4. N. Engel and W. Steglich, Angew. Chem., 90, 719 (1978).
5. H. Berner, G. Schulz, and H. Reinshagen, Monatsh. Chem., 108, 285 (1977).
6. B. A. Trofimov, S. E. Korostova, A. I. Mikhaleva, L. N. Balabanova, A. N. Vasil'ev, and M. V. Sigalov, USSR Inventor's Certificate No. 601282; Byull. Izobret., No. 13, 79 (1978).
7. A. Lochman, Organic Syntheses [Russian translation], Collective Vol. 2, Moscow (1949), p. 393.

PREPARATION OF 1-(4-NITROPHENYL)-2-FORMYLPYRROLE FROM FURFURAL

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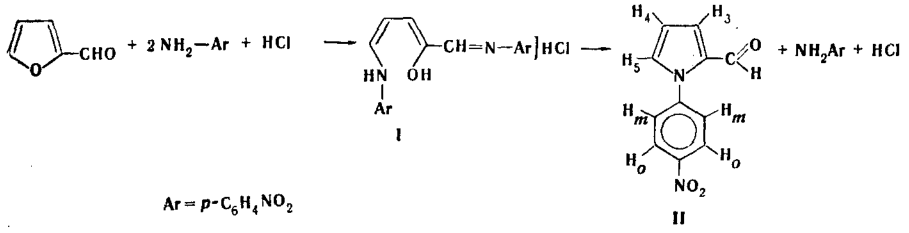
The products of the condensation of furfural with p-nitroaniline in an acidic medium in various solvents were investigated. It was established that the well-known method gives 1-(4-nitrophenyl)-2-formylpyrrole in no higher than 55% yield and 2,3-bis(4-nitrophenylamino)-2-formylpyrrole in 27% yield. A method based on a previously described method is recommended (the products are obtained in up to 72% yields).

The condensation of furfural with aromatic amines is of interest as a method for the conversion of compounds of the furan series to pyrrole derivatives. 1-(4-Nitrophenyl)-2-formylpyrrole (II) can be obtained by this method from p-nitroaniline through Stenhouse salt I [1-3]:



A method [1] involving the use of ethanol as the solvent and a method [2] that differs from the former in that methanol is used in place of ethanol and less hydrochloric acid is employed have been proposed for the synthesis of II. The Janovsky method [2] is well known; the Lüpke method [1] is described in a literature source that is difficult to obtain. In the opinion of the authors, both methods ensure quantitative yields. In the first case these yields are achieved by repeated precipitation of the reaction product after evaporation of the alcohol, while in the second case they are obtained by direct isolation of the reaction products from the reaction mixtures.

However, Petit and Pallaud [3] note the difficulties involved in the preparation of formylpyrrole II, viz., resinification and a decreased yield. Replacement of the hydrochloric acid by a cation-exchange resin did not improve the results very much [3]. The synthesis of formylpyrrole has not found wide laboratory application, although this compound is extremely promising as an intermediate for the preparation of various N-substituted pyrroles.

It is known that the reaction of furfural with aromatic amines may proceed via different pathways, depending on the synthetic conditions and the structure of the amine. The formation of pyridinium salts in addition to pyrrole derivatives is possible in an acidic medium [1, 4]; diaminocyclopentenones were obtained in a neutral medium [4]. The formation of aminopyrrolinones is also assumed [5].

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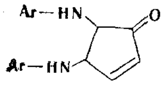
TABLE 1. Yields and Compositions of the Reaction Products in Various Solvents at Various pH Values of the Media (for a furfural to p-nitroaniline ratio of 1:2)

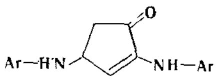
Expt. No.	HCl moles	Solvent	pH±0,05	Overall yield of the mixture of products based on II, %	Yield, %		Amount of resin in the reaction product, %
					II	III (IV)	
1	0,5	Methanol	0,8	98	54	27	—
2	1	Methanol	0,7	68	37	—	40
3	0,2	Ethanol	2,0	73	11	38	—
4	0,5	Ethanol	1,6	83	37	28	—
5	1	"	1,3	70		—	—
6	2	"	1,1	44	33	—	20
7	4	"	0,8	69	28	—	55
8	1	Propyl alcohol	1,6	58	49	(5)	—
9	1	Isopropyl alcohol	1,8	51	36	(9)	—
10	1	DMF	2—3,6	122	—	(75)	—
11	1	Acetic acid	1,0	54	32	—	35

The compositions of the reaction products obtained by the methods described in [1-3] have not been previously verified.

