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SYNTHESIS OF 5-ARYLPYRIMIDINE-2-CARBOXYLIC ACIDS AND THE LIQUID-CRYSTAL CHARACTERISTICS OF THEIR ARYL ESTERS

M. A. Mikhaleva, G. A. Kolesnichenko, K. I. Rubina, Yu. Sh. Gol'dberg, V. A. Savel'ev, L. Ya. Leitis, M. V. Shimanskaya, and V. P. Mamaev

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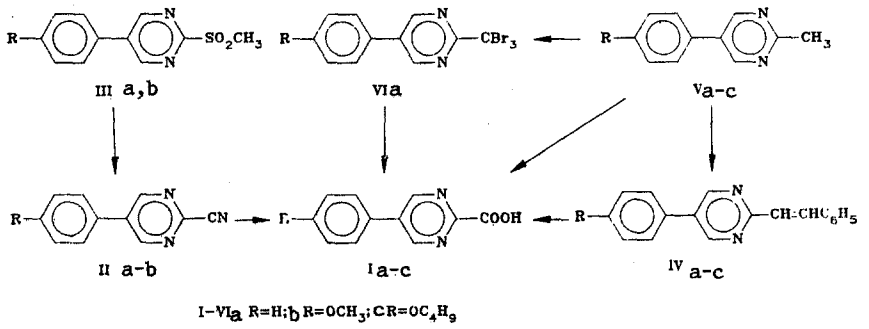
5-Arylpyrimidine-2-carboxylic acids were synthesized by the hydrolysis of 5-aryl-2-cyanopyrimidines and the oxidation of 5-aryl-2-styrylpyrimidines under the conditions of phase-transfer catalysis. The aryl esters of the acids were obtained, and their liquid-crystal characteristics were studied. The p-substituted aryl esters of 5-phenylpyrimidine-2-carboxylic acid do not exhibit mesomorphism, but the introduction of a butyloxy group at the p position of the phenyl residue leads to the appearance of nematic characteristics. Aryl 5-phenylpyrimidinylcarbonyloxybenzoates are nematic liquid crystals with a thermally stable meso phase and an existence range of 50-80°C.

The pyrimidine analogs of biphenyls have been widely studied [3, 4] in connection with advances in the study of cyanobiphenyls and the increased interest in liquid crystals with positive dielectric anisotropy [1, 2]. An important position among the various types of liquid-crystalline compounds is occupied by the esters, but with the large number of researches into liquid-crystalline aryl benzoates (e.g., [5-7]) the esters of heterocyclic acids have hardly been studied at all; there are only data on the nematic characteristics of the allyl esters of pyridine acids [8].

We have realized the synthesis of aryl pyrimidine-2-carboxylates, which are the analogs of mesomorphous compounds of the aromatic series [9-11], and we investigated their liquid-crystal characteristics. To obtain the acids I we used the traditional methods for synthesis of pyrimidine-2-carboxylic acids [12], i.e., hydrolysis of the cyanopyrimidines (II) obtained from the sulfones III and oxidation of styrylpyrimidines IV or methylpyrimidines V. Here special attention was paid to the possibility of producing the pure product, which is of primary significance during the synthesis of liquid-crystalline compounds.

SCHEME 1



I-VIa R=H; b R=OCH3; c R=OC4H9

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk 630090. Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 380-388 March, 1986. Original article submitted February 12. 1985.

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TABLE 1. p-Substituted Phenyl Pyrimidine-2-carboxylates

Compound	Transition T, °C		ΔT†, °C	IR, spectrum, ν, cm⁻¹	Found, %			Molecular formula	Calculated, %			Yield, %
	T_{nem}	T_{is}			C	H	N		C	H	N	
IX	—	208—210	—	1775, 2230	76,4	3,99	11,1	$C_{24}H_{15}N_3O_2$	76.4	3,98	11,1	61
XIIa	—	119—120	—	1760	75,7	6,30	8,32	$C_{22}H_{22}N_2O_2$	76,2	6,36	8,10	90
XIIb	—	140—142	—	1760	72,8	5,89	7,86	$C_{22}H_{22}N_2O_3$	72,9	6,07	7,73	83
XIIc	—	190—195	—	1770, 2230	71,8	3,94	13,6	$C_{18}H_{11}N_3O_2$	71,8	3,66	13,9	50
XIId	165	210	45	1770, 2240	70,4	5,13	11,2	$C_{22}H_{19}N_3O_3$	70,7	5,10	11,2	21
XIIIa	145	225	80	1740, 1760	74,7	5,44	5,94	$C_{29}H_{26}N_2O_4$	74,7	5,58	6,02	59
XIIIb	155	230—235	75	1740, 1760	72,5	5,24	6,06	$C_{29}H_{26}N_2O_5$	72,2	5,40	5,82	37
XIIIc	225	270 decomp.	45	1750, 1765, 2235	71,6	3,62	9,80	$C_{25}H_{15}N_3O_4$	71,8	3,56	9,98	95
XIV	—	270 decomp.	—	1700, 1770	—	—	8,65	$C_{18}H_{12}N_2O_4$	—	—	8,75	56

