SYNTHESIS OF 2-(4-n-ALKYLPHENYL)-5-n-ALKYLPYRIDINES

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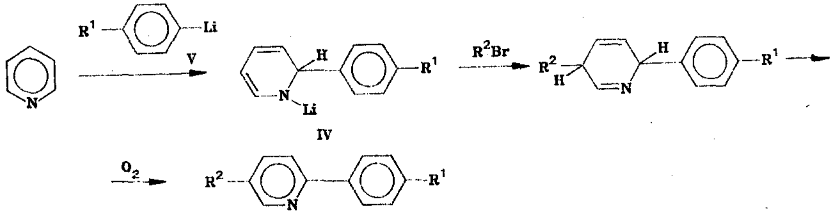
New liquid-crystalline 2-(4-alkylphenyl)-5-alkylpyridines were synthesized by the reaction of 2-(4-alkylphenyl)-1-lithio-1,2-dihydrophyridines with alkyl bromides. The compounds obtained have relatively low melting points and narrow temperature ranges of the existence of a nematic meso phase; the thermal stability of the meso phase is determined by the length of the alkyl group in the pyridine and benzene parts of the molecule.

It is known that replacement of the benzene ring by a pyridine ring makes it possible to substantially expand the class of potentially mesomorphic compounds; moreover, owing to the contribution of the heteroatom, it becomes possible to vary the direction and magnitude of the dipole moment, the effective tension, the viscosity, and the range of operating temperatures [1].

We have previously reported [2] the synthesis and properties of liquid-crystalline 2-(4-alkoxyphenyl)-5-n-alkylpyridines I and 2-n-alkyl-5-(4-n-alkyl- and alkoxyphenyl)pyridines II. It seemed of interest to investigate the previously undescribed alkyl analogs III of I, which we obtained via the previously proposed method for the synthesis of 2-phenyl-5-alkylpyridines [3] by alkylation of 2-(4-alkylphenyl)-1-lithio-1,2-dihydropyridines IV.



IIIa-i $R^1 = C_nH_{2n+1}$, $R^2 = C_nH_{2n+1}$

The starting 4-n-alkylbromobenzenes [4, 5] were obtained by acylation of bromobenzene with the complex of the corresponding acid chloride with aluminum chloride at 70°C with subsequent reduction of the resulting ketone by hydrazine in an alkaline medium.

In an attempt to isolate complexes IV ($R^1 = C_2H_5$—C_7H_{15}) we found that their solubility in ether increases with an increase in the length of the alkyl chain, and large losses consequently develop in this step. In addition, the overall yields of pyridines III with allowance for isolation of complex IV (R^1 = H) [3] and without its isolation are virtually the same (12-18%). We therefore excluded the step involving the isolation of complex IV. Different temperature conditions (0, 25, 40°C) for the preparation of complex IV and its alkylation do not have a substantial effect on the overall yields of pyridines III.

The properties and physicochemical parameters of the synthesized pyridines III are presented in Table 1. In contrast to biphenyl the III molecule, inasmuch as it is unsymmetrical for substituents, markedly changes the mesomorphic properties (the temperatures of the phase transitions) as a function of the length of the alkyl chain in the pyridine and benzene parts. Thus an increase in the length of the alkyl chain in the pyridine part of IIIb-i as compared with the benzene part leads to an increase in both the melting point and the clarification temperature (Table 1).

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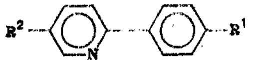
TABLE 1. Properties of 2-(4-Alkylphenyl)-5-n-alkylpyridines