We have established by means of thin-layer chromatography (TLC) that a compound identified as 2,3-bis(4-nitrophenylamino)-4-cyclopentenone (III) is formed along with aldehyde II in the synthesis by the method in [2]. Formylpyrrole II was obtained free of other compounds by the method in [1]. When we replaced ethanol by dimethylformamide (DMF), we obtained 2,4-bis(4-nitrophenylamino)-2-cyclopentenone (IV) by the same method.



III



IV

Ar = $p\text{-}C_6H_4NO_2$

Compounds III and IV are similar to formylpyrrole II with respect to their appearance and solubility in alcohol and acetone. They were previously obtained by another method [4]; however, their formation in an acidic medium was not described.

We investigated the effect of the pH of the medium and the nature of the solvent on the reaction products and ascertained the conditions under which the formation of formylpyrrole II predominates.

We used the methods for the preparation of II [1, 2] as the basis for our study. Solvents of the aprotic type, viz., pyridine and DMF, solvents with weakly expressed acidic properties, viz., methanol, ethanol, propyl alcohol, and isopropyl alcohol, and acidic solvents, viz., formic and acetic acids, were tested. The amount of added hydrochloric acid was varied.

The reaction mixture (consisting of water, the solvent, furfural, p-nitroaniline, hydrochloric acid, and the reaction products) was a complex buffer solution. By measuring its pH we determined the apparent acidity, which varied as a function of the amount of acid and the nature of the solvent but remained constant in the course of the synthesis (Table 1). The acidity of the solution decreased (pH 2→3.6) as the reaction proceeded only when DMF was used (experiment No. 10); this can be explained by the presence of a large amount of base in the reaction mixture, which exceeds the capacity of the buffer, and by the formation of a compound with a higher basicity than that of the p-nitroaniline consumed in the reaction.

The reaction does not occur in pyridine and Stenhouse salt I is not formed — the solution did not take on the dark-crimson color that is characteristic for it; no reaction products whatsoever were isolated. In formic acid the reaction proceeded exclusively to favor the formation of unidentified substance V. The results of these two experiments are presented in Table 1.

TABLE 2. Principal Characteristics of III-V

Compound	mp,* °C	Found, %			Empirical formula	Calculated, %			R_f
		C	H	N		C	H	N	
III	183—184	57,4	4,00	00	$C_{17}H_{14}N_4O_5$	57,6	3,98	15,8	0,69
IV	193—194	57,7	3,99	00	$C_{17}H_{14}N_4O_5$	57,6	3,98	15,8	0,23
V	192	51,6	4,34	00	—	—	—	—	0,19

*From ethanol.

TABLE 3. Spectral Characteristics of the Synthesized Compounds

Compound	λ_{max}, nm	IR spectrum, cm^{-1}					
		C=O	C=C	NH	NO_2		
					ν_{as}	ν_s	ν_{C-N}
II	284	1670	1600	—	1520	1352	866
III	382	1730	1600	3317, 3360	1472, 1490	1310, 1330	838, 850
IV	384	1720	1610	3345. 3377	1475, 1490	1300, 1320	840
V	324	1700	1575	3630,* 3425, 3480	1510	1340	860

*In $CHCl_3$.

The conditions of the Janovsky method [2] were observed in experiment No. 1, while the conditions of the Lüpke method [1] were observed in experiment No. 5. The yield of the initially isolated reaction product based on II is presented in Table 1 for comparison with the previously described method; its composition and the possibility of the presence of other compounds in it were not taken into account. When the mixture contained III and IV (experiments Nos. 1, 3, 4, 8, and 9), the molecular mass of which is 354, i.e., greater than that of II (216), we obtained numbers that were known to be too high, whereas in experiment No. 10 in which aldehyde II was absent the yield turned out to be absurd. The amount of resin formed is given in Table 1 in percent relative to the overall yield of the reaction products.

All of the experiments were carried out at 70 ± 1°C, since overheating increases the degree of resinification, while the yield of II decreases at lower temperatures.

The literature does not contain information regarding spectral data for II. We measured its PMR, IR, and UV spectra, which confirm its structure quite clearly.

