REACTION OF DIHALOCARBENES WITH 2-(BENZYLIDENEAMINO)PYRIDINES. CYCLIZATION OF 2-(BENZYLIDENEAMINO)PYRIDINIUM DIHALOMETHYLIDS TO GIVE 2-ARYL-3-HALOIMIDAZO[1,2-*a*]PYRIDINES

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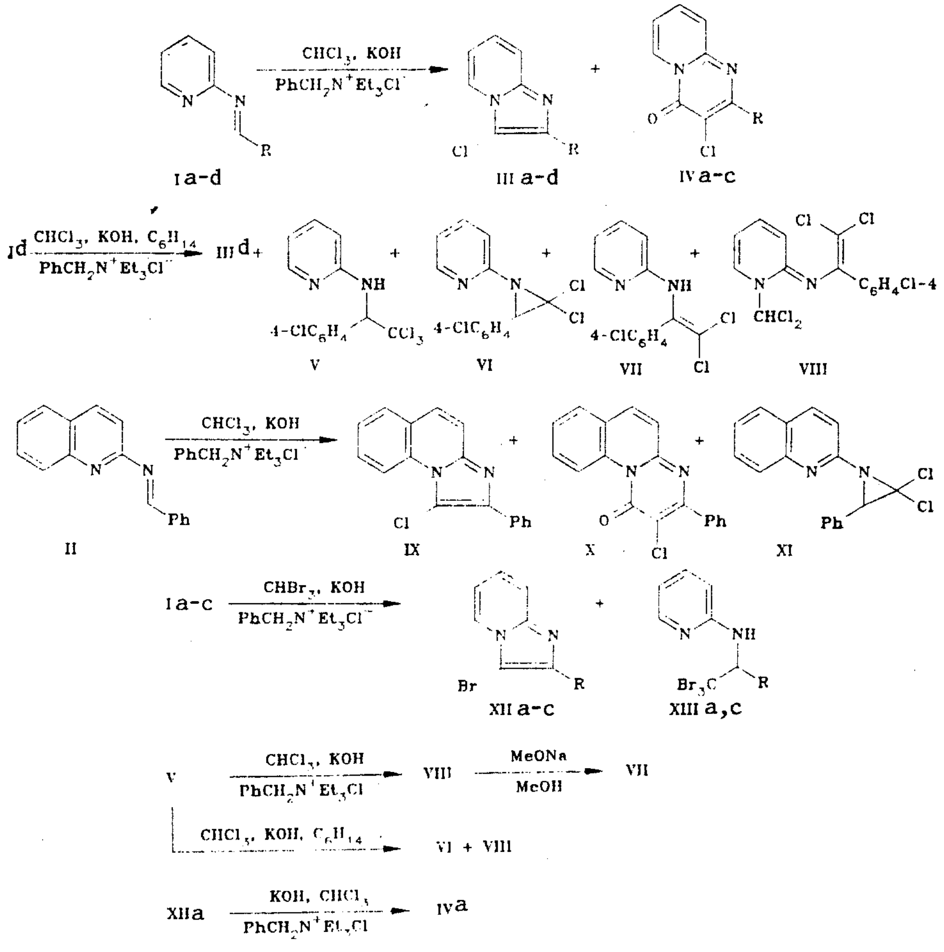
Pyridinium dichloromethylids, formed in the reaction of dichlorocarbene with 2-(benzylideneamino)pyridines, undergo intramolecular 1,5-cyclization to give 2-aryl-3-chloroimidazo[1,2-a]pyridines, which undergo partial conversion to 2-aryl-3-chloro-4H-pyrido[1,2-a]pyrimidin-4-ones under the reaction conditions. 2-Aryl-3-bromoimidazo[1,2-a]pyridines and 2-[N-(1-aryl-2,2,2-tribromoethyl)amino]pyridines, respectively, are obtained in the reaction of dibromocarbene and the tribromomethyl anion generated in the reaction of bromoform with potassium hydroxide.