*Compound IX was crystallized from benzene, XIIa from hexane, XIIb and XIIIa, b from ethanol, and XIIc, d and XIIIc from ethyl acetate. T_{nem} is the temperature of the nematic mesophase, and T_{is} the temperature of the isotropic mesophase. †ΔT is the existence range of the mesomorphous state.

The acid (Ia) was obtained with yields of 60-70% both by the hydrolysis of cyanopyrimidine IIa and by the oxidation of styrylpyrimidine IVa under the conditions of phase-transfer catalysis or of methylpyrimidine Va by selenium dioxide with prolonged boiling in pyridine. In order to replace the toxic selenium dioxide we studied the possibility of synthesizing the acids I from the derivatives V under the conditions of phase-transfer catalysis, the effectiveness of which in oxidation reactions is well known [13]. The experiments showed that the oxidation of Va by permanganate does not occur at room temperature in the two-phase dichloroethane—water (benzene—water, o-dichlorobenzene—water) system in the presence of typical phase-transfer catalysts (18-crown-6, $Bu_3(C_6H_5CH_2)N^+Cl^-$, $Bu_4N^+Br^-$); when the temperature was increased decomposition of the pyrimidine ring was observed, and only benzoic acid was isolated from the reaction mixture. The oxidation of the pyrimidine V by atmospheric oxygen in the presence of V—Mo—O catalyst (V:Mo, 3:1) and Pd-Cu-NaY zeolite at 400-440°C under pulsed conditions (4-methylpyrimidine is oxidized to 4-formylpyrimidine with high selectivity under these conditions [14]) led to the formation of carbon oxides and resinous products. Oxygen-containing organic compounds were not found in the reaction products. During the production of the acid Ia from 2-bromomethyl derivative VIa [15], according to mass spectrometry, bromine-containing products were detected in the product as impurities.

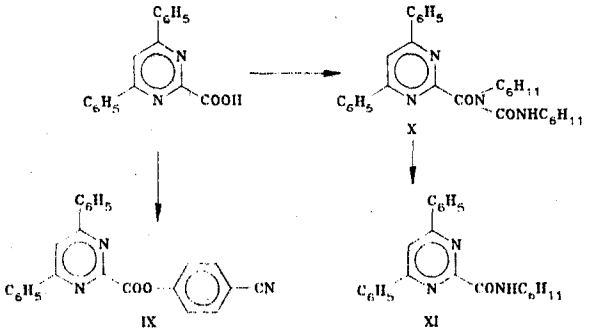
Similarly, only p-methoxybenzoic acid is formed from methylpyrimidine Vb during oxidation under the conditions of phase-transfer catalysis; it was possible to obtain the acid Ib by the oxidation of styrylpyrimidine IVb in the two-phase benzene—aqueous potasssium permanganate system in the presence of tributylbenzylammonium chloride. In the case of the butyloxyphenyl derivatives IVc, Vc, however, oxidation under analogous conditions did not lead to the corresponding acid Ic as a result, evidently, of the oxidative elimination of the butyloxy group. The hydrolysis of the cyanopyrimidine IIc gave a mixture of the acid Ic, its amide VIIc, and 2-hydroxy-5-(p-butyloxyphenyl)pyrimidine (VIIIc), the ratio of which depended on the hydrolysis conditions. When 10-15% sodium hydroxide was used at a bath temperature of 90-100°C, hydrolysis only took place slowly (TLC), and the acid Ic and the amide VIIc were found in the reaction mixture. If the temperature was increased to 100-120°C, the initial cyano derivative disappeared after 1 h, but the 2-hydroxy derivative VIIIc began to appear. During hydrolysis at a bath temperature of 130°C the latter was the only reaction product. These compounds cannot be separated by recrystallization and are difficult to separate by chromatography on account of the similarity in their R_f values. The hydrolysis of the cyano derivative IIb takes place similarly (according to IR spectroscopy and TLC).

From the acids Ia, c we than obtained their aryl esters in order to investigate their mesomorphous characteristics. Various methods have been described for the production of the aryl esters of carboxylic acids, but the most widespread method is the reaction of phenols with acid chlorides [16]. Since the pyrimidine-2-carboxylic acids do not always form acid chlorides readily [15], we checked the applicability of the carbodiimide method [17, 18]

and the method employing the triphenylphosphine–carbon tetrachloride complex [19] for the production of the aryl pyrimidine-2-carboxylates in the case of 4,6-diphenylpyrimidine-2-carboxylic acid. The synthesis of the aryl esters of pyrimidinecarboxylic acids has not been described in the literature. There are only patent data on the production of p-nitrophenyl pyrimidine-5-carboxylate in the presence of dicyclohexylcarbodiimide (DCC) [20].

