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SYNTHESIS OF MESOMORPHIC 2-ALKYL-5-(p-CYANOPHENYL)PYRIDINES

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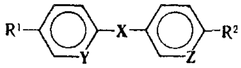
A new series of liquid–crystal derivatives of 2-alkyl-5-(p-cyanophenyl)pyridines were obtained by halogenation of 2-alkyl-5-phenylpyridines under the conditions of the Birckenbach–Gubo–Waters reaction with subsequent conversion of the 2-alkyl-5-(p-bromo- or iodophenyl)pyridines to the cyano derivatives.

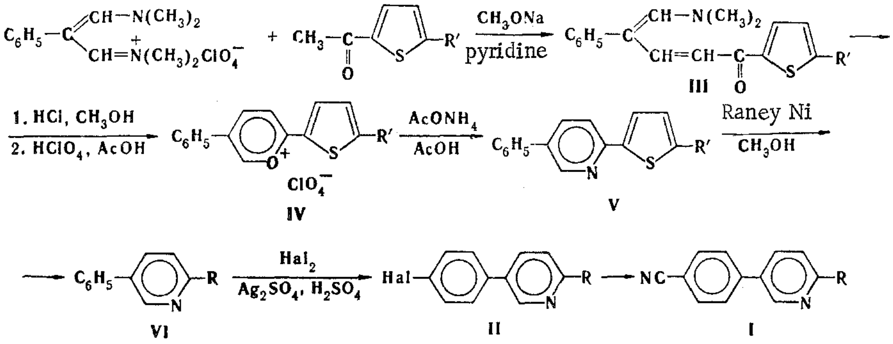
In previous research on the Liquid–crystal properties of α- and β-substituted pyridines [1-3] it was shown that in the case of β-X-substituted pyridines both the thermal stability of the mesophase and the melting point decrease significantly (when X = $CH{=}N$, X = COO). In the case of α- and β-phenylpyridines (X = a single bond) the melting point and the thermal stability of the mesophase, as well as the dielectric properties, of the liquid crystals obtained have a more complex relationship [4, 5].



Y=N, Z=H α-substituted

Y=H, Z=N β-substituted

It seemed of interest to compare two series of mesomorphic compounds, viz., our previously described 2-cyano-5-(p-alkylphenyl)pyridines [6] and 2-alkyl-5-(p-cyanophenyl)pyridines, which differ with respect to the position of the nitrile group. The synthesis of the latter was realized via the scheme



$R = C_4H_9, C_6H_{13}, C_9H_{19}$

We presented the method used to obtain the intermediate 2-alkyl-5-phenylpyridines (VI) in [4, 7]. In a preparative respect this method is simpler, it seems to us, than the known scheme for the synthesis of VI through organolithium derivatives [8]. Since exclusively the p-substituted compounds have mesomorphic properties, we made a detailed study of the orientation of the incorporation of substituents in the halogenation of β-phenylpyridines (VI) by the bromine or iodine cation under the conditions of the Bircenbach–Gubo–Waters reaction [9]. The para isomer was isolated in 64% yield in the nitration of β-phenylpyridine in sulfuric acid at 100°C [10]. We therefore expected that the principal product in the halogenation of β-phenylpyridine would also be the para isomer. An analysis of the reaction mixture by means of gas–liquid chromatography (GLC) shows that the principal product in the iodination of VI is actually the para isomer (R = H, 82% IIa; R = C_4H_9, 66% IIb; R = C_6H_{13},

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79% IIc), which was isolated in pure form; its structure was established by means of PMR spectroscopy. Thus signals of the protons in the 1 and 4 positions with corresponding chemical shifts in $CDCl_3$ of 8.52 (1H, dd, J_{12} = 5 Hz, J_{14} = 1.8 Hz, 1-H) and 8.72 ppm (1H, dd, J_{41} = 1.8 Hz and J_{43} = 0.7 Hz, 4-H) are isolated in the spectrum of IIa. The signals of the protons in the 2 and 3 position are overlapped by the signals of the protons of the phenyl ring. The four protons of the phenyl ring give a complex spectrum corresponding to a four-spin AA'XX' system, which indicates the para orientation of the iodine in the phenyl ring. The spectra of IIb and IIc are similar. In addition, starting pyridines VIa-c and an isomer with an unestablished structure and a shorter retention time than for the para isomer (R = H, 12%; R = C_4H_9, 11%; R = C_6H_{13}, 7%) were detected in the reaction products. In the case of bromination under similar conditions we were able to isolate the para isomer only for VI with R = C_6H_{13} and C_9H_{19}. An analysis of the reaction mixture obtained in the bromination of 3-phenylpyridine by means of GLC demonstrated that the mixture contained, in addition to starting VIa (17%), the para isomer (52%), an isomer with an unestablished structure with a retention time similar to that of the iodination product (13%), and two products (10 and 8%) with retention times that are considerably greater than for the para isomer. The latter are probably dibromination products.

