of trans isomer Va in the form of an oil. IR spectrum (film): 1730 (CO) and 1615 cm⁻¹ (C₆H₅). UV spectrum (in heptane): λ_{max} 307 (ϵ 67) and 253 nm (shoulder, ϵ 470).

Decahydro-4-quinolone Ethylene Ketals (VII-IX). A mixture of 3 mmole of the mixture of isomers IV-VI, 3 mmole of p-toluenesulfonic acid, 6 mmole of ethylene glycol, and 30 ml of absolute benzene was refluxed with a Dean-Stark trap for 4 h (with chromatographic monitoring), after which the mixture was made alkaline with aqueous NaOH, and the benzene layer was washed with water until the wash liquid was neutral and dried with Na₂SO₄. The solvent was removed to give a mixture of cis- and trans-amino ketals VII-IX. The individual isomers were isolated by chromatography with a column filled with neutral Al_2O_3 by successive elution with petroleum ether and petroleum ether-ether (15:1, 10:1, 5:1, and 3:1). The chromatographically homogeneous fractions were combined and evaporated to give chromato-graphically individual isomers of ethylene ketals VIIa,b-IXa,b.

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6-SUBSTITUTED 1-HETARYLAMINO-3-ARYLOXINDOLES

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6-Substituted l-hetarylamino-3-aryl-2,3-dihydro-2-indolones were obtained by cyclization of diarylglycolic acid hetarylhydrazides in concentrated H_2SO_4 . The ability of the compounds obtained to undergo acylation was demonstrated. A cyclization mechanism is proposed. The IR, PMR, and mass spectra of the synthesized compounds were studied.

It is known that diarylglycolic acid 2-aryl-1,2-dialkylhydrazides are converted to cinnolones under the influence of concentrated sulfuric acid [1], whereas diarylglycolic acid 2-acyl-1-arylhydrazides are converted to 1-acyl-amino-3,3-diarylindolones [2]. We have studied the reaction with concentrated sulfuric acid of diarylglycolic acid 2-pyridyl-(IIa-c [3]), 2-quinolyl-(IId,e [4]), and 8-quinolylhydrazides (IIf-h, Table 1); the latter were synthesized by the method in [5] by the reaction of oxalic acid ethyl ester 8-quinolyl-hydrazide (I) with Grignard reagents:



Intensely colored halochromic salts are formed when hydrazides IIa-h are added to concentrated sulfuric acid [6]. The color of the solution vanishes on standing as a consequence of conversion of the carbonium ion to stable colorless substances, which are isolated from the reaction mixtures by dilution with water and neutralization. According to the

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TABLE 1. Diarylglycolic Acid 8-Quinolylhydrazides

Com- pound	Ar	mp,°C	Found, %			Empirical formula	С	Yield,		
			c	н	N		,C	н	N,	%
llf Ilg Ilh	C6H5 p-FC6H4 p-ClC6H4	$188 - 189 \\ 174 - 175 \\ 205 - 206$	74,5 68,0 62,9	5,3 4,4 3,8	11,1 10,0 9,2	$\begin{array}{c} C_{23}H_{19}N_{3}O_{2}\\ C_{23}H_{17}F_{2}N_{3}O_{2}\\ C_{23}H_{17}Cl_{2}N_{3}O_{2}\end{array}$	74,8 68,1 63,0	5,2 4,2 3,9	11,4 10,4 9,6	90 61 76

TABLE 2. 6-Substituted 1-Hetarylamino-3-aryloxindoles

Com- pound	Ar	Hetaryl	mp, °C	Found, %			Empirical	Catc., %			Yield, %
				С	н	N	formula	с	н	N	
[][a]]]b]]]c	C ₈ H ₅ p-FC ₆ H ₄ p-ClC ₆ H ₄	2-Pyridyl 2-Pyridyl 2-Pyridyl	136—137 136—137 132 dec.	75,5 67,5 61,4	5,2 4,0 3,6	13,8 13,2 11,2	C19H15N3O C19H13F2N3O C19H13Cl2N3O	75,7 67,7 61,6	5,0 3,9 3,5	13,9 12,8 11,4	61 49 46
]]]d	ρ -FC ₆ H ₄	2-Quinolyl	147—148	71,5	4,1	11,0	$C_{23}H_{15}F_2N_3O$	71,3	3,9	10,9	43
llle lllf lllg lllh	p-ClC ₆ H ₄ C ₆ H ₅ p-FC ₆ H ₄ p-ClC ₆ H ₄	2-Quinolyl 8-Quinolyl 8-Quínolyl 8-Quinolyl	dec. 209—210 179—180 181—182	66,0 78,4 71,2 65,9	3,8 4,7 3,8 3,8	9,9 11,6 10,7 9,8	C ₂₃ H ₁₅ Cl ₂ N ₃ O C ₂₃ H ₁₇ N ₃ O C ₂₃ H ₁₅ F ₂ N ₃ O C ₂₃ H ₁₅ Cl ₂ N ₃ O	65,7 78,6 71,3 65,7	3,6 4,9 3,9 3,6	10,0 11,9 10,9 10,0	54 50 79 64