It was shown that, unlike pyrimidine-5-carboxylic acid [20], in reaction with p-cyanophenol in THF in the presence of DCC 4,6-diphenylpyrimidine-2-carboxylic acid forms a compound which corresponds in its spectral characteristics to the ureide X and not the aryl ester IX (Scheme 2).

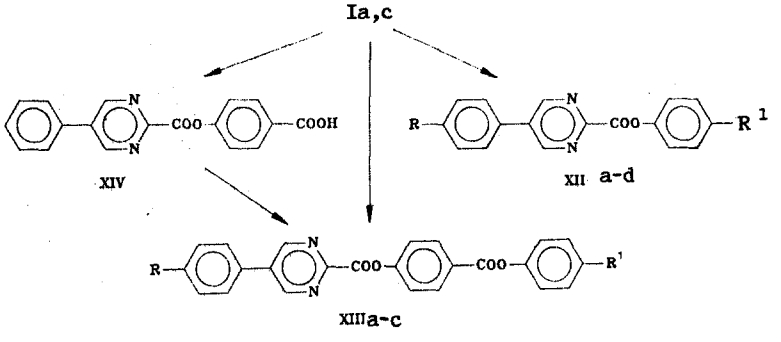
SCHEME 2



Compounds of such a type are formed as a result of the rearrangement of the corresponding O-acylisourea formed initially in the reactions with DCC [17]. During vacuum distillation compound X was converted into the amide (XI). The p-cyanophenyl ester IX was obtained from p-cyanophenol and 4,6-diphenylpyrimidine-2-carboxylic acid with a good yield by means of the PPh_3–CCl_4 complex [19] and also by the traditional method through the acid chlorides [6].

We obtained the esters XII by the reaction of the acids I with p-substituted phenols according to the method in [9] (scheme 3).

SCHEME 3



XII XIII a–c R=H, d R=OC_4H_9; a $R^1=C_5H_{11}$, b $R^1=OC_5H_{11}$, c, d R^1=CN

The esters XIII with two bridging groups were obtained by different methods [6, 16]; for $R^1 = C_5H_{11}$ and OC_5H_{11} the synthesis was realized similarly to the previous synthesis from the acid Ia and the aryl p-hydroxybenzoate [7], and in the case of R^1 = CN we first obtained the carboxy ester XIV, which we then converted into the ester XIIIc through the acid chloride by reaction with p-cyanophenol. The obtained esters XII and XIII were easy to isolate from the reaction mixture and were purified well by recrystallization. Thin-layer chromatography was only suitable for isolation or purification in the case of the esters not containing CN groups. During chromatography on silica gel and elution with alcohol the latter were converted into the corresponding ethyl esters.

TABLE 2. 2,5-Disubstituted Pyrimidines

Compound	T_{mp} °C*	M(M_{calc})	R_f	IR spectrum, ν, cm⁻¹	Found, %			Molecular formula	Calculated, %			Yield, %
					C	H	N(Br)		C	H	N(Br)	
Ia	223	200	0,2—0,3	1730	66,0	4,00	14,2	$C_{11}H_8N_2O_2$	66,0	4,00	14,0	71
Ib	230—231	—	—	—	62,9	4,18	12,7	$C_{12}H_{10}N_2O_3$	62,6	4,38	12,2	42
Ic	170—175‡	272	0,50	1720	—	—	10,0	$C_{15}H_{16}N_2O_3$	—	—	10,3	61
IIb	182—187	—	0,75	1260, 2250	67,9	4,30	20,0	$C_{12}H_9N_3O$	68,2	4,30	19,9	63
IIIa	181—182	—	0,45	—	56,6	4,60	11,7	$C_{11}H_{10}N_2O_2$	56,5	4,30	11,9	30
IIIb	184—185	—	0,65	1135, 1310	54,5	4,91	10,6	$C_{12}H_{12}N_2O_3$	54,6	4,55	10,6	73
Vb	137—138	—	0,35	—	72,2	5,83	14,0	$C_{12}H_{12}N_2O$	72,0	6,00	14,0	83
Vc	113—115	—	0,35	—	74,8	7,45	11,4	$C_{15}H_{18}N_2O$	74,4	7,44	11,6	95
VIa	163—165 subl.	404	0,90	—	32,4	1,72	6,80 (59,0)	$C_{11}H_7Br_3N_2$	33,0	1,61	6,49 (59,0)	68
VIIc	150—160 †	271, 1322 (271, 1321)	0,52	1690, 3200, 3280 sh 3400	—	—	—	$C_{15}H_{17}N_3O_2$				—
VIIIc	195—199	244	0,44	1680 b.r.	69,5	6,71	11,5	$C_{14}H_{16}N_2O_2$	68,9	6,55	11,5	55 ‡

*Compounds Ia, b, VIIIc were crystallized from ethyl acetate, IIb from a mixture of ethanol and carbon tetrachloride, IIIa, b from ethanol, Vb from heptane, and Vc from methanol.

