shifts are due to primary coordination of $Eu(FOD)_3$ with the ring nitrogen atom in structure Ia. The conclusion regarding the primary existence of the investigated structures in the amino form makes it possible to conclude that the half-chair conformation is the most stable conformation for them. The absence of doubled signals in the spectra constitutes evidence that these compounds are isomerically homogeneous (they have one variant of orientation of the CH_3 groups relative to the plane of the ring). It is difficult to make an unambiguous choice between the cis and trans isomers. However, an examination of Dreiding models of I with allowance for the observed paramagnetic shifts makes it possible to prefer the cis-axial isomer.

EXPERIMENTAL

The PMR spectra of the compounds at various temperatures and in various solvents were recorded with a BS-487-C spectrometer with hexamethyldisiloxane as the internal standard; the operating frequency of the spectrometer was 80 MHz.

Amides II-V and p-toluenesulfonic acid amide V were obtained by acylation of 2H,6H-2,6-dimethyl-4-amino-1,3,5-dithiazine (Ia) with the anhydrides and chlorides of the corresponding acids. 6H-2,6-Dimethyl-4-amino-2,3-dihydro-1,3,5-thiadiazine was synthesized by the method in [5].

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1-ARYLAMINO-3-PHENYL-2,3-DIHYDRO-2-INDOLONES

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UDC 547.754'756'759

α-Chlorodiphenylacetyl chloride reacts with arylhydrazines to give 1-arylamino-3-phenyl-2,3-dihydro-2-indolones, which undergo acetylation at the nitrogen and oxygen and undergo benzoylation at the nitrogen atom.

It is known that α-chlorodiphenylacetyl chloride reacts with 1,1-dimethylhydrazine [1] and 1-methyl-1-benzylhydrazine [2] to give 1-amino-3-phenyl-2,3-dihydro-2-indolone derivatives. We studied this reaction in the case of monosubstituted hydrazines, viz., arylhydrazines Ia-m. In this reaction one may assume the formation of derivatives of diazetidinone, indolone IV, and cinnolone; however, judging from the data from the IR, PMR, and mass spectra, indolones IVa-m are formed, as in the case of 1,1-disubstituted hydrazines.

The occurrence of the reaction through intermediate III is proved by alternative synthesis of IVa, d from phenylhydrazide VIIa [3] and p-tolylhydrazide VIId [4] of benzilic acid. We were unable to isolate intermediate III, which indicates its high reactivity, in contrast to the anilide [5, 6] or 4-methylphenylamide [7] of α-chlorodiphenylacetic acid. The synthesized compounds are presented in Table 1.

In the IR spectrum of derivative IVa the band of the amide C=O group lies at 1725 cm^{-1}, while the NH band is found at 3320 cm^{-1} in the crystalline state and at 3350 cm^{-1} in

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A. M. Gor'kii Perm State University, Perm 614000. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 488-490, April, 1981. Original article submitted April 8, 1980.

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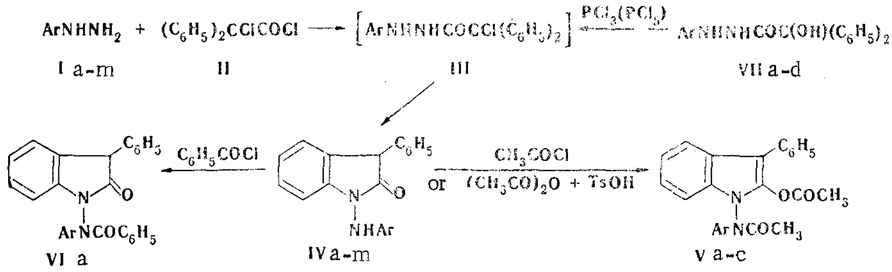