results of elementary analysis and data from the IR, PMR, and mass spectra, 6-substituted l-hetarylamino-3-aryloxindoles (IIIa-h, Table 2) are formed as a result of the investigated reaction.

A band of an amide carbonyl group at $1721-1735 \text{ cm}^{-1}$ and a band of an NH group at $3290-3340 \text{ cm}^{-1}$ are observed in the IR spectra of crystals of the synthesized compounds; the band of the NH group is shifted to $3360-3365 \text{ cm}^{-1}$ in the spectrum of a solution in CHCl₃. The PMR spectrum of IIIa in pentafluorochlorobenzene contains a singlet of a 3-H proton of 4.94 ppm, a singlet of the proton of the NH group at 8.15 ppm, and signals of aromatic and pyridine protons at 6.61-8.03 ppm. The mass spectrum* of IIa contains a molecular-ion peak (M⁺) at 301 and peaks of fragment ions at 272 (17), 257 (8), 208 (32), 196 (34), 180 (13), 165 (27), and 156 (5). The principal fragmentation processes of the molecular ion of IIIa under electron impact are detachment of a 2-C₅H₄NNH group and decarbonylation.

The proposed reaction mechanism includes the formation of an unstable aziridinone from the carbonium ion and its rearrangement to an indolene, as in the synthesis of indolene derivatives by the reaction of di- and monosubstituted hydrazines and α -chlorodiphenylacetyl chloride [7, 8].



In the case of IIIa we demonstrated the ability of the synthesized compounds to undergo acylation. 1-(p-Bromobenzoy1-2-pyridy1)amino-2-(p-bromocarbobenzoyy)-3-phenylindole (IVa) was obtained by the reaction of IIIa with p-bromobenzoy1 chloride in pyridine. Treatment of this product with 5% alcoholic alkali gives 1-(p-bromobenzoy1-2-pyridy1)amino-3-phenyloxindole (VIa). Compound VIa was also obtained by alternative synthesis by the reaction of benzilic acid N-(p-bromobenzoy1)-2-pyridy1hydrazide (Va) with concentrated sulfuric acid:

*The m/z values (intensities in percent with respect to the maximum peak) are given.



The NH (3310 cm⁻¹) and C=O (1727 cm⁻¹) bands vanish in the IR spectrum of IVa, while C=O (ester, 1750 cm⁻¹) and C=O (amide, 1695 cm⁻¹) bands appear. The NH band (3310 cm⁻¹) vanishes in the IR spectrum of crystals of VIa, and a C=O band (1693 cm⁻¹) appears.

EXPERIMENTAL

The IR spectra of mineral oil suspensions and solutions of the compounds in $CHCl_3$ were recorded with an IKS-22 spectrometer. The PMR spectrum of a 10% solution of IIIa in penta-fluorochlorobenzene was recorded with a BS-487 C spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The mass spectra of IIIa was recorded with an AEI MC-30 spectrometer at 80°C and an ionization energy of 70 eV. The individuality of the synthesized compounds was monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates in an ether-acetone-benzene system (3:1:3) with development with iodine vapors.

Oxalic Acid Ethyl Ester 8-Quinolylhydrazide (I). A solution of 10 g (0.062 mole) of 8-quinolylhydrazine [9] in a mixture of 40 g of diethyl oxalate and 60 ml of ethanol was allowed to stand for 24 h, after which the precipitate was removed by filtration and recrystallized from ethyl acetate to give 7.4 g (46%) of hydrazide I with mp 171-172°C. Found: N 16.4%. $C_{13}H_{13}N_{3}O_{3}$. Calculated: N 16.2%.

Benzilic Acid 8-Quinolylhydrazide (IIf). A 2.59-g (0.01 mole) sample of hydrazide I was added to a Grignard reagent obtained from 15.7 g (0.1 mole) of bromobenzene and 2.4 g (0.1 mole) of magnesium in absolute ether. The reaction mixture was stirred at room temperature for 5 min, after which it was decomposed with a saturated solution of ammonium chloride. The product was separated and recrystallized from ethanol to give 3.3 g (90%) of IIf with mp 188-189°C. Compounds IIg, h were similarly obtained.