Thus our studies showed that the Birckenbach–Gubo–Waters reaction can be used successfully to obtain 3-(p-iodophenyl)pyridines.

The p-iodo(bromo)phenylpyridines were converted via the usual scheme to cyano derivatives I, of which the homolog with R = C_6H_{13} forms a monotropic liquid crystal, while another (R = C_9H_{19}) displays enantiotropic liquid–crystal properties.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in $CDCl_3$ at 20°C were recorded with a Varian-HA 100D spectrometer with tetramethylsilane as the internal standard. Gas–liquid chromatography (GLC) was carried out with an LKhM-8MD chromatograph with a column (1 m × 3 mm) with a stationary phase consisting of SE-30 on Chromosorb at a carrier-gas flow rate of 3.6 liters/h. The temperatures of the transitions were determined with a Mettler FP-52 apparatus equipped with an MIN-8 polarization microscope.

2-(2-Thienyl)-5-phenylpyrylium Perchlorate (IVa). A 20-ml sample of a 3 M solution of sodium methoxide was added dropwise with vigorous stirring at 40°C to a solution of 18 g (0.06 mole) of 1-dimethylamino-3-dimethylimmonio-2-phenylpropene perchlorate and 7.6 g (0.06 mole) of α-acetylthiophene in 50 ml of anhydrous pyridine. After 10 h, the solvent was removed in vacuo, and the residue was decomposed with 100 ml of water and extracted with 300 ml of chloroform. The organic layer was chromatographed on activity II aluminum oxide, the eluate was evaporated in vacuo, and 50 ml of methanol and 10-15 ml of 10% aqueous hydrochloric acid solution were added to the residue. After 30 min, the reaction product was diluted with 300 ml of water and extracted with ether. The ether was removed by distillation, and 10 ml of glacial acetic acid and 10 ml of 70% $HClO_4$ were added to the residue. After 30 min, 150 ml of dry ether was added, and the precipitated pyrylium salt was removed by filtration and washed with dry ether to give 12 g (59%) of a product with mp 196°C (from acetic acid). Found C 53.2; H 3.4%. $C_{15}H_{11}ClO_5S$. Calculated: C 53.2; H 3.3%. Similarly, 2-ethyl-5-acetylthiophene gave salt IVb, with mp 142°C (from acetic acid), in 53% yield. Found: C 55.8; H 4.4%. $C_{17}H_{15}ClO_5S$. Calculated: C 55.7; H 4.1%. Salt IVc, with mp 138°C (from acetic acid), was isolated in 51% yield from 2-amyl-5-acetylthiophene. Found: C 58.9; H 5.0%. $C_{20}H_{21}ClO_5S$. Calculated: C 58.8; H 5.1%.

2-(2-Thienyl)-5-phenylpyridine (Va). A mixture of 12 g (0.035 mole) of crude pyrylium salt, 40 g of ammonium acetate, and 150 ml of acetic acid was refluxed for 2 h, cooled, and poured into 500 ml of water. The precipitate was removed by filtration, washed with water, air dried, and recrystallized from hexane with the addition of aluminum oxide to give 4.5 g (53.5%) of a substance with mp 108°C. Found: C 75.5; H 4.8; N 5.6%. $C_{15}H_{11}NS$. Calculated: C 75.9; H 4.7; N 5.9%. 2-(2-Ethyl-5-thienyl)-5-phenylpyridine (Vb), with mp 85°C (from hexane), was similarly obtained in 42% yield. Found: C 76.6; H 5.8; N 5.5%. $C_{17}H_{15}NS$. Calculated: C 76.9; H 5.7; N 5.3%. 2-(2-Amyl-5-thienyl)-5-phenylpyridine (Vc), with mp 92°C (from hexane), was obtained in the same way. Found: C 78.0; H 7.1; N 4.4%. $C_{20}H_{21}NS$. Calculated: C 78.1; H 6.9; N 4.6%.