The PMR spectrum of II contains the signal of an aldehyde proton at 9.59 ppm. The H_o and H_m protons of the benzene ring are represented by two doublets: H_o, 8.29 ppm, J = 9 Hz; H_m, 7.53 ppm, J = 9 Hz. The 3-H and 5-H protons show up in the form of a multiplet at 7.17 ppm. The 4-H proton gives a triplet at 6.48 ppm.

The IR spectrum of II contains absorption bands that confirm the presence of the principal fragments of the molecule. The UV spectrum is similar to the spectra of unsubstituted formylpyrrole and furfural.

The physicochemical characteristics of all of the compounds obtained in the synthesis are presented in Tables 2 and 3.

The IR spectra of III and IV are very similar and contain intense bands in the region corresponding to the stretching vibrations of carbonyl and NH groups; this constitutes evidence for the presence of a conjugated keto group and two secondary amino groups.

Compound III is labile and is converted to the more stable IV isomer, which does not undergo reconversion, when it is refluxed for a long time in alcohol solution. Both compounds react with concentrated hydrochloric acid to give a color reaction for Stenhouse salt I, and formylpyrrole II was obtained after prolonged refluxing of solutions of them in alcohol with HCl, which was accompanied by considerable resinification. These peculiarities in the chemical behavior of III and IV were also observed by Lewis and Malqiney [4] and also confirm their identification. Both cyclopentanones are separated satisfactorily on Silufol, and their R_f values (Table 2) differ from the R_f values for formylpyrrole (R_f 0.72).

Compound V was isolated in the form of almost colorless crystals. Its IR spectrum in mineral oil contains an absorption band at 1700 cm^{-1}, which may correspond to the stretching vibrations of a conjugated carbonyl group. The broad diffuse band at 3020-3280 cm^{-1} constitutes evidence for the presence of an NH or OH group tied up in hydrogen bonds. The spectrum of a dilute solution of this substance in chloroform contains more distinct bands that are shifted somewhat to the higher-frequency region (Table 3). Compound V does not undergo the transformations that III and IV do. Stenhouse salt I is not formed when concentrated hydrochloric acid is added. Without additional studies the structure of V still remains unestablished.

The data obtained showed that the yields of reaction products do not depend directly on the pH of the solution. However, this sort of dependence does exist in a certain solvent. The highest yield of II in the absence of side products was obtained in ethanol at pH 1.3 (experiment No. 5). Compound III is formed at lower acidities (experiments Nos. 3 and 4), while resinification occurs at higher acidities (experiments Nos. 6 and 7). Resinification is not observed in methanol even at a low pH value (experiment No. 1).

On the basis of the material stated above it may be concluded that the highest yield of formylpyrrole II is obtained at a strictly definite acidity as a function of the solvent. The Lüpke method [1] meets this requirement, and the specified amount of acid ensures the optimal pH of the medium (experiment No. 5). The formation of a side product is not observed under these conditions. However, the yield does not exceed 67-70%. The repeated precipitation of the reaction product proposed by Lüpke gives only a slight increase in the yield, since p-nitroaniline, when it is used in a twofold excess, contaminates the desired product significantly, and its purification requires many recrystallizations.

In addition, Lüpke does not precisely specify the temperature conditions of the synthesis, and this may be the reason for the depressed yield. We noted that heating is of great value in the preparation of formylpyrrole. The formation of side products, viz., III and IV, is possible in the cold, and II was isolated only when the reaction mixture was heated. We established an optimal temperature of 70 ± 1°C.

Thus the Lüpke method [1] with precise specification of the temperature for the synthesis can be recommended for the preparation of 1-(4-nitrophenyl)-2-formylpyrrole (II). However, the Janovsky method [2] leads, in addition to the desired product, to the formation of 2,3-bis(4-nitrophenylamino)-4-cyclopentenone and cannot be used for the preparation of formylpyrrole, since its yield does not exceed 55%.

EXPERIMENTAL

Thin-layer chromatography (TLC) was carried out on Silufol UV-254 plates in a dioxane–hexane system (1:2) with development with a hydrochloric acid solution of 4-(N,N-dimethylamino)benzaldehyde. The nominal pH values were determined with a pH-121 pH meter by means of an ÉSL-43-07 glass electrode and an ÉVL-1M3 silver chloride electrode with calibration with respect to aqueous buffer solutions. The UV spectra of solutions of the compounds were recorded with a Specord UV-vis spectrophotometer. The IR spectra of mineral oil suspensions of the compounds between NaCl plates were recorded with a UR-20 spectrometer. The PMR spectrum of a solution in dichloroethane was recorded with VS49H spectrometer at 100 MHz with a resolution of 50 Hz relative to tetramethylsilane.