<u>1-(2-Pyridylamino)-3-phenyloxindole (IIIa).</u> A 1.0-g (3.1 mmole) sample of IIa was added in portions to 30 ml of concentrated H_2SO_4 , during which the initial red-violet coloration changed to light yellow. The mixture was maintained at room temperature for 15 min, after which it was poured into 700 ml of water, and the aqueous mixture was neutralized to pH 7 with 25% aqueous NaOH solution. The precipitate was separated and recrystallized from heptane to give 0.58 g (61%) of oxindole IIIa with mp 136-137°C. Compounds IIIb-h were similarly obtained.

<u>l-(p-Bromobenzoyl-2-pyridyl)amino-2-(p-bromocarbobenzoxy)-3-phenylindole (IVa).</u> A mixture of 0.4 g (1.3 mmole) of IIIa with 0.4 g (0.018 mole) of p-bromobenzoyl chloride in 10 ml of dry pyridine was heated at 90°C for 1 h, after which it was poured into 40 ml of water. The precipitate was separated and recrystallized from alcohol to give 0.35 g (40%) of IVa with mp 222°C (dec.). Found: Br 23.7; N 6.4%. $C_{33}H_{21}Br_2N_3O_3$. Calculated: Br 24.0; N 6.3%.

Benzilic Acid N-(p-Bromobenzoyl)-2-pyridylhydrazide (Va). A mixture of 1.0 g (3.1 mmole) of hydrazide IIa with 0.7 g (3.1 mmole) of p-bromobenzoyl chloride in 20 ml of dry pyridine was heated at 90°C for 1 h, after which it was poured into 60 ml of water, and the precipitate was separated and recrystallized from ethanol to give 1.2 g (76%) of Va with mp 196-197°C. Found: Br 16.0; N 8.2%. $C_{26}H_{20}BrN_3O_3$. Calculated: Br 15.9; N 8.5%.

 $\frac{1-(p-Bromobenzoy1-2-pyridy1)amino-3-phenyloxindole (VIa).}{A) A 1.0-g (0.002 mole)}$ sample of Va was subjected to reaction with concentrated H₂SO₄ as in the synthesis of oxindole IIIa. Workup gave 0.42 g (44%) of VIa with mp 199-200°C. Found: Br 16.8; N 8.3%. C₂₆H₁₈BrN₃O₂. Calculated: Br 16.5; N 8.7%.

B) A mixture of 0.2 g (0.3 mmole) of IVa with 10 ml of a 5% solution of KOH in ethanol was refluxed for 5 min, after which it is diluted with 5 ml of water, and the mixture was cooled to give 0.15 g (85%) of oxindole VIa with mp 199-200°C. According to TLC data, the product was identical to the compound obtained by method A.

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CONDENSATION OF AZAFLUORENES WITH AROMATIC

ALDEHYDES UNDER PHASE-TRANSFER-CATALYSIS

CONDITIONS

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Aryl-substituted (in the oxirane ring) spiro[azafluorene-9,2'-oxiranes] were obtained, and their configuration was established. The substances that are formed under phase-transfer catalysis conditions in the condensation of 1-azafluorene with benzaldehyde were studied. A relationship between the ratio of aryl-substituted (in the oxirane ring) isomeric spiro[azafluorene-9,2'-oxiranes] and the position of the nitrogen atom in the azafluorene fragment was established.

Spiro compounds that contain azafluorene and oxirane fragments have been obtained in up to 50% yields by Darzens method under phase-transfer catalysis conditions from 4-azafluorene and 3-methy1-2-azafluorene and benzaldehyde. 9,9-Dichloroazafluorenes and bis(9azafluorenylidenes) were isolated in addition to the spiro compounds in these reactions [1].

In the present communication we present the results of experiments on the condensation of 1-azafluorene (I) with benzaldehyde in the presence of 50% aqueous sodium hydroxide solution, carbon tetrachloride, and catalytic amounts of triethylbenzylammonium chloride (TEBAC).

By chromatographic separation of the complex mixture of products of this reaction we isolated the Z and E isomers of 9-benzylidene-1-azafluorene (IIa,b), 9,9-dichloro-1-aza-fluorene (III), 3-phenylspiro[1-azafluorene-9,2'-oxirane] (IV), and a small amount of

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