Ar = a C_6H_5; b 2-$CH_3C_6H_4$; c 3-$CH_3C_6H_4$; d 4-$CH_3C_6H_4$; e 2,4-$(CH_3)_2C_6H_3$; f 2,5-$(CH_3)_2C_6H_3$; g 2-ClC_6H_4; h 4-ClC_6H_4; i 2,4-$Cl_2C_6H_3$; j 2-BrC_6H_4; k 4-BrC_6H_4; *l* 4-IC_6H_4; m 4-$CH_3OC_6H_4$

solution in $CHCl_3$. The PMR spectrum of IVa in dioxane contains a singlet of a proton attached to C_3 at 4.68 ppm, a singlet of an NH group at 7.68 ppm, and signals of aromatic protons at 6.58-7.25 ppm. The mass spectrum of IVa contains a molecular-ion peak (M^+) at m/e 300 (90% relative intensity), as well as peaks at 271 (30), 208 (35), 195 (100), 180 (69), 165 (58), 160 (32), 152 (30), 132 (34), 104 (24), 92 (23), 77 (64), 65 (32), 51 (22), 39 (21), 29 (40). The principal fragmentation processes of IVa in the case of electron impact are detachment of an NHC_6H_5 group and decarbonylation.

Compounds IVa-c were acetylated with acetyl chloride in benzene or with acetic anhydride in the presence of p-toluenesulfonic acid to give 1-(N-acetyl-N-aryl)amino-2-acetoxy-3-phenylindoles Va-c; this is in agreement with the chemical behavior of 3-phenyloxindole in acetylation [8]. The NH band at 3315-3325 cm^{-1} (for crystals) and the C=O band at 1720-1730 cm^{-1} vanish in the IR spectra of Va-c, but C=O bands appear at 1735 and 1690 cm^{-1}. The acetyl derivatives are presented in Table 2.

The benzoylation of IVa with benzoyl chloride in benzene (for 1-4 h) takes place only at the nitrogen atom to give 1-(N-benzoyl-N-phenyl)amino-3-phenyl-2,3-dihydro-2-indolone (VIa); the NH band (3320 cm^{-1}) of a crystalline sample vanishes in the IR spectrum in this case, but a C=O band (1680 cm^{-1}) appears.

TABLE 1. 1-Arylamino-3-phenyl-2,3-dihydro-2-indolones (IVa-m)

Compound IV	mp,* °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
a	166—167	80,3	5,2	9,4	$C_{20}H_{16}N_2O$	80,0	5,3	9,3	60
b	125—126	79,9	5,7	8,8	$C_{21}H_{18}N_2O$	80,3	5,7	8,9	53
c	139—140	80,2	5,8	8,8	$C_{21}H_{18}N_2O$	80,3	5,7	8,9	55
d†	110—111	80,3	5,7	8,7	$C_{21}H_{18}N_2O$	80,3	5,7	8,9	58
e	135—136	80,4	6,3	8,3	$C_{22}H_{20}N_2O$	80,6	6,1	8,5	23
f	164—165	80,8	6,0	8,1	$C_{22}H_{20}N_2O$	80,6	6,1	8,5	60
g	146—147	72,1	4,6	8,3	$C_{20}H_{15}ClN_2O$	71,9	4,5	8,4	24
h†	147—148	71,8	4,5	8,0	$C_{20}H_{15}ClN_2O$	71,9	4,5	8,4	67
i	134—135	65,0	3,9	7,5	$C_{20}H_{14}Cl_2N_2O$	64,8	3,8	7,5	14
j	144—145	63,3	3,9	7,3	$C_{20}H_{15}BrN_2O$	63,3	4,0	7,4	48
k†	150—151	63,2	3,9	7,3	$C_{20}H_{15}BrN_2O$	63,3	4,0	7,4	70
l	146—147	56,4	3,6	6,8	$C_{20}H_{15}IN_2O$	56,3	3,5	6,6	56
m	147—148	75,1	5,4	8,1	$C_{21}H_{18}N_2O_2$	75,6	5,4	8,5	28

*The compounds were recrystallized: IVe from heptane, IVg from CCl_4, IVi from cyclohexane, and the remaining compounds from alcohol.

†Compounds IVd, h, k form crystal solvates with benzene with mp 62-63, 83-84, and 93-94°C, respectively.

