CONVERSIONS OF 9-BROMO(CYANO)-4-AZAFLUORENES AND 1,2-DI(4-AZAFLUOREN-9-YL)ETHANE UNDER CONDITIONS OF THE MICHAEL REACTION

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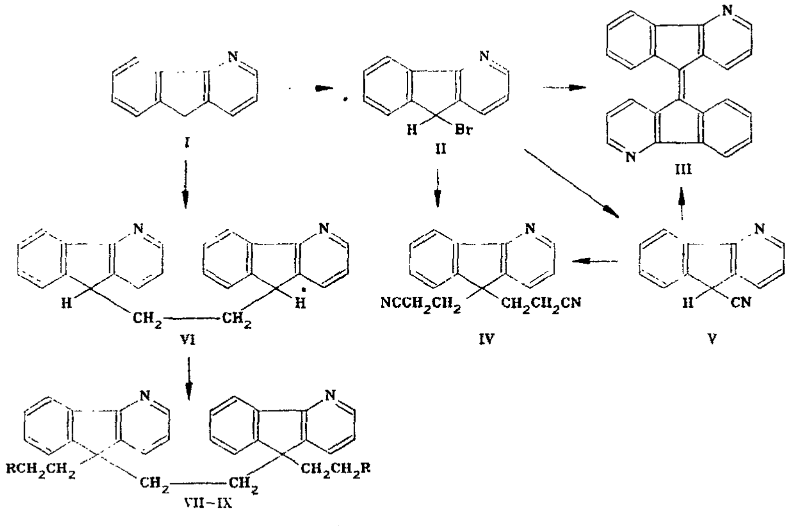
9-Bromo(cyano)-4-azaflourenes are converted to di(4-azafluorylidene-9) or 9,9-di(β-cyanoethyl)-4-azafluorene under the conditions of the Michael reaction (acrylonitrile, ethoxytrimethylphenylammonium), depending on the temperature. 1,2-Di(4-azafluoren-9-yl)ethane was synthesized, and its cyanoethylation was performed.

Earlier we studied the cyanoethylation of 3-methyl-2-azafluorene as well as 4-azafluorene (I), in the presence of ethoxytrimethylphenylammonium (kR). In both cases only the 9,9-di(β-cyanoethyl) derivatives of these azafluorenes were obtained [1, 2]. We were interested in determining the conversions that occur with 9-bromo-4-azafluorene (II) under the same conditions [3], where a different chemistry of the reactions is possible.

Without heating, the initial bromide II (80%) and di(4-azafluoryliden-9) (III) (12%) were isolated. There were no cyanoethylation products. In view of the fact that the only new product in this case is the dimer III, we suggested that a singlet carbene is formed from the bromide II under the influence of the catalyst, and it dimerizes.

Upon heating, 9,9-di(β-cyanoethyl)-4-azafluorene (IV) was obtained in a 74% yield. In this case the singlet carbene formed, probably at the first step, is rapidly converted to a triplet form, which interacts with two molecules of acrylonitrile as a biradical. Evidently 9,9-di(4-azafluoren-9-yl)-4-azafluorene is formed according to the same radical mechanism; it is obtained in a yield of 60% when the bromide II is treated with an alcohol solution of potassium hydroxide with heating [3].



VII R=CN; VIII R=COOH; IX R=CON(C_2H_5)$_2$

It could be assumed that under the same conditions analogous conversions should also occur with 9-cyano-4-azafluorene (V), synthesized from the bromide II and sodium cyanide. Compounds III (26%) and IV (57%) were isolated from the products.