†After TLC.

‡In the condensation reaction.

Liquid-Crystalline Characteristics of Esters XII and XIII. The esters XIIa-c did not exhibit mesomorphous characteristics even in the presence of the CN group (XIIc), although the previously described benzene analogs of the esters XIIb, c, i.e., p-cyanophenyl [9] and p-amyloxyphenyl [11] biphenylcarboxylates, were nematic liquid crystals. As noticed earlier for Schiff bases [21], the introduction of a pyrimidine ring in place of the benzene ring in this case also leads to loss of the liquid-crystal characteristics. In the presence of a substituent at the p position (the ester XIId) the compound becomes mesomorphous, and a nematic meso phase appears. In this case it is possible to draw an analogy both with the appearance of nematic characteristics in biphenylcarboxylic esters [10, 11] and in the similarity in the clearing temperatures of their cyanophenyl esters [10].

Similarly, diesters XIII are nematic liquid crystals (Table 1). In compounds XIIIa, b the mesophase appears at lower temperatures than in the ester XIId, while the cyano derivative XIIIc is characterized by high-temperature transitions. The existence range of the liquid-crystal state in these compounds amounts to 80°C.

EXPERIMENTAL

The IR spectra were recorded in tablets with potassium bromide on a UR-20 spectrometer. The PMR spectra of compounds Ia, b, IVa-c were recorded on a Bruker WH-90/DS spectrometer in chloroform with TMS as internal standard. The spectra of the other compounds were recorded on a Varian A56/60 spectrometer in deuterochloroform with HMDS as internal standard. The molecular weights were determined by mass spectrometry on a high-resolution MS-902 instrument. The phase transition temperatures were measured on a small-scale heater bench of the Boetius type with an RNMK-0.5 visual facility. Thin-layer chromatography was performed in the 20:1 chloroform–alcohol system on Silufol UV-254 plates and silica gel L50/40.

The characteristics of the obtained compounds are given in Tables 1 and 2.

5-Phenylpyrimidine-2-carboxylic Acid (Ia). A. A suspension of 1.27 g (7 mmoles) of the cyanopyrimidine IIa in 25 ml of a 15% sodium hydroxide solution was boiled for 0.5 h and cooled. The precipitate was filtered off and washed with chloroform and with alcohol. The obtained salt was suspended in 30 ml of water and acidified to pH 2-3 with dilute hydrochloric acid. The acid Ia was filtered off and dried in air. The yield was 1 g.

B. To a solution of 2.15 g (8.3 mmoles) of styrylpyrimidine IVa and 0.26 g (0.83 mmoles) of tributylbenzylammonium chloride in 35 ml of benzene, cooled to 15°C, we added dropwise a solution of 2.63 g (17 mmoles) of potassium permanganate in 55 ml of water at such a rate that the temperature of the reaction mixture did not exceed 20°C. The mixture was stirred at 15-20°C for 0.5 h, the manganese dioxide was filtered off, the aqueous layer was separated and acidified to pH 2-4, and the precipitated acid Ia was filtered off. The yield was 1.07 g (68%). PMR spectrum, 7.49-7.84 (m, 5H, H_{arom}), 9.16 ppm (s, 2H, 4,6-H of pyrimidine ring).

C. To a solution of 2.04 g (12 mmoles) of methylpyrimidine Va [22] in 25 ml of pyridine, while boiling, we added 2 g (18 mmoles) of selenium dioxide in small portions over 4 h. The mixture was cooled, the precipitated selenium was filtered off, and the solvent was distilled. The distillation residue was dissolved in 25 ml of 0.1 N sodium hydroxide solution, filtered, and acidified to pH 4 with hydrochloric acid. The precipitate was filtered off, and 0.91 g (61%) of the acid Ia was obtained.