1-(4-Nitrophenyl)-2-formylpyrrole (II). A 3.5-g (0.025 mole) sample of p-nitroaniline and 1.08 ml (0.0125 mole) of furfural were dissolved in 50 ml of ethanol, and the solution was heated to 70°C. A 4.5-ml (0.0125 mole) sample of a 10% solution of hydrochloric acid was then added to the mixture, after which 50 ml of water was added slowly, and the mixture was heated at 70°C for 2 h. The solution was cooled, and the resulting precipitate was removed by suction filtration and washed with aqueous alcohol (60-70%). Recrystallization from ethanol gave 1.8 g (67%) of II.

LITERATURE CITED

1. H. Lüpke, "Uber die Bildung von Pyrrol- und Pyridin-Derivaten aus Furfurol," Dissertation, Berlin (1939), p. 39.

2. Organic Syntheses [Russian translation], Collective Vol. 1, Izv. Akad. Nauk SSSR, Moscow (1950), p. 120.
3. R. Petit and R. Pallaud, Compt. Rend., 258, 230 (1964).
4. K. G. Lewis and C. R. Malqiney, Tetrahedron, 33, 463 (1977).
5. I. S. Barvinok and V. S. Kuprin, Z h. Obshch. Khim., 31, 632 (1961).

SYNTHESIS AND PROPERTIES OF SUBSTITUTED INDOLO-3-CYANINE DYES

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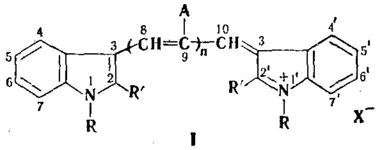
Indolo-3,3'-mono- and indolo-3,3'-trimethylidynecyanines that contain substituents in the indole rings and in the polymethine chain (in the case of trimethylidynecyanines) were synthesized by condensation of 2-alkyl- and 2-arylindoles, respectively, with ethyl orthoformate and tetraalkylacetals of substituted malonic dialdehydes in anhydrous benzene in the presence of acetyl chloride or thionyl chloride. The colors of the products were studied, and the polarographic potentials of the oxidation and reduction half waves were determined. A relationship between the indicated characteristics of indolo-3-cyanines and their structure was established.

Cyanine dyes that are derivatives of 2-arylindiles occupy an important position among spectral sensitizers of silver halide photographic emulsions [1, 2]. These compounds are effective electron acceptors and are suitable for use in direct positive photomaterials.

In this connection, we decided to synthesize new substituted (in the indole ring and in the polymethine chain) indolo-3,3'-cyanine dyes, to study their colors and sensitizing action, to determine the polarographic potentials of the oxidation and reduction half waves, and to establish a relationship between the indicated characteristics of these dyes and their structure.

With this in mind we synthesized symmetrical indolo-3,3'-cyanines with the general structure (I)



I

$R{=}H$ or CH_3, $R'{=}CH_3$, C_6H_5 or Ar, $A{=}H$ or Hal, $n{=}0$ or 1, X^- — acid residue

Indolo-3-monomethylidynecyanines (n = 0) were obtained by condensation of the corresponding 2-arylindoles with ethyl orthoformate in anhydrous benzene at room temperature [3]. Symmetrical indolo-3-trimethylidynecyanines (n = 1) were synthesized by condensation of 2-alkyl- and 2-arylindoles with tetraalkylacetals of malonic dialdehydes in anhydrous benzene in the presence of thionyl chloride or acetyl chloride at room temperature [4].

The spectral and redox characteristics of the synthesized dyes in a mixture (5:1) of nitromethane and acetic acid are presented in Table 1. The data in Table 1 show that the colors of the indolo-3,3'-cyanines depend to an appreciable extent on the character and position of the substituents in the indole heteroresidues and the polymethine chain. Replacement of the hydrogen atom attached to the indole nitrogen atom of 2-phenylindole by a methyl group leads to a hypsochromic shift of the absorption maximum. The dyes that contain phenyl groups in the 2 and 2' positions of the indole residues are considerably more deeply

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