2-Butyl-5-phenylpyridine (VIa). A mixture of 3.5 g (0.015 mole) of 2-(2-thienyl)-5-phenylpyridine in 200 ml of methanol and 35 g of Raney Ni was stirred thoroughly and refluxed.

After 6 h, another 10 g of Raney Ni was added. At the end of the reaction (as monitored from the disappearance of the starting compound on the chromatogram), the mixture was filtered, the mother liquor was evaporated in vacuo, and the residue was extracted with benzene and chromatographed on aluminum oxide. The eluate (benzene) was distilled, and the residue [2 g (64%) of an oil] was halogenated without further purification. PMR spectrum (in $CDCl_3$): 7.11 (1H, dd, J_{21} = 8 Hz, J_{23} = 0.8 Hz, 2-H), 7.64 (1H, dd, J_{12} = 8 Hz, J_{13} = 2.7 Hz, 1-H), and 8.67 ppm (1H, dd, J_{31} = 2.7 Hz, J_{32} = 0.8 Hz, 3-H). Found C 85.7; H 8.2; N 6.1%. $C_{15}H_{17}N$. Calculated: C 85.3; H 8.1; N 6.6%. 2-Hexyl-5-phenylpyridine (VIb) was similarly obtained in 56% yield. Found: C 85.5; H 8.7; N 5.8%. $C_{17}H_{21}N$. Calculated: C 85.3; H 8.8; N 5.9%.

2-Nonyl-5-phenylpyridine (VIc) was similarly obtained in 61% yield. Found: C 85.6; H 9.8; N 4.6%. $C_{20}H_{27}N$. Calculated: C 85.4; H 9,7; N 5.0%.

3-(p-Iodophenyl)pyridine (IIa). A 2.6-g (0.01 mole) sample of finely ground iodine was added in portions at room temperature to a vigorously stirred mixture of 1.55 g (0.01 mole) of 3-phenylpyridine, 1.56 g (0.005 mole) of Ag_2SO_4, and 15 ml of 90% sulfuric acid. After 2 h, the precipitate was removed by filtration and washed with a small amount of sulfuric acid. The mother liquor was diluted with water, made alkaline (while cooling) with concentrated sodium hydroxide solution, and extracted with benzene. The benzene layer was washed with water and chromatographed on activity II aluminum oxide. The eluate was evaporated in vacuo, and the residue (1.8 g) was recrystallized from hexane to give 0.7 g (25%) of a substance with mp 117°C. Found C 46.7; H 3.1; N 5.2%. $C_{11}H_8IN$. Calculated: C 47.0; H 2.9; N 5.0%. 2-Butyl-5-(p-iodophenyl)pyridine (IIb), with mp 68°C, was similarly isolated in 30% yield. Found: C 53.6; H 4.6; N 4.1%. $C_{15}H_{16}IN$. Calculated: C 53.4; H 4.8; N 4.2%. 2-Hexyl-5-(p-iodophenyl)-pyridine (IIc), with mp 67°C, was isolated in 31% yield. The PMR spectra of IIb and IIc were similar to the spectrum of IIa. Found: C 56.0; H 5.3; N 3.7%. $C_{17}H_{20}IN$. Calculated: C 55.9; H 5.7; N 3.8%.

2-Hexyl-5-(p-bromophenyl)pyridine (IId). A 1.6-g (0.01 mole) sample of bromine was added slowly dropwise with stirring at room temperature to a solution of 2.4 g (0.01 mole) of 2-hexyl-5-phenylpyridine and 1.56 g (0.005 mole) of Ag_2SO_4 in 15 ml of 90% sulfuric acid. After 2 h, the precipitated AgBr was removed by filtration and washed with a small amount of sulfuric acid. The mother liquor was diluted with water and made alkaline while cooling. The reaction mixture was worked up as described above to give 0.77 g (24%) of a substance with mp 48°C (from hexane). The signals of the protons of the pyridine ring gave the following signals in the PMR spectrum of a solution in $CDCl_3$: 7.81 (1H, dd, J_{12} = 8 Hz, J_{13} = 2.7 Hz, 1-H), 7.08 (1H, dd, J_{21} = 8 Hz, J_{23} = 0.8 Hz, 2-H), and 8.59 ppm (1H, dd, J_{31} = 2.7 Hz, J_{32} = 0.8 Hz, 3-H). The protons of the phenyl ring give a spectrum corresponding to a four-spin AA'XX' system. Found: C 64.4; H 6.1; N 4.3%. $C_{17}H_{20}BrN$. Calculated: C 64.1; H 6.3; N 4.4%. 2-Nonyl-5-(p-bromophenyl)pyridine (IIe), with mp 44°C, was similarly isolated in 20% yield. Found: C 66.5; H 7.4; N 4.0%. $C_{20}H_{26}BrN$. Calculated: C 66.7; H 7.3; N 3.9%.

