$\frac{1-(p-Bromobenzoy1-2-pyridy1)amino-3-phenyloxindole (VIa).}{A) A 1.0-g (0.002 mole)}$ 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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bis[9-(1-azaf1uorenylidene)] (V).



I-V 1-aza, R=H, $Ar=C_6H_5$; VI, VII 2-aza, $R=CH_3$; VIII-X 4-aza, R=H, $Ar=C_6H_4NO_2-p$

Compounds III-V are analogs of the compounds obtained in the condensation of 4- and 2-azafluorenes with benzaldehyde under phase-transfer catalysis conditions [1]. Isomers of benzylidene derivative II, which were previously obtained in our laboratory by direct condensation of 1-azafluorene (I) with benzaldehyde [2], were isolated in 11% yield in the same experiment.

The condensation (similar to the aldol condensation) of 1-azafluorene (I) with benzaldehyde evidently takes place in the presence of sodium hydroxide and TEBAC, and the resulting secondary alcohol undergoes dehydration to benzylidene derivatives II. The fact that the only product in the reaction of 3-methyl-2-azafluorene (VI) with benzaldehyde in the presence of aqueous sodium hydroxide solution and TEBAC in benzene is phenyl[9-(3-methyl-2azafluorenyl)]carbinol (VII), which is evidently more stable than the analogous alcohol formed from 1-azafluorene (I), serves as a confirmation of this assumption.

The reaction of 4-azafluorene (VIII) with p-nitrobenzaldehyde was carried out under phase-transfer catalysis conditions, and the principal products were 9,9-dichloro-4-aza-fluorene (IX) and 3'-(p-nitrophenyl)spiro[4-azafluorene-9,2'-oxirane] (X).

The spiro[azafluoreneoxiranes] that we previously obtained on the basis of 2- and 4azafluorenes were isolated in the form of Z and E isomers that differ with respect to the orientation of the phenyl group in the oxirane ring with respect to the pyridine ring of the azafluorene fragment [1].



These isomers are readily distinguished from the PMR spectra. As a consequence of steric hindrance the phenyl group in both isomers is nonplanar relative to the azafluorene skeleton, and the azafluorene proton that is closest to it (1-H for the Z isomer and 8-H for the E isomer) therefore falls into the region of the diamagnetic effect of the ring current of the benzene ring, which shifts its signals 0.8-0.9 ppm to the strong-field region as compared with 9-unsubstituted azafluorenes [3].

The pronounced difference in the PMR spectra made it possible to determine the ratio of the Z and E isomers of the spiro compounds formed in the condensation of 2- and 4-azafluorenes with benzaldehyde. This ratio, which was determined on the basis of a comparison of the intensities of the signals of the 8-H and 3'-H protons, is 4:5 for 2-azafluorene and 5:4 for 4-azafluorene. Spiro compounds IV and X described in the present communication were isolated only in the form of the E isomer. The PMR spectrum of spiro compound IV, which is presented in Fig. 1, confirms its configuration, since the signal of the 8-H proton is observed at anomalously strong field (6.69 ppm).

On the basis of a comparison of the ratios of the Z and E isomers of phenyl-substituted (in the oxirane ring) spiro compounds formed from 2- and 4-azafluorenes and considering the



Fig. 1. PMR spectrum of 3'-phenylspiro[1-azafluorene-9,2'-oxirane]: a) experimental spectrum; b) iteration calculation of ABCD and ABC systems for the protons in the 5,6,7, and 8 in the 2,3, and 4 positions, respectively.

fact that only the E isomer is formed from 1-azafluorene, it may be assumed that the repulsive interaction of the unshared electron pair of the nitrogen atom of the pyridine ring of the azafluorene fragment and the π system of the benzene ring affects their configuration. This interaction is manifested most markedly in the case of 1-azafluorene, and, as a result, only the E isomer is formed.

EXPERIMENTAL

The PMR spectra of the compounds were recorded with Brucker WP-80 (80 MHz) and Nicolet NT-360 (360 MHz) spectrometers. The mass spectra were obtained with an MKh-1303 spectrometer at an ionizing-electron energy of 70 eV. Thin-layer chromatography (TLC) was carried out on activity II aluminum oxide by elution with heptane-ether (1:3).

