$. Calculated: C 77.4; H 4.8; N 11.3%; M 248. IR spectrum: λ_{max} 300 nm, (log ε), 4.091. A compound identical to IIIa was obtained by the indicated treatment of the chlorine-containing derivative IIf because of reductive dehalogenation.

1-(p-Methoxyphenyl)-4-methyl-1,2-dihydropyrrolo[3,4-b]indol-3-one (IIIb). A 10-ml sample of acetic acid saturated with hydrogen bromide was added at 0° to a mixture of 1.74 g (0.01 mole) of 1-methyl-2-carboxamidoindole and 1.36 g (0.01 mole) of anisaldehyde at 0°. The solution of bromide IV was cooled for 30 min, after which it was allowed to stand at room temperature for 15 h. It was then washed three times with hexane–ether (1 : 1) and twice with hexane and triturated in ethanol. The resulting crystals were removed by filtration and purified by crystallization from ethanol to give 2.1 g (72%) of IIIb with mp 221-222°. PMR spectrum, ppm: 8.22-7.50, 9H; 5.84, 1H; 3.97, 3H (N_4-CH_3); 3.77, 3H (OCH_3). Found: C 74.4; H 5.5; N 8.5%. $C_{18}H_{16}N_2O_2$. Calculated: C 74.0; H 5.5; N 9.6%.

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PYRIMIDINYLFORMAZANS

I. SYNTHESIS AND STUDY OF UNSYMMETRICAL 1-(4,6-DIMETHYL-2-PYRIMIDINYL)-5-ARYLFORMAZANS

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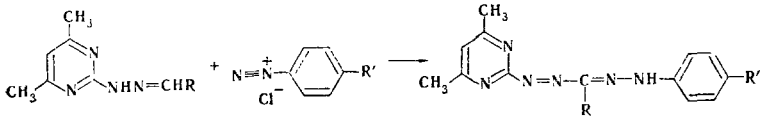
1-(4,6-Dimethyl-2-pyrimidinyl)-3-methyl(aryl)-5-arylformazans, the structures of which depend on the substituents attached to 3-C, were obtained by diazo coupling of arenediazonium salts with 4,6-dimethyl-2-pyrimidinylhydrazones.

Pyrimidinylformazans have been described only in [1]. The present research was carried out in order to ascertain the effect of the pyrimidine ring and the substituents in it on the electronic spectra of formazans.

The 1-(4,6-dimethyl-2-pyrimidinyl)-3-methyl(aryl)-5-arylformazans (III-IX) were synthesized by diazo coupling of arenediazonium salts II with 4,6-dimethyl-2-pyrimidinylhydrazones of benzaldehyde, p-chlorobenzaldehyde, and acetaldehyde (Ia-c).



I II III-IX

I—II a $R=CH_3$, $R'=H$; b $R=C_6H_5$, $R'=CH_3$; c $R=p\text{-}ClC_6H_4$, $R'=NO_2$; III $R=CH_3$, $R'=H$; IV $R=CH_3$, $R'=CH_3$; V $R=CH_3$, $R'=NO_2$; VI $R=C_6H_5$, $R'=H$; VII $R=C_6H_5$, $R'=CH_3$; VIII $R=C_6H_5$, $R'=NO_2$; IX $R=p\text{-}ClC_6H_4$, $R'=H$

Pyrimidinylformazans III-IX are orange to red-brown or greenish-black crystalline substances that can be stored for a long time without decomposition. Deeply colored solutions of the salts are formed when these compounds are dissolved in alcoholic alkali. The salts of formazans V and VIII, which contain a nitro group (Table 1), are most deeply colored (blue-violet). The color of the alcohol solutions of the formazans changes to light-yellow when they are acidified, and this color vanishes on standing.

An intense absorption band of NH stretching vibrations at 3370-3380 cm^{-1} is observed in the IR spectra of III-V with a methyl group attached to 3-C. They consequently have an open structure (probably trans-anti or trans-syn forms [2, 3]).

The spectrum of formazan IX does not contain the band of an NH bond, whereas the spectra of VI and VII have a very weak absorption band at 3360-3365 cm^{-1}. This provides a basis for the assumption that formazans with a phenyl group attached to 3-C exist in the s-cis conformation of the trans-syn form, which is stabilized by

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