2-Nonyl-5-(p-cyanophenyl)pyridine (Ib). A mixture of 0.36 g (0.001 mole) of 2-nonyl-5-(p-bromophenyl)pyridine, 5 ml of N-methylpyrrolidone, and 0.18 g (0.002 mole) of CuCN was refluxed with vigorous stirring until the starting IIe vanished (according to chromatographic analysis). The reaction mixture was cooled and poured into 25 ml of 12% ammonium hydroxide, and the reaction product was extracted with benzene and chromatographed on activity II aluminum oxide. The solvent (benzene) was removed by distillation, and the residue was recrystallized from hexane to give 0.18 g (59%) of a substance with T_{C-S} 42°C (the temperature of transition from the crystalline to the smectic state) and T_{S-I} 54°C (the temperature of transition from the smectic state to an isotropic liquid). Found: C 82.0; H 9.0; N 9.0%: $C_{21}H_{26}N_2$. Calculated: C 82.3; H 8.6; N 9.1%. 2-Hexyl-5-(p-cyanophenyl)pyridine (Ia), with mp 52°C and T_i 26°C (the temperature of transition from an isotropic liquid to a nematic mesophase), was similarly obtained. Found: C 82.0; H 7.7; N 10.3%. $C_{18}H_{20}N_2$. Calculated: C 81.8; H 7.6; N 10.6%.

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KINETICS OF N-OXIDATION OF COMPOUNDS OF THE QUINOLINE SERIES AND ISOMERIC BENZOQUINOLINES BY PERBENZOIC ACID IN CHLOROFORM AND AQUEOUS DIOXANE

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The kinetics of the N-oxidation with perbenzoic acid of 15 derivatives of quinoline and benzoquinoline in chloroform and 19 compounds in 50% aqueous dioxane at 20, 25, 30, and 35°C were subjected to a comparative study. The rate constants, parameters of the Arrhenius equation, and the activation energies for the N-oxidation of the indicated monoazines were determined. A scale of the reactivities of derivatives of the quinoline series and benzoquinolines was calculated within the framework of general perturbation theory.

The idea that the initial step in many reactions involving electrophilic and nucleophilic substitution in the monoazine series is coordination at the ring nitrogen atom of both a kinetically independent electropositive particle and the electropositive part of an ion pair has become a firmly established principle. It is evident that the reactivity of the monoazine will be determined essentially as a function of the character of such coordination, in the same way as the behavior of the free bases and conjugate acids [1].

For a better understanding of the peculiarities of the behavior of monoazines in the reactions indicated above we needed some kind of model reaction for which at least formal kinetics would be applicable. The N-oxidation of derivatives of the pyridine series is a prime reaction of this sort [2]. In connection with the fact that the literature does not contain kinetic data on N-oxidation and the fact that the nucleophilicities of derivatives of the quinoline series and benzoquinolines have not been calculated, it seemed of interest to investigate the kinetics of oxidation of the indicated monoazines by the method and under the conditions described in [2]. For this, we studied the kinetics of N-oxidation with perbenzoic acid of 15 derivatives of quinoline and benzoquinoline in chloroform and 19 compounds in 50% aqueous dioxane at 20, 25, 30, and 35°C.

It is essential to note that a direct relationship between the consumption of perbenzoic acid and the concentrations of the resulting N-oxides was established in [2-5].

At a molar ratio of the organic base to the peracid of ~1:0.5 the N-oxidation reaction was described satisfactorily by a second-order equation for unequal concentrations. The somewhat arbitrary selection of monoazines for the kinetic measurements was determined by the fact that the principal goal was to develop a general approach to the evaluation of the nucleophilicity of a monoazine with respect to the electron-deficient δ^+ (OH) group of the peracid within the framework of perturbation theory.

In the present research we determined the parameters of the Arrhenius equation and the activation entropies of the indicated heterocycles. We calculated a scale of the nucleo-

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