The reaction of dichlorocarbene with pyridine and 3- and 4-substituted pyridines yields pyridinium dichloromethylids, which give products of 1,3-dipolar cycloaddition with electron-deficient dipolarophiles [1, 2]. 2-Substituted pyridines are inert in this reaction [2].



I, III, IV, XII, XIII a R=Ph; b R=4-MeOC$_6$H$_4$; c R=4-BrC$_6$H$_4$; d R=4-ClC$_6$H$_4$

In the present research we investigated the reaction of dichlorocarbene and dibromocarbene, generated from the haloforms and potassium hydroxide in the presence of benzyltriethylammonium chloride, with 2-(arylmethyleneamino)pyridines Ia-d and 2-(benzylideneamino)quinoline (II).

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2-Aryl-3-chloroimidazo[1,2-*a*]pyridines IIIa-d and 2-aryl-3-chloro-4H-pyrido[1,2-*a*]pyrimidin-4-ones IVa-c were isolated in 34-41% and 1-20% yields, respectively, as a result of the reaction of dichlorocarbene with pyridines Ia-d in chloroform (see Tables 1 and 2). Signals of the protons of the pyridine part of the molecule at 8.05 (dt, 5-H), 6.85 (dt, 6-H), 7.20 (dd, 7-H), and 7.60 ppm (dt, 8-H), as well as signals of protons of a benzene ring (7.0-8.2 ppm), are observed in the PMR spectra of IIIa-d. The presence of an absorption band at 1350 cm^{-1}, which has the highest intensity, is characteristic for the IR spectra of IIIa-d. The data from the UV spectra of IIIa, b are in agreement with the data presented in [3].

Intense absorption bands of stretching vibrations of a C=O bond at ~1690 cm^{-1} are observed in the IR spectra of IVa-c. In the PMR spectra of these compounds the signal of the 6-H proton is shifted to weak field (~9 ppm).

Compounds V-VIII, in addition to imidazopyridine IIId, were obtained from Id when the reaction was carried out in a mixture of chloroform and hexane (1:1 by volume). In addition to signals of aromatic protons (see Table 1), two doublets at 5.41 (NH) and 6.11 ppm (CH) (J = 9.5 Hz) are present in the PMR spectrum of V. The IR spectrum of V contains a band at 3435 cm^{-1} (ν_{NH}). A molecular-ion peak (m/z 334) is present in the mass spectrum of this substance, while the most intense peak is the peak of the $[M - CCl_3]^+$ ion (m/z 217). The PMR spectrum of VI contains a singlet signal of an aziridine proton at 4.21 ppm (see [4]). The PMR spectrum of VII contains a broad signal of a proton of an NH group, to which the band at 3395 cm^{-1} in the IR spectrum corresponds. The mass spectrum of this compound contains a molecular-ion peak (m/z 298), while the most intense peak is the peak of the $[M - Cl]^+$ ion (m/z 263). In the PMR spectrum of VIII multiplet signals of protons of a 1,2-dihydropyridine ring are found at stronger field than the corresponding protons of V-VIII; in addition, there is a singlet signal at 8.64 ppm ($NCHCl_2$). A $\nu_{C=N}$ band (1653 cm^{-1}) is present in the IR spectrum of VIII. A molecular-ion peak (m/z 380) is present in the mass spectrum of VIII, while the most intense peak is the peak of the $[M - Cl - HCl]^+$ ion (m/z 309). The position of the long-wave maximum (360 nm) in the UV spectrum of VIII constitutes evidence for the presence of a conjugated π system that is more extended than in V-VII (see Table 1). The structure of VIII is also confirmed by its conversion to amine VII by the action of sodium methoxide in methanol.

In addition to analogs of III and IV — 2-phenyl-1-chloroimidazo[1,2-*a*]quinoline (IX) and 3-phenyl-2-chloro-1H-pyrimido[1,2-*a*]quinolin-1-one (X) — 2-(3-phenyl-2,2-dichloroaziridin-1-yl)quinoline (XI) is formed in the reaction of substituted quinoline II with dichlorocarbene. The PMR spectra of IX-XI contain multiplet signals of aromatic protons, while the spectrum of XI contain, in addition, a singlet signal of an aziridine proton at 4.43 ppm. The parameters of the UV spectrum of X are in essential agreement with the data for the same compound synthesized by a different method [3].