D. To a stirred solution of 1.5 g (3.6 mmoles) of tribromomethylpyrimidine VIa in 10 ml of glacial acetic acid we added dropwise 5 ml of a 2 N aqueous solution of silver nitrate. The mixture was heated in the dark for 1.5 h. The cooled suspension was treated with 1 ml of 5 N hydrochloric acid. The precipitate was filtered off and washed with 50 ml of alcohol. The alcohol filtrate was evaporated, and 0.64 g of the precipitate was obtained. It was washed with ether and with methanol, sublimed at 150°C (1 mm Hg), and recrystallized from ethyl acetate. The acid Ia was obtained with a yield of 0.40 g (56%). The IR spectra of the acids obtained by methods A and D were identical. The mass spectrum contained a line with m/z 325, corresponding to the dibromomethyl derivative.

5-(p-Methyoxyphenyl)pyrimidine-2-carboxylic Acid (Ib). Compound Ib was obtained similarly to Ia by method B from styrylpyrimidine IVb. PMR spectrum: 3.44 (s, 3H, OCH_3), 6.71-7.31 (m, 4H, H_{arom}), 8.62 ppm (s, 2H, 4,6-H of pyrimidine ring).

5-(p-Butyloxyphenyl)pyrimidine-2-carboxylic Acid (Ic), 5-(p-Butoxyphenyl)-2-carbamoylpyrimidine (VIIc), and 2-Hydroxy-5-(p-butyloxyphenyl)pyrimidine (VIIIc). A suspension of 2 g (7.9 mmoles) of the cyanopyrimidine IIc [3] was heated and shaken with 50 ml of a 15% solution of sodium hydroxide at 120°C for 1 h. The mixture was cooled, and the precipitated sodium salt was filtered off and washed with water and with alcohol. It was suspended in 30 ml of water and acidified to pH 2-3 with a 20% solution of hydrochloric acid. The precipitate was filtered off and washed with water and with alcohol. We obtained 2 g of a mixture of the acid Ic, the amide VIIc, and the hydroxypyrimidine VIIIc. IR spectrum: 1610, 1630 sh, 1680, 1720 cm^{-1}. R_f 0.40 (dark luminescence) 0.45-0.50 (two light spots). The mixture was not separated during recrystallization from alcohol, ethyl acetate, or benzene, or by reprecipitation by dissolution in alkali and careful acidification. By twofold separation by preparative TLC we obtained 1.3 g of the acid Ic and a small amount of the amide VIIc. The hydroxypyrimidine VIIIc was obtained with a yield of 0.1 g; R_f 0.45, mp 199-200°C (from ethyl acetate). It was identical with an authentic sample in its IR spectrum.

2-Cyano-5-phenylpyrimidine (IIa). A suspension of 6.8 g (29 mmoles) of the pyrimidine IIIa and 2.5 g (39 mmoles) of potassium cyanide in 130 ml of N-methylpyrrolidone was stirred at room temperature for 1 h, at 50°C for 2 h, and at 65°C for 4 h. The mixture was poured into 40° ml of water and extracted with ether (4 × 150 ml). The extract was washed with 300 ml of water, dried with magnesium sulfate, and evaporated. The yield of the cyano derivative IIa was 3.7 g (70%); mp 128-129°C (from alcohol). Published data [23]: mp 129-130°C.

2-Cyano-5-(p-methoxyphenyl)pyrimidine (IIb). To a solution of 8 g (36 mmoles) of the pyrimidine IIIb in 200 ml of DMFA we added 2.34 g (36 mmoles) of potassium cyanide. The mixture was heated at 100°C for 3 h. A sample of the reaction mixture (10 ml) was then diluted with water (1:1). The precipitate was filtered off, dissolved in 10 ml of methylene chloride, filtered, and evaporated. The product was recrystallized from a mixture of carbon tetrachloride and alcohol, and 0.1 g of the cyanopyrimidine IIb was obtained. PMR spectrum: 3.85 (s, 3H, CH_3); 7.07 and 7.50 (d, 2H, J = 9 Hz, H_{arom}); 9.00 ppm (s, 2H, 4,6-H of pyrimidine ring).

The DMFA was distilled from the remaining quantity of the reaction mixture. The residue was extracted with methylene chloride (4 × 100 ml), the extract was evaporated, and 6 g of a mixture containing two compounds with R_f 0.70 and 0.75 was obtained. A sample of the mixture (0.76 g) was boiled with 10 ml of a 15% solution of sodium hydroxide. The undissolved part was filtered off and recrystallized from alcohol, and 2-dimethylamino-5-(p-methoxyphenyl)pyrimidine was obtained; mp 127-130°C. The yield was 0.25 g (29%). PMR spectrum: 3.12 (s, 6H, NCH_3), 3.70 (s, 3H, OCH_3), 6.90 and 7.30 (d, 2H, J = 9 Hz, H_{arom}), 8.43 ppm (s, 2H, 4,6-H of pyrimidine ring). Found %: C 67.9; H 6.45; N 18.4. $C_{13}H_{15}N_3O$. Calculated %: C 68.1; H 6.55; N 18.3.