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In the condensation of 4-azafluorene (I) with ethylene glycol in the presence of sodium, 1,2-di(4-azafluoren-9-yl)ethane (VI) was formed with a yield of 50%. An analogous condensation of fluorene was studied in [4, 5]. To synthesize functionally substituted derivatives of compound VI, we carried out its cyanoethylation. The 1,2-di[9-(β-cyanoethyl)-4-azafluoren-9-yl]ethane (VII) obtained in this case was then converted to the dibasic acid VIII, and from the latter we isolated 1,2-di[9-(β-diethylcarbamoylethyl)-4-azafluoren-9-yl]ethane (IX) through its dihydrochloride.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 instrument in tablets with KBr; the PMR spectra were recorded on a Tesla BS-467 spectrometer (60 MHz), with a TMS internal standard. The mass spectra were obtained on a MX-1303 instrument. Column chromatography and thin-layer chromatography were conducted on aluminum oxide of II degree of activity.

Di(4-azafluorylidene-9) (III) and 9,9-di(β-cyanoethyl)-4-azafluorene (IV). A. A solution of 0.5 g (2 mmoles) of the bromide II, 0.54 g (10 mmoles) of acrylonitrile, and 0.1 ml of an alcohol solution of kR in 15 ml of anhydrous benzene was mixed for 4 h at 20°C. Then 30 ml of water was poured in. The benzene layer was shaken with water, separated, and dried with potash. The residue after the benzene was distilled off was chromatographed, with a 3:1 mixture of ether and hexane as the eluent. We isolated 0.4 g (80%) of the bromide II and 0.08 g (12%) of compound III, mp 288-289°C [3]. In an analogous experiment, conducted at 0°C, the bromide II was isolated with a yield of 64%, while compound III was isolated with a yield of 14%.

B. The same amounts of the reagents were taken for the reaction. The process was conducted for 8 h at 60°C. Analogously we isolated 0.41 g (74%) of the dicyanoethyl derivative IV, mp 132-133°C [2].

9-Cyano-4-azafluorene (V). A solution of 4.5 g (18 mmole) of the bromide II and 2 g (4.3 mmoles) of sodium cyanide in 50 ml of ethanol and 15 ml of water was exposed for 3 h at 60°C. The alcohol was distilled off, neutralized to pH 9 with soda, and extracted with chloroform. The residue after the chloroform was distilled off was chromatographed (system the same). We isolated 2.15 g (61%) of compound V, colorless crystals, mp 229-230°C (from a 1:2 mixture of hexane and benzene). PMR spectrum: 4.83 ppm (1H, $C_{(9)}$—H). IR spectrum: 2240 cm^{-1} (CN). Found: N 14.5%; M^+ 192. $C_{13}H_8N_2$. Calculated: N 14.6%; M 192.

We mixed 0.2 g (1.04 mmoles) of compound V, 0.54 g (10.1 mmoles) acrylonitrile, and 0.1 ml of an alcohol solution of kR in 15 ml of anhydrous benzene for 3 h at 20°C. The benzene layer was shaken with water and dried with potash. The residue after the benzene was distilled off was chromatographed, with a 1:1 mixture of ether and hexane as the eluent, then ethyl acetate. Yield 0.09 g (26%) of the dimer III and 0.16 g (57%) of the dinitrile IV.

1,2-Di(4-azafluoren-9-yl)ethane (VI). We dissolved 0.2 g (8.7 moles) of sodium in 3 g (48 mmoles) ethylene glycol, added 1 g (5.9 mmoles) of the azafluorene I, and heated for 22 h at 230°C. The mixture was cooled, 20 ml of water was added, and it was extracted with chloroform. The residue after the chloroform was distilled off was chromatographed (eluent ether-hexane, 3:1). We isolated 1.1 g (50%) of the compound VI: mp 174-175°C (from a 2:1 mixture of hexane and benzene). Found: C 86.6; H 5.6; N 7.5%; M^+ 360. $C_{26}H_{20}N_2$. Calculated: C 86.7; H 5.6; N 7.8%; M 360.