2-Aryl-3-bromoimidazo[1,2-*a*]pyridines XIIa-c and 2-[N-(1-aryl-2,2,2-tribromoethyl)amino]pyridines XIIIa, c were obtained in the reaction of azomethines Ia-c with bromoform and potassium hydroxide. The spectral characteristics of XIIa-c are similar to those for chlorides IIIa-c (see Table 1). In addition to multiplet signals of aromatic protons, two doublet signals at 6.1 (CH) and 5.5 ppm (NH) (J = 9.5 Hz) are present in the PMR spectra of XIIIa, c. The absorption at 3430 cm^{-1} in the IR spectra of XIIIa, c corresponds to stretching vibrations of an NH group. Molecular-ion peaks (m/z 432 and 510, respectively) are present in the mass spectra of XIIIa, c, while the most intense peaks are the peaks of $[M - CBr_3]^+$ ions (m/z 183 and 261, respectively). It has been previously shown that the reaction of dichlorocarbene with pyridines [1, 2, 5] and benzylideneanilines [5] gives pyridinium and iminium dichloromethylids. The former undergo 1,3-dipolar cycloaddition reactions, while the latter undergo cyclization to the corresponding aziridines more readily than they give adducts with dipolarophiles [5]. Quinolinium dichloromethylid has low activity, while 2-substituted pyridinium dichloromethylids are inert in 1,3-dipolar cycloaddition reactions [2]. This is probably associated with the nonplanar structures of the indicated ylids, which hinder intermolecular cycloaddition reactions.