2-Methylsulfonyl-5-phenylpyrimidine (IIIa). By stirring we dissolved 9.69 g (48 mmoles) of 2-methylthio-5-phenylpyrimidine [22] in 100 ml of glacial acetic acid. The mixture was heated to 60°C, and 25 ml of 30% hydrogen peroxide was added drop by drop. The mixture was heated for 6 h, the solution was poured into 100 ml of water, the precipitate was filtered off and washed with 50 ml of 10% sodium bicarbonate solution and to a neutral reaction with water, and 3.2 g of the pyrimidine IIIa was obtained.

2-Methylthio-5-(p-methoxyphenyl)pyrimidine. A mixutre of 30 g (90 mmoles) of 2-(p-methoxyphenyl)-3-dimethylaminopropenylidenedimethylamine perchlorate [24] and 13.1 g (60 mmoles) of methylisothiourea sulfate in 150 ml of absolute pyridine was heated at 80°C for 6 h. The mixture was poured onto a mixture of 900 g of ice with 110 ml of concentrated sulfuric acid. The precipitate was filtered off, and 19.75 g (94%) of the product was obtained; mp 79°C (from hexane). Found %: C 62.6; H 5.43; N 12.0. $C_{12}H_{12}N_2O$. Calculated %: C 62.5; H 5.18; N 12.0.

2-Methylsulfonyl-5-(p-methoxyphenyl pyrimidine (IIIb). To a suspension of 10.58 g (46 mmoles) of 2-methylthio-5-(p-methoxyphenyl)pyrimidine in 90 ml of glacial acetic acid we added 23 ml of 30% hydrogen peroxide. The mixture was stirred at 50°C for 6 h and added to 200 ml of water. The precipitate was filtered off, washed to a neutral reaction with 100 ml of 10% sodium bicarbonate solution and then with water, and dried. We obtained 8.8 g of the pyrimidine IIIb.

2-Styryl-5-phenylpyrimidine (IVa). A mixture of 17 g (100 mmoles) of the pyrimidine Va and 11.7 g (110 mmoles) of benzaldehyde was stirred at 150-160°C for 4.5 h, cooled, and dissolved in 50 ml of acetone. Water was added (100 ml) until a precipitate separated. The precipitate was filtered off and recrystallized from petroleum ether. The yield of styryl-pyrimidine IVa was 18 g (70%); mp 143°C. PMR spectrum: 7.15-8.16 (m, 12H, H_{vinyl} and H_{arm}), 8.90 ppm (s, 2H, 4,6-H of pyrimidine ring). The following two compounds were obtained similarly.

2-Styryl-5-(p-methoxyphenyl)pyrimidine (IVb). The yield was 64% mp 166-168°C. PMR spectrum: 3.89 (s, 3H, OCH_3), 6.96-8.02 (m, 11H, H_{vinyl} and H_{arom}) 8.93 ppm (s, 2H, 4,6-H of pyrimidine ring).

2-Styryl-5-(p-butyloxyphenyl)pyrimidine (IVc). The yield was 67%; mp 135-138°C. PMR spectrum: 1.00 (t, 3H, J = 6 Hz, CH_3), 1.31-2.00 (m, 4H, CH_2), 4.02 (t, 2H, J = 6 Hz, OCH_2), 7.24 (q, A_2B_2, J = 8 Hz, 4H, H_{arom}), 8.78 ppm (s, 2H, 4,6-H of pyrimidine ring).

2-Methyl-5-(p-methoxyphenyl)pyrimidine (Vb) and 2-methyl-5-(p-butyloxyphenyl)pyrimidine (Vc). The compounds were obtained by a method similar to that in [22].

2-Tribromomethyl-5-phenylpyrimidine (VIa). To a boiling solution of 8.5 g (50 mmoles) of the pyrimidine (Va) and 24.6 g (300 mmoles) of sodium acetate in 150 ml of glacial acetic acid we added 24 g (150 mmoles) of bromine in 10 ml of glacial acetic acid. The mixture was stirred for 0.5 h and left over night. The precipitate was filtered off and washed with 100 ml of a saturated solution of sodium bicarbonate and with water. We obtained 12.15 g of the pyrimidine VIa.