TABLE 2. 1-(N-Acetyl-N-aryl)amino-2-acetoxy-3-phenylindoles (Va-c)

Compound V	mp, °C (from alcohol)	N found, %	Empirical formula	N calc., %	Yield, %
a	153—154	7,2	$C_{24}H_{20}N_2O_3$	7,3	72
b	145—146	6,9	$C_{25}H_{22}N_2O_3$	7,0	76
c	127—128	6,9	$C_{25}H_{22}N_2O_3$	7,0	83

EXPERIMENTAL

The IR spectra of mineral oil suspensions and solutions of the compounds in $CHCl_3$ were recorded with a UR-20 spectrometer. The PMR spectrum of a solution in dioxane was recorded with a Tesla BS-487C spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The mass spectrum of IVa was recorded with a Varian MAT-311 spectrometer with direct introduction of the substance into the ion source at an ionization energy of 70 eV at 50°C. The purity of all of the synthesized compounds was verified by thin-layer chromatography (TLC) on Silufol UV-254 plates in a benzene—ethyl acetate system (5:1).

1-Phenylamino-3-phenyl-2,3-dihydro-2-indolone (IVa). A) A solution of 26.51 g (0.1 mole) of II in 100 ml of ether was added at −20°C to a solution of 32.44 g (0.3 mole) of phenylhydrazine in 100 ml of diethyl ether, and the mixture was allowed to stand at 20°C for 8 h. A solution of 10 g of NaOH in 150 ml of water was added, the mixture was stirred for 20 min, and the remaining precipitate was treated with ether and water and crystallized from alcohol to give 18.02 g of IVa with mp 166-167°C. Found: N 9.4%. $C_{20}H_{16}N_2O$. Calculated: N 9.3%. The reaction also proceeds smoothly in up to 70% yields in benzene and THF; the desired product was obtained in 5% yield in DMF, and resinous products were formed in ethanol.

B) A mixture of 3.18 g (0.01 mole) of benzilic acid phenylhydrazide (VIIa) and 1.37 g (0.01 mole) of PCl_3 in 15 ml of dioxane was heated on a water bath for 1 h, after which it was allowed to stand for 12 h. It was then poured into a saturated solution of $NaHCO_3$ in water, and the resulting precipitate was dried and extracted with 40 ml of boiling toluene. Workup of the solution yielded 0.9 g (30%) of IVa, which was purified by recrystallization from alchol with activated charcoal. The reaction of VIIa with PCl_5 was carried out similarly; after treatment with $NaHCO_3$, the residue was crystallized from alcohol to give the product in 42% yield.

No melting-point depression was observed for a mixture of the compounds obtained by methods A and B, and their IR spectra were identical; however, method A gave a purer product. Compounds IVb, c, k were formed in low yields by method B and were detected by TLC on Silufol by comparison with genuine samples.

1-(4-Methylphenylamino)-3-phenyl-2,3-dihydro-2-indolone (IVd). A solution of 6.35 g (25.8 mmole) of II in 15 ml of THF was added at −20°C to 9.45 g (77.5 mmole) of 4-methylphenylhydrazine in 40 ml of THF. After 8 h, 7.75 g of the hydrochloride of Id was removed by filtration, the filtrate was evaporated, and the residue was treated with 55 ml of benzene. Filtration gave 5.62 g of the adduct of IVd with benzene with mp 62-63°C; crystallization from alcohol gave 4.68 g (58%) of IVd with mp 110-111°C. Found: N 8.7%. $C_{21}H_{18}N_2O$. Calculated: N 8.9%. Compounds IVb, c, e-m were similarly obtained. Compound IVd was obtained in 30% yield by method B from VIId and PCl_5.

1-(N-Benzoyl-N-phenyl)amino-3-phenyl-2,3-dihydro-2-indolone (VIa). A mixture of 1 g (3.3 mmole) of IVa with 2 ml of benzoyl chloride was heated on a water bath for 2 h, and the mixture was poured into 50 ml of water. The resulting precipitate was washed with ether and crystallized from benzene to give 0.89 g (66%) of VIa with mp 170-172°C. Found: N 6.9%. $C_{27}H_{20}N_2O_2$. Calculated: N 6.9%.

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