3'-Phenylspiro[1-azafluorene-9,2'oxirane] (IV). A solution of 1 g (6 mmole) of 1azafluorene, 0.8 g (7.5 mmole) of benzaldehyde, and 18 mg of TEBAC in 3 ml of carbon tetrachloride was added with vigorous stirring in a stream of nitrogen to 3 ml of 50% aqueous sodium hydroxide solution. After 10 min, the mixture was treated with 10 ml of water, and the organic layer was separated. The solvent was removed by distillation, and the residue (1.5 g) was chromatographed on aluminum oxide by elution with heptane-ether (9:1). Workup of the initial fractions gave 0.02 g (1.3%) of light-yellow crystals of Z isomer IIa of the benzylidene derivative with mp 116-117.5°C (from heptane) and $R_{\rm f}$ 0.69 [2]. Subsequent elution gave 0.15 g (9.7%) of yellow crystals of E isomer IIb with mp 71-72°C (from heptane) and R_f 0.55 [2]. Elution then gave 0.32 g (22.8%) of colorless crystals of dichloride III with mp 132-133°C (from heptane) and R_f 0.42. PMR spectrum spectrum (CDCl₃): 8.56 (1H, 2-H) and 7.29-7.59 ppm (6H, m, aromatic protons). Found: C 61.4; H 3.3; Cl 29.6; N 6.1%; M⁺ 235. C₁₂H₇Cl₂N. Calculated: C 61.3; H 3.0; Cl 29.8; N 6.0%; M 235. Subsequent elution gave 0.38 g (23.8%) of colorless crystals of spiro compounds IV with mp 102-104°C (from heptane) and $\rm R_{f}$ 0.29. PMR spectrum (CDCl_3), 30°C, azafluorene protons, iteration calculation by means of the ITRCAL program: 8.51 (2-H), 7.32 (3-H), 7.93 (4-H), 7.72 (5-H), 7.37 (6-H), 7.06 (7-H), and 6.69 ppm (8-H); [J, Hz: 4.9 (2-3), 1.3 (2-4), 7.6 (3-4), 7.5 (5-6), 1.1 (5-7), 0.7 (5-8), 7.6 (6-7), 1.1 (6-8), 7.6 (7-8)]; 5.0 (broad s, 3'-H), and 7.3-7.5 ppm (weak m, C₆H₅). Found: C 84.4; H 5.1; N 5.0%; M⁺ 271. C₁₉H₁₃NO. Calculated: C 84.2; H 4.8; N 5.2%; M 271. The last compound eluted was V [0.01 g (1%)] in the form of bright-orange crystals with mp 258-259°C. PMR spectrum (d₆-DMSO): 8.98 (2H, s, 8-H), 8.44 (2H, s, 2-H), and 7.26-7.31 ppm (10H, m, aromatic protons). Found: M⁺ 330. C₂₄H₁₄N₂. Calculated: M 330.

<u>Phenyl[3-methyl-9-(2-azafluorenyl)]carbinol (VII)</u>. A 15-mg sample of TEBAC, a solution of 1 g (5.5 mmole) of azafluorene VI in 3 ml of benzene, and 0.7 g (6.9 mmole) of benzaldehyde were added with stirring to 3 ml of 50% aqueous sodium hydroxide, and the mixture was stirred for 2 h. The resulting precipitate was washed with water and dried to give 1 g (63.5%) of colorless crystals of carbinol VII with mp 215-220°C (from ethanol). PMR spectrum, 360 MHz (d_6 -DMSO), 50°C: 2.49 (3H, m, CH₃), 4.43 (1H, d, 9-H), 5.02 (1H, d),

5.79 (broad s, OH), 7.35 (2H, m, 6-H and 7-H), 7.52 (1H, broad s, 4-H), 7.64 (1H, m, 8-H), 7.77 (1H, m, 6-H), 8.55 (1H, broad s, 1-H), and 7.1 ppm (5H, broad s, C₆H₅). Found: C 83.0; H 5.5; N 4.8%. C₂₀H₁₇NO. Calculated: C 83.6; H 5.9; N 4.9%.

<u>3'-(p-Nitrophenyl)spiro[4-azafluorene-9,2'-oxirane]</u> (X). A mixture of 3 ml of 50% aqueous sodium hydroxide, 1 g (6.0 mmole) of 4-azafluorene (VIII), 1.27 g (8.4 mmole) of p-nitrobenzaldehyde, 15 mg of TEBAC, 3 ml of carbon tetrachloride, and 20 ml of benzene was stirred in a stream of nitrogen for 1 h, after which the mixture was worked up and the products were isolated as in the preparation of IV. This procedure gave 0.32 g (22.7%) of colorless crystals of dichloride IX with mp 139-140°C (from heptane) [1] and 0.25 g (15.4%) of colorless crystals of spiro compound X with mp 164-165°C (from heptane). PMR spectrum (d₆-DMSO), 60°C, azafluorene protons, DSS as the internal standard: 7.85 (1-H), 7.32 (2-H), 8.57 (3-H), 7.89 (5-H), 7.41 (6-H), 7.1 (7-H), and 6.53 ppm (8-H); oxirane ring: 5.33 (1H, broad s, 3'-H); p-NO₂C₆H₄, AA'BB' system: 8.16 (2H, m, AA') and 7.70 ppm (2H, m, BB').

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REACTION OF DIMETHYLAMINOVINYLPYRIMIDINES

WITH CARBOXYLIC ACID CHLORIDES

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Phenacyl- and trichloroacetonylpyrimidines were obtained in the reaction of dimethylaminovinylpyrimidines with carboxylic acid chlorides. It is shown that substituents in the pyrmidine and triazine rings affect the course of this reaction.

Dimethylaminovinylpyrimidines and -triazines are formed relatively easily in the reaction of methylpyrimidines and -triazines with dimethylformamide dimethylacetal [1]. The higher reactivities of enamines may make it possible to use the indicated compounds for the preparation of various derivatives of pyrimidines and triazines.

In the present research we studied the reaction of enamines of the pyrimidine and triazine series with carboxylic acid chlorides.

It is known that 2-phenacylnitrobenzene is formed in the reaction of β -dimethylamino-2-nitrostyrene with o-fluorobenzoyl chloride as a result of electrophilic attack on the α -carbon atom [2].

We subjected 4-(β -dimethylaminovinyl)pyrimidine (Ia), 5-nitro-2,4-dimethoxy-6-(β -dimethylaminovinyl)pyrimidine (Ib), 4-methyl-6-(β -dimethylaminovinyl)pyrimidine (Ic), and 2,4-bis(trichloromethyl)-6-(β -dimethylaminovinyl)triazine (II) to reaction with benzoyl chloride.

4-Phenacylpyrimidine (IVa) was obtained in the reaction of enamine Ia with benzoyl chloride in benzene in the presence of triethylamine at 20° C. The reaction probably proceeds through intermediate IIIa.

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