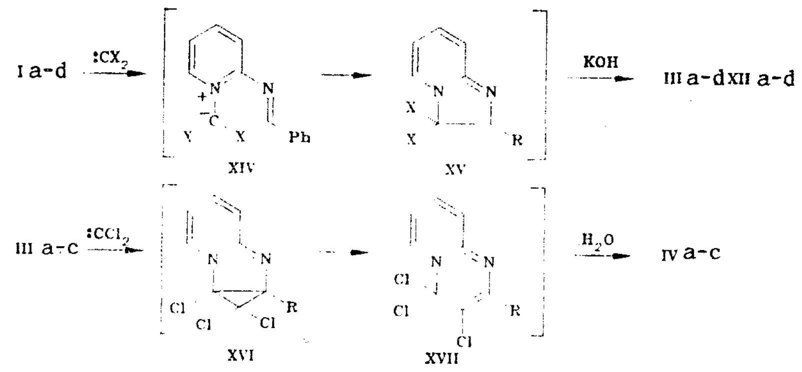

TABLE 1. UV and PMR Spectra of Ic and III-XIII

Compound	Empirical formula	mp, °C*	UV spectrum, λ_{max}, nm (log ε)	PMR spectrum, δ, ppm; J, Hz	Yield, %
Ic	$C_{12}H_9BrN_2$	104 . . . 106		6,95 . . . 7,88 (7H, m, C_6H_4, 3—5-H Py); 8,42 (1H, d, $J=9$, 6-H Py); 9,08 (1H, s, N═CH)	60
IIIa**	$C_{13}H_9ClN_2$	125 . . . 126 (120 . . . 122 (sublimation)[10])	245 (4,64), 319 (3,89)	6,91 (1H, dt, , 6-H); 7,23 (1H, ddd, , 7-H); 7,65 (1H, dt, 8-H); 8,08 (1H, dt, , 5-H); 7,37 (1H, m, 4-H Ph); 7,48 (2H, m, 3—5-H Ph); 8,14 (2H, m, 2,6-H Ph); $J_{55}=J_{67}=6{,}8$, $J_{57}=J_{58}=J_{68}=1$, $J_{78}=9{,}0$	34
IIIb	$C_{14}H_{11}ClNO_2$	120 . . . 121	255 (4,68), 330 (4,04)	3,83 (3H, s, MeO); 6,82 (1H, dt, , 6-H); 7,16 (1H, ddd, , 7-H); 7,58 (1H, dt, , 8-H); 8,02 (1H, dt, 5-H); 6,98 and 8,08 (4H, d, $J=9$, C_6H_4); $J_{56}=J_{67}=7$, $J_{57}=J_{58}=J_{68}=1$, $J_{78}=9$	35
IIIc	$C_{13}H_9BrClN_2$	142,5 . . . 143,5	252 (4,68), 319 (3,96)	6,88 (1H, dt, , 6-H); 7,20 (1H, ddd, , 7-H); 7,58 (1H, dt, , 8-H); 8,04 (1H, dt, , 5-H): 7,39 8,05 (4H, d, $J=9$, C_6H_4); $J_{56}=J_{67}=7$, $J_{57}=J_{58}=J_{68}=1$, $J_{78}=9$	40
IIId	$C_{13}H_9Cl_2N_2$	143 . . . 144	250 (4,61), 320 (3,89)	6,85 (1H, dt, , 6-H); 7,18 (1H, ddd, , 7-H); 7,58 (1H, dt, , 8-H); 8,04 (1H, dt, , 5-H); 7,39 and 8,05 (4H, d, $J=9$, C_6H_4); $J_{56}=J_{67}=7$, $J_{57}=J_{58}=J_{68}=1$, $J_{78}=9$	41
IVa	$C_{14}H_9ClN_2O$	165 . . . 166 (164 [11]; 171 . . . 173 from benzene[12])	265 (4,28), 353 (4,00)	7,08 . . . 7,26 (1H, m); 7,43 . . . 7,49 (3H, m); 7,68 . . . 7,87 (4H, m); 9,04 (1H, dt, , $J=7$; 1,6-H)	20
IVb	$C_{15}H_{11}ClN_2O_2$	177 . . . 178 (175 . . . 175,5 from ethanol[3])	300 (2,68), 352 (4,05), 364 (4,01)	3,88 (3H, s, MeO); 7,00 and 8,24 (4H, d, $J=9$, C_6H_4); 7,10 . . . 7,22 (1H, m), 8,01 . . . 8,07 (2H, m); 9,02 (1H, dt, $J=7{,}5$; 1, 6-H)	16
IVc	$C_{14}H_8BrClN_2O$	269,5 . . . 270,5			<1
V	$C_{13}H_{10}Cl_4N_2$	141 . . . 142	243 (4,27); 295 (3,60)	5,41 (1H, br d, , NH); 6,11 (1H, d, CH); 6,48 (1H, dt, 3-H Py); 6,62 (1H, ddd, 5-H Py); 7,39 (1H, ddd, 4-H Py); 8,09 (1H, dt, 6-H Py); 7,31 and 7,34 (4H, d, $J=8{,}6$, C_6H_4); $J_{NH,CH}=9{,}5$, $J_{34}=8{,}4$, $J_{35}=J_{36}=J_{46}=1$, $J_{45}=7{,}2$, $J_{56}=5{,}0$	9
VI	$C_{13}H_9Cl_3N_2$	114 . . . 115	246 (4,22), 271 (3,65)	4,21 (1H, s, CH); 7,08 (1H, ddd, , 5-H Py); 7,18 (1H, dt, , 3-H Py); 7,72 (1H, ddd, , 4-H Py); 8,34 (1H, ddd, 6-H Py); $J_{34}=8{,}8$, $J_{35}=J_{36}=1$, $J_{45}=7$, $J_{46}=2$, $J_{56}=5$	19
VII	$C_{13}H_9Cl_3N_2$	94 . . . 95	251 (4,24), 301 (4,06)	6,01 (1H, dt, , 3-H); 6,65 (1H, ddd, , 5-H); 6,68 (1H, br.s., NH); 7,25 (1H, ddd, , 4-H); 8,06 (1H, ddd, , 6-H); 7,30 and 7,50 (4H, d, $J=9$, C_6H_4); $J_{34}=8{,}3$, $J_{35}=J_{36}=0{,}9$, $J_{45}=7{,}3$, $J_{46}=2$, $J_{56}=5{,}0$	<1