III

Compound	R¹	R²	mp (tr. temp.),* °C	Found, %			Empirical formula	Calc., %			Yield, %
				C	H	N		C	H	N	
IIIa	H	C_4H_9	34(–)	85,2	8,2	6,6	$C_{15}H_{17}N$	85,3	8,1	6,6	18
IIIb	C_4H_9	C_7H_{15}	38,9(44,5)	85,4	10,0	4,6	$C_{22}H_{31}N$	85,4	10,1	4,5	14
IIIc	C_7H_{15}	C_4H_9	17,0(16,2†)	85,3	10,1	4,6	$C_{22}H_{31}N$	85,4	10,1	4,5	15
IIId	C_4H_9	C_5H_{11}	17,4(21,8)	85,3	9,6	5,1	$C_{20}H_{27}N$	85,3	9,7	5,0	14
IIIe	C_5H_{11}	C_4H_9	16,5(3,6†)	85,4	9,7	4,9	$C_{20}H_{27}N$	85,3	9,7	5,9	16
IIIf	C_2H_5	C_6H_{13}	41,9(–)	85,3	9,4	5,3	$C_{19}H_{25}N$	85,4	9,4	5,2	18
IIIg	C_6H_{13}	C_2H_5	12,0(–)	85,3	9,5	5,2	$C_{19}H_{25}N$	85,4	9,4	5,2	12
IIIh	C_2H_5	C_8H_{17}	47,4(–)	85,3	9,9	4,8	$C_{21}H_{29}N$	85,4	9,9	4,7	16
IIIi	C_4H_9	C_8H_{17}	50,4(45,1†)	85,3	10,2	4,5	$C_{23}H_{33}N$	85,4	10,3	4,3	16

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*The abbreviation "tr. temp." pertains to the temperature of transition of the nematic meso phase to an isotropic liquid.

†Monotropic transition.

EXPERIMENTAL

The PMR spectra of solutions in CCl_4 were obtained with a Tesla BS-497 spectrometer at a frequency of 100 MHz relative to tetramethylsilane (TMS). The purity of the compounds obtained was monitored by thin-layer chromatography (TLC) on Silufol UV-254.

4-Acylbromobenzenes VII. A 1-mole sample of anhydrous aluminum chloride was added in portions with stirring at room temperature to 1.1 moles of the aliphatic acid chloride, after which the mixture was heated at 40°C until it becomes homogeneous. Bromobenzene (2 moles) was than added dropwise at room temperature, and the mixture was heated at 80°C for 2 h. It was then cooled and poured over ice. Chloroform (300 ml) was added, and the organic layer was separated, washed with water, dried over calcium chloride, and distilled in vacuo. The yields ranged from 70% to 80%. The melting and boiling points of the compounds were in agreement with the values described in [4].

4-Alkylbromobenzenes VIII. These compounds were obtained by the Wolff–Kisner reaction in the Huang-Minlon modification [5].

2-(4-Alkylphenyl-5-alkylpyridines III. A solution of 0.3 mole of pyridine in 80 ml of absolute ether was added at room temperature in the course of 1 h in a stream of argon to a solution of the 4-alkylphenyllithium (obtained from 0.4 mole of the 4-alkylbromobenzene and 6 g of lithium in 150 ml of absolute ether), and the mixture was stirred for 3-4 h. A solution of 0.3 mole of the corresponding alkyl bromide in 50 ml of absolute ether was added slowly dropwise at room temperature, and the mixture was refluxed for 1 h and allowed to stand overnight in a stream of nitrogen. It was then poured into 500 ml of water at 0°C, and the organic layer was separated, washed with water, and dried over Na_2SO_4. The solvent was removed by distillation, and the residue was distilled in vacuo. The high-boiling fraction with bp 160-200°C (2-3 mm) was collected and chromatographed with a column packed with activity II aluminum oxide by successive elution with hexane and hexane–benzene (1:2). The product had R_f 0.46 (Silufol UV-254, benzene). The solvent was removed by distillation, and the residue was recrystallized from acetone at –40°C. PMR spectrum of IIId (CCl_4): 1.03-1.4 [16H, m, $(CH_3)_2$, $(CH_2)_5$]; 2.6 (4H, m, CH_2Py, CH_2Ar); 2.70 (2H, 3-H, 5-H) and 7.90 (2-H, 6-H), spectrum of the AA'BB' type; 7.30-7.70 (2H, m, γ- and β-H); 8.53 ppm (1H, m, α-H).

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