1,2-Di[9-(β-cyanoethyl)-4-azafluoren-9-yl]ethane (VII). We mixed 0.59 g (1.6 mmoles) of compound VI, 4 g (75.4 mmoles) of acrylonitrile, 0.1 ml kR, and 30 ml of toluene for 3 h at 60°C. The toluene layer was shaken with water, and dried with potash. The residue after the toluene was distilled off was chromatographed, with ether as the eluent. We isolated 0.52 g (68%) of compound VII, mp 288-289°C (from benzene). IR spectrum: 2250 cm^{-1} (CN). Found: C 82,4; H 5.5; N 11.8%; M^+ 466. Calculated C 82.4; H 5.6; N 12.0%; M 466.

1,2-Di[9-β-carboxyethyl)-4-azafluoren-9-yl]ethane (VIII). A solution of 0.84 g (1.8 mmoles) of the dinitrile VII and 7.64 g (0.14 mole) potassium hydroxide in 12 ml of ethanol was boiled for 18 h. It was neutralized to pH 7 with 70% sulfuric acid. The residue was washed with water and dried. We obtained 0.48 g (53%) of the dibasic acid VIII, mp 310°C (with dec.). Found: 5.3%; M^+ 504. $C_{32}H_{28}N_2O_4$. Calculated: N 5.6%; M 504.

1,2-Di[9-(β-diethylcarbamoylethyl)-4-azafluoren-9-yl]ethane (IX). A solution of 0.48 g (0.9 mmole) of the diacid VIII and 2.5 g (21 mmoles) of thionyl chloride in 25 ml of absolute ether was boiled for 3 h. After the ether and thionyl chloride were distilled off, 3.53 g (48 mmoles) diethylamine was added to the residue, and it was heated with boiling for 2 h. The excess diethylamine was distilled off, 30 ml of water was added, and soda was added to pH 10. The reaction products were extracted with ether and then chromatographed; the eluent was ether. Yield 0.2 g (35%) of compound IX; mp 158-159°C (from a 1:2 mixture of hexane and benzene). IR spectrum: 1650 cm^{-1} ($CONR_2$). Found: C 77.9; H 7.6; N 9.1%; M^+ 614. $C_{40}H_{46}\cdot N_4O_2$. Calculated: C 78.1; H 7.5; N 9.1%; M 614.

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FLUORESCENCE AND PHOTOCYCLIZATION OF N-NAPHTHYL-SUBSTITUTED PYRIDINIUM CATIONS

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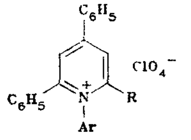
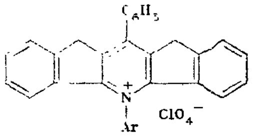
The spectral-fluorescent and photochemical properties of 1-naphthyl-2,4-di- and 2,4,6-triphenylpyridinium perchlorates were investigated in solutions at 293 and 77°K. The anomalously large Stokes shift of the fluorescence was due to the adiabatic change in the structure of the molecules as a result of rotations of the C- or N-aryl substituents. The observed phosphorescence arises as a result of intramolecular T-T transfer of energy to the N-naphthyl radical. 1-Naphthyl-2,4-diphenylpyridinium cations are capable of photocyclization with the formation of intensely fluorescent derivatives of benzo[b or c]pyrido[1,2-f]phenanthridinium, isolated with high yields in preparative photolysis.

In arylsubstituted pyridinium cations, deactivation of the lower excited singlet state occurs both as a result of the formation of photochemically stable coplanar structures that fluoresce with an anomalous Stokes shift and as a result of a competing process of photocyclization with the participation of the N-phenyl substituent. The relative rates of these reactions depends substantially on steric and electronic factors [1, 3]. The purpose of this work was to study the processes of deactivation of the excited states of N-naphthyl-substituted pyridinium cations and to perform a photochemical synthesis of new polycyclic heteroaromatic systems with directed variation of the structure of the initial compounds. The objects of investigation were N-naphthylpyridinium perchlorates I-IV and model compounds V and VI.



I-IV



V,VI

I, II, V Ar=1-napthyl III, IV, VI Ar=2-napthyl; I, III R=C_6H_5; II, IV R=H

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