VIII	$C_{14}H_9Cl_5N_2$	60...61	260 (4,17), 360 (3,68)	6,03 (1H, ddd, 5-H); 6,22 (1H, dt, 3-H); 6,86 (1H, ddd, 4-H); 7,58 (1H, ddd, 6-H); 8,64 (1H, s, $CHCl_2$), 7,26 and 7,48 (4H, d, $J=8{,}8$, C_6H_4); $J_{34}=9{,}4$, $J_{35}=J_{36}=0{,}9$, $J_{45}=6{,}4$, $J_{46}=1{,}7$, $J_{56}=7{,}4$	18
IX	$C_{17}H_{11}ClN_2$	124...126	244 (4,61), 249 (4,61), 255 (4,56), 261 (4,46), 321 (3,86), 330 (3,84)	7,34...7,58 (7H, m); 7,64...7,79 (1H, m); 8,01...8,10 (2H, m); 9,17 (1H, ddd, $J=8$, 2, 1, 9-H)	8
X	$C_{18}H_{11}ClN_2O$	188,5...189,5 (184...185 from butanol [3])	250 (4,40), 278 (4,46), 374 (4,06), 392 (3,98)	7,27...7,79 (8H, m); 7,87...7,97 (2H, m); 9,84 (1H, ddd, $J=9$, 2, 1, 10-H)	5
XI	$C_{17}H_{12}Cl_2N_2$	95...97; 117...119***		4,43 (1H, s, CH); 7,35 (1H, d, 3-H); 7,43 (1H, ddd, 6-H); 7,62 (1H, ddd, 7-H); 7,77 (1H, dd, 5-H); 7,90 (1H, br d, 8-H); 8,15 (1H, d, 4-H); 7,55...7,58 (2H, m, Ph); 7,37...7,44 (3H, m, Ph); $J_{34}=8{,}6$, $J_{56}=7{,}9$, $J_{57}=1{,}2$, $J_{67}=6{,}8$, $J_{68}=1{,}1$, $J_{78}=8{,}4$	6
XIIa	$C_{13}H_9BrN_2$	83...84 (63,0...64,5 (sublimation) [10]; 83...85 [13]; 88...90 from octane [14])	244 (4,65), 326 (3,87)	6,86 (1H, dt, 6-H); 7,20 (1H, ddd, 7-H); 7,61 (1H, dd, 8-H); 8,14 (1H, d, 5-H); 7,33...7,56 (3H, m, Ph); 8,08...8,17 (2H, m, Ph); $J_{56}=J_{67}=7$, $J_{57}=J_{68}=1$, $J_{78}=9$	7
XIIb	$C_{14}H_{11}BrN_2O$	101...103	255 (4,65), 328 (3,98)	3,83 (3H, s, MeO); 6,88 (1H, dt, 6-H); 7,22 (1H, ddd, 7-H); 7,64 (1H, d, 8-H); 8,12 (1H, dt, 5-H); 6,98 and 8,05 (4H, d, $J=9$, C_6H_4); $J_{56}=J_{67}=7$, $J_{57}=J_{68}=1$, $J_{78}=9$	10
XIIc	$C_{13}H_8Br_2N_2$	156...157	251 (4,62), 319 (3,94)	6,90 (1H, dt, 6-H); 7,26 (1H, ddd, 7-H); 7,62 (1H, dt, 8-H); 8,14 (1H, dt, 5-H); 7,58 and 8,02 (4H, d, $J=9$, C_6H_4); $J_{56}=J_{67}=7$, $J_{57}=J_{58}=J_{68}=1$, $J_{78}=9$	13
XIIIa	$C_{13}H_{10}Br_3N_2$	114...116		5,51 (1H, br d, NH); 6,13 (1H, d, CH); 6,51 (1H, d, 3-H); 6,62 (1H, ddd, 5-H); 7,31...7,48 (4H, m, 4-H, Ph); 8,12 (1H, m, 6-H); 7,66...7,76 (2H, m, Ph); $J_{NH,CH}=9{,}5$, $J_{34}=8{,}5$, $J_{35}=1$, $J_{45}=7$, $J_{56}=5$	5
XIIIc	$C_{13}H_{10}Br_4N_2$	148...150		5,47 (1H, br.d, NH); 6,11 (1H, d, CH); 6,49 (1H, d, 3-H); 6,62 (1H, ddd, 5-H); 7,40 (1H, ddd, 4-H); 8,09 (1H, dt, 6-H); 7,40...7,64 (4H, m, C_6H_4); $J_{NH,CH}=9{,}5$, $J_{34}=8{,}5$, $J_{35}=J_{36}=J_{46}=1$, $J_{45}=7$, $J_{55}=5$	