2-Hydroxy-5-(p-butyloxyphenyl)pyrimidine (VIIIc). To a mixture of 1.12 g (3 mmoles) of 2-(p-butyloxyphenyl)-3-dimethylaminopropenylidenedimethylamine perchlorate [24] and 0.24 g (4 mmoles) of urea we added 5 ml of absolute methanol. The mixture was heated to boiling, and a solution of sodium methoxide (from 0.16 g of metallic sodium and 3 ml of methanol) was slowly added drop by drop. The mixture was heated for 3 h and cooled, and 50 ml of water and 5 ml of acetic acid were added. The product was rubbed until a uniform suspension was obtained. The fine precipitate was filtered off and washed with water and several times with ether. We obtained 0.4 g of the hydroxypyrimidine VIIIc.

p-Cyanophenyl 4,6-Diphenylpyrimidine-2-carboxylate (IX). A. A mixture of 2 g (7.25 mmoles) of 4,6-diphenylpyrimidine-2-carboxylic acid [25] and 14 ml of thionyl chloride in 150 ml of benzene was boiled in the presence of six drops of DMFA for 24 h. The mixture was distilled to dryness, a further 30 ml of dry benzene was added, the mixture was again distilled to dryness, and the residue was kept under vacuum (2.6-3.0 kPa) for 5-7 min. The acid chloride was dissolved in 35 ml of pyridine, 0.86 g (7.2 mmoles) of p-cyanophenol was added, and the mixture was stirred at room temperature for five days. It was then poured onto 150 g of ice with 35 ml of concentrated sulfuric acid. The precipitate was filtered off and washed with water, alcohol, and ether, and 1.66 g of the ester IX was obtained.

B. A mixture of 2 g (7.25 mmoles) of the acid, 0.7 g (6 mmoles) of p-cyanophenol, 1.9 g (7.2 mmoles) of triphenylphosphine, 0.73 g (7.2 mmoles) of triethylamine, and 1.1 g (7.2 mmoles) of carbon tetrachloride in 10 ml of acetonitrile was stirred at room temperature for 6 h. The precipitated ester IX was filtered off and washed with chloroform. The yield was 1.5 g (66%); mp 208-209°C (from ethyl acetate).

N-Cyclohexyl-4,6-diphenylpyrimidine-2-carboxamide (XI). To a solution of 1 g (3.6 mmoles) of 4,6-diphenylpyrimidine-2-carboxylic acid and 0.96 g (7.2 mmoles) of p-cyanophenol in 50 ml of dry THF we added dropwise a solution of 1.5 g of DCC in 20 ml of dry THF. The mixture was stirred at room temperature for 9 h and evaporated. The residue was rubbed with 15 ml of ether, and the ureide X was filtered off; mp 179-181°C (from ethyl acetate). IR spectrum: 1640, 1680, 1705, 3290 cm^{-1}. The ureide (X) was sublimed under vacuum at 150-160°C (2 mm Hg), and the amide (XI) was obtained; mp 218-223°C. IR spectrum, 1635, 3330 cm^{-1}. Found %: N 11.9; M 357. $C_{23}H_{23}N_3O$. Calculated %: N 11.7; M. 357.

p-Cyanophenyl 5-Phenylpyrimidine-2-carboxylate (XIIc). A mixture of 1 g (5 mmoles) of the acid Ia, 0.47 g (4.2 mmoles) of p-cyanophenol, 1.31 g (5 mmoles) of triphenylphosphine, 0.5 g (5 mmoles) of triethylamine, and 0.77 g of carbon tetrachloride in 6.5 ml of acetonitrile was stirred at room temperature for 10 h. The precipitate was filtered off and washed with acetonitrile, and compound XIIc was obtained.

p-Amylphenyl (XIIa) and p-amyloxyphenyl (XIIc) esters of the acid Ia were obtained similarly.

p-Cyanophenyl 5-(p-Butyloxyphenyl)pyrimidine-2-carboxylate (XIId). A mixture of 1.3 g (4.8 mmoles) of the acid Ic, 0.48 g (4 mmoles) of p-cyanophenol, 1.26 g (4.8 mmoles) of triphenylphosphine, 0.47 ml (4.8 mmoles) of carbon tetrachloride, and 0.67 ml (4.8 mmoles) of triethylamine was stirred on a magnetic stirrer for 6 h. The precipitate was filtered off and washed with acetonitrile, heptane, and ether, and 0.9 g of the precipitate was obtained. It was rubbed with 30-40 ml of benzene and filtered. The solution was evaporated, and 0.38 g of the ester XIId was obtained. The product was purified by recrystallization from a 1:1 mixture of benzene and petroleum ether and then from ethyl acetate. By purification by TLC and elution with alcohol we only obtained the ethyl ester of the acid Ic, which was identical with an authentic sample.