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*The compounds were crystallized: IIIa-c and IVa from acetone, IVb from benzene, IVc from ethanol, IIId, XIIc, and XIIIc from ether, V, VII-XI, and XIIIa from hexane, VI from hexane—ether, and XIIa from octane.

**^{13}C NMR spectrum, δ, ppm ($CDCl_3$): 105.6 s, 112.7 d, 117.7 d, 122.6 d, 124.6 d, 127.5 d, 128.2 d, 128.4 d, 132.7 s, 140.0 s, 143.8 s.

***These are the melting points of the polymorphic forms (prisms and needles, respectively).

TABLE 2. Mass Spectra of V, VII, VIII, and XIIIa, c*

Compound	m/z (I_{rel}, %)
V	334 (4) M^+, 301 (20), 299 (20), 219 (34), 218 (16), 217 (100), 202 (8), 105 (8), 91 (9), 79 (10), 78 (34)
VII	298 (2) M^+, 267 (11), 265 (66), 263 (100), 230 (7), 228 (21), 170 (4), 159 (8), 152 (7), 78 (26), 51 (9)
VIII	384 (24), 382 (38), 380 (25), M^+, 313 (35), 311 (98), 309 (100), 263 (23), 202 (33), 172 (32), 170 (50), 78 (76)
XIIIa	432 (0,5) M^+, 357 (7), 355 (14), 353 (7), 195 (8), 194 (4), 184 (14), 183 (100), 105 (3), 102 (8), 78 (17)
XIIIc	510 (0,5) M^+, 437 (11), 435 (34), 433 (34), 431 (13), 263 (98), 261 (100), 82 (14), 80 (15), 79 (17), 78 (54)

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*The data for the M^+ ions and the 10 most intense ions are presented.

Ylids XIV, which are formed from azomethines Ia-d, also do not react with dimethyl maleate but undergo intramolecular 1,5-cyclization to give dihydroimidazopyridines XV, and dehydrochlorination of the latter gives IIIa-d and XIIa-d. Imidazopyridines IIIa-c react with dichlorocarbene to give adducts XVI, opening of the three-membered ring in which and subsequent hydrolysis lead to pyridones IVa-c. The formation of IV from azomethines I through chlorides III is confirmed by a study of the progress of the reaction by means of liquid chromatography, as well as by obtaining IVa in the reaction of bromide XIIa with dichlorocarbene. In agreement with the proposed reaction scheme, the introduction of acceptor R substituents into the aryl group reduces the activity of the C=C bond in III and decreases the yields of pyridone products IV (Table 1).

It should be noted that only the pyridine nitrogen atom is involved in the reaction of dichlorocarbene with I, and reaction with the azomethine C=N bond, which should lead to the formation of a gem-dichloroaziridine, does not occur [the corresponding aziridine (for example, VI) is stable under the reaction conditions]. This fact is probably due to a decrease in the nucleophilicity of the azomethine nitrogen atom due to the electron-acceptor effect of the pyridine ring and polarization in the CH=N—C=N system. At the same time, aziridine XI was obtained in addition to IX and X in the reaction of quinoline II with dichlorocarbene. This change in the regioselectivity of the reaction is probably associated with the greater steric shielding of the endocyclic nitrogen atom in II as compared with I (see [6]).

An unusual result was obtained when the reaction was carried out with azomethine Id in hexane; in addition to IIId, we isolated a product of addition of the trichloromethyl anion to the C=N bond, viz., chloride V, which subsequently undergoes conversion to VI-VIII. This change in the pathway of the reaction of Id probably constitutes evidence that the formation of dichlorocarbene is hindered and the activity of the trichloromethyl ion increases when chloroform is diluted with hexane.

In addition to bromides XIIa-c, which are formed from ylids XIV, the reaction of azomethines Ia-c with bromoform and alkali gives products of addition of the tribromomethyl anion to the C=N bond. The formation of the latter occurs even in a solution that does not contain hexane; this is associated with the greater nucleophilicity of the tribromomethyl anion as compared with the trichloromethyl anion [7].

EXPERIMENTAL

The progress of the reactions was monitored by TLC on Silufol UV-254 plates. Analysis of the reaction mixtures by GLC was carried out with an LKhM-80MD chromatograph with a 2000 × 2 mm stainless-steel column with 3% SE-30 on a Chromaton-N-Super support as the stationary phase; analysis by liquid chromatography was carried out with a Milikhrom chromatograph with a 50 × 2 mm stainless-steel column packed with Silasorb 600 (5 μ) and elution with hexane—ether (3-4:1). The IR spectra of 1% solutions in $CHCl_3$ (in CCl_4 for VI and VIII) were recorded with a UR-20 spectrometer. The PMR spectra of 5% solutions in $CDCl_3$ were obtained with Tesla BS-567A (100 MHz) and Bruker WM (270 MHz) spectrometers with hexamethyldisiloxane (HMDS) as the internal standard. The UV spectra of solutions of the compounds [$0.2\text{-}1.4) \cdot 10^{-4}$ mole/liter] in 96% ethanol (in hexane for V-VIII) were recorded with Specord M-40 and Perkin—Elmer M-402 spectrophotometers. The mass spectra were obtained with an MKh-1303 mass spectrometer with direct introduction of the samples into the ion source at an ionizing-electron energy of 60 eV. 2-(Arylmethyleneamino)pyridines Ia-d and 2-(benzylideneamino)quinoline (II) were obtained from benzaldehydes and 2-aminopyridine [8] or 2-aminoquinoline [3]. Chloroform purified to remove ethanol was used for the reactions [9]. The isolation of the reaction products by column chromatography was carried out on silica gel L (100-160 μ). The analytical characteristics of the new compounds were in agreement with the calculated values.

Reactions of Ia-d and II with Dichlorocarbene in Chloroform. A 36-63-mmole sample of powdered KOH was added in small portions with stirring in an argon atmosphere at -20°C in the course of 5-12 h to a solution of 9 mmole of freshly distilled or recrystallized Ia-d or II and 0.62 g (2.7 mmole) of benzyltriethylammonium chloride in 60 ml of chloroform until the reaction was complete (monitoring by TLC or liquid chromatography). The reaction mixture was then filtered through a Schott filter and evaporated, and the products were isolated by column chromatography [elution with hexane—ether (5:1) or hexane—ethyl acetate (4:1)]. In addition to products III, IV, and IX-XI (Table 1), workup gave 20-30% of the corresponding benzaldehyde formed by hydrolysis of the starting azomethines during the reaction and during chromatography.