Ethyl 5-(p-Butyloxyphenyl)pyrimidine-2-carboxylate. A mixture of 0.13 g (0.48 mmoles) of the acid Ic, 3 ml of alcohol, and three drops of concentrated hydrochloric acid was boiled for 5 h and cooled. The precipitate was filtered off and washed with ether. The yield was 0.1 g (70%); mp 150.5-151.5°C (from alcohol). IR spectrum: 1730 cm^{-1}. Found %: C 68.1; H 6.68; N. 9.39; M 300. $C_{17}H_{20}N_2O_3$. Calculated %: C 68.1; H 6.66; N 9.33; M 300.

p-Ethyl- and p-Ethoxyphenyl p-(5-Phenyl-2-pyrimidylcarbonyloxybenzoate (XIIIa, b). We mixed 2.4 mmoles of the acid Ia, 2 mmoles of p-ethyl- or p-ethoxyphenyl p-hydroxybenzoate [7], and 2.4 mmoles each of triphenylphosphine, carbon tetrachloride, and triethylamine. The mixture was stirred at room temperature on a magnetic stirrer for 7-10 h. The precipitated ester was filtered off and washed with hexane and with ether.

p-Cyanophenyl p-(5-Phenyl-2-pyrimidoylcarbonyloxy)benzoate (XIIIc). To a suspension of 0.64 g (2 mmoles) of the acid XIV in 20 ml of absolute benzene we added 3 ml of thionyl chloride. The mixture was boiled for 10 h, and the benzene and thionyl chloride were distilled to dryness. To the residue we added 10 ml of benzene. The mixture was again distilled to dryness, the residue was kept under vacuum (2.6-3.0 kPa) for 0.5 h, and 0.77 g of the acid chloride XIV was obtained. IR spectrum: 1760 br, 1780 cm^{-1}.

To a suspension of 0.75 g (2.22 mmoles) of the acid chloride in 10 ml of pyridine we added 0.26 g (2.18 mmoles) of p-cyanophenol. The mixture was stirred at room temperature for 4 h. The precipitate was filtered off, washed with 10 ml of 10% hydrochloric acid and to a neutral reaction with water, and dried in air. We obtained 0.8 g of the ester XIIIc.

p-(5-Phenyl-2-pyrimidylcarbonyloxy)benzoic Acid (XIV). A mixture of 2 g (10 mmoles) of the acid Ia with 15 ml of thionyl chloride in 100 ml of absolute benzene with the addition of 1 ml of DMFA was boiled for 15 h. The mixture was distilled to dryness, 50 ml of benzene was added to the residue, and the mixture was again distilled to dryness. The residue (the chloride of the acid Ia) crystallized in the form large needless. IR spectrum 1740 w, 1775 cm^{-1}. To the acid chloride Ia we added 30 ml of dry pyridine and 0.7 g of p-hydroxybenzoic acid. The reaction mixture was kept at room temperature for three days. The precipitate was filtered off, washed to a neutral reaction with water which had been acidified with hydrochloric acid, and dried. We obtained 1.8 g of the acid XIV.

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REACTIONS OF AZINIUM IONS.

4.* REACTIONS OF QUINOXALINIUM SALTS WITH NITROALKANES — SINGLE-STAGE PATH TO TETRAAZAHETEROCYCLES WITH BRIDGED AND FRAMEWORK STRUCTURES

V. N. Charushin, D. M. Petrova,
O. N. Chupakhin, E. O. Sidorov,
G. G. Aleksandrov, A. I. Chernyshev,
N. A. Klyuev, and N. N. Sorokin

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The addition of the carbanions of nitroalkanes of N-alkylquinoxalinium salts in an alcohol medium leads to dibenzo[d,k]-1,3,6,10-tetrasubstituted tricyclo[7.3.1.$0^{2,7}$]- and tetracyclo[7.3.1.$0^{2,7}0^{6,13}$]tridecanes.

The reactions of azinium ions with the carbanions of nitroalkanes take place in various ways. Thus, the N-methoxypyridinium ion adds nitroalkanes in the presence of sodium ethoxide at position 2 with subsequent opening of the pyridine ring [2]. More complex transformations were observed in the reaction of nitroalkanes with quaternary isoquinolinium salts, in which complex polycyclic systems with a framework structure are formed as a result of the successive combination of two isoquinolinium molecules [3]. In the present work we give the results from an investigation into the reactions of nitroalkanes with quaternary quinoxalinium salts, which are susceptible (unlike other azinium ions) to the formation of products from the diaddition of nucleophiles at positions 2 and 3 [4-7].

In fact, a common feature of the investigated transformations of quinoxalinium salts under the influence of trinitroalkane anions is the formation of tetrahydroquinoxalines from them as a result of the diaddition of the nucleophiles. However, the outcome of the reactions depends on the nature of the reagents, the solvent, and also the base.

When dissolved in an excess of nitroethane in the presence of diethylamine, N-methylquinoxalinium iodide (Ia) gives a high yield (87%) of the diaddition product II, melting at

*For Communication 3, see [1].

S. M. Kirov Ural Polytechnical Institute, Sverdlovsk 620002. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 389-399, March, 1986. Original article submitted February 21, 1985.

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