Reaction of Id with Chloroform and Potassium Hydroxide in Hexane. A 4-g (70 mmole) sample of powdered KOH was added in small portions with stirring in an argon atmosphere at -20°C in the course of 7 h to a solution of 3.19 g (14.7 mmole) of Id and 1 g (4.4 mmole) of benzyltriethylammonium chloride in a mixture of 60 ml of chloroform and 60 ml of hexane, after which the reaction mixture was filtered and evaporated in vacuo. Column chromatography of the residue [elution with hexane—ether (10:1)] yielded, successively, 0.99 g (18%) of 1-(dichloromethyl)-2-[2,2-dichloro-1-(4-chlorophenyl)vinylamino]-1,2-dihydropyridine (VIII), 0.18 g (9%) of 4-chlorobenzaldehyde, 0.82 g (19%) of 2-[2,2-dichloro-3-(4-chlorophenyl)aziridin-1-yl]pyridine (VI), 0.45 g (9%) of 2-[2,2,2-trichloro-1-(4-chlorophenyl)ethylamino]pyridine (V), 0.02 g (0.5%) of 2-[2,2-dichloro-1-(4-chlorophenyl)vinylamino]pyridine (VII), and 0.68 g (20%) of imidazopyridine IIId.

Reaction of V with Chloroform and Potassium Hydroxide. A 50-mg sample of powdered KOH was added with stirring at -20°C in the course of 50 min to a solution of 50 mg (0.15 mmole) of V and 15 mg of benzyltriethylammonium chloride in 2 ml of chloroform. Column chromatography [elution with hexane—ether (10:1)] gave 45 mg (79%) of VIII.

Reaction of V with Chloroform and Potassium Hydroxide in Hexane. A 0.12-g sample of powdered KOH was added with stirring at -20°C in the course of 1 h to a solution of 50 mg (0.15 mmole) of V and 15 mg of benzyltriethylammonium chloride in a mixture of 1 ml of hexane and 1 ml of chloroform. Column chromatography [elution with hexane—ether (10:1)] of the reaction mixture gave 15 mg (26%) of VIII and 17 mg (38%) of aziridine VI.

Reaction of VIII with Sodium Methoxide. A 0.1-g (0.26 mmole) sample of VIII was added to a solution of sodium methoxide obtained from 30 mg of sodium and 2 ml of methanol, and the mixture was heated at 55°C for 1 h. The reaction mixture was then cooled and filtered through a thin layer of silica gel, the filtrate was washed with hexane—ether (1:1) and evaporated, and the residue was recrystallized from hexane to give 45 mg (58%) of VII.

Reaction of Ia-c with Bromoform and Potassium Hydroxide. A 27-45-mmole sample of powdered KOH was added in small portions with stirring in an argon atmosphere at -20°C in the course of 6-8 h to a solution of 9 mmole of Ia-c and 0.62 g (2.7 mmole) of benzyltriethylammonium chloride in 60 ml of bromoform (with monitoring of the reaction by TLC), after which the reaction mixture was filtered. The filtrate was evaporated in vacuo, and the residue was subjected to column chromatography [elution with hexane—ether (3-5:1)] to give XIIa-c and XIIIa, c (Table 1) and 20-30% of the corresponding benzaldehyde — the product of hydrolysis of the starting Ia-c.

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SPECTRAL AND QUANTUM-CHEMICAL STUDY OF SOME HETEROANALOGS OF 1,4-BIS(5-PHENYL-2-AZOLYL)BENZENES

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The effect of structural changes in the molecules of thiophene and furan analogs of 1,4-bis(5-phenyl-2-azolyl)benzenes on their electronic spectra was studied by the MO LCAO method within the π-electron approximation.

One of the most effective organic luminophores that are widely used in scintillation technique is 1,4-bis(5-phenyl-2-oxazolyl)benzene (POPOP, I).

I

The spectral-luminescence properties of POPOP and its various functional substituted derivatives have been investigated quite thoroughly [1].

The aim of the present research was to study the spectral-luminescence properties of our previously synthesized [2] heteroanalogs of I containing alternating oxazole, 1,3,4-oxadiazole, thiophene, and furan residues in various combinations (see Table 1).

The absorption spectrum of POPOP in toluene consists of one intense (ε 52,000) slightly structure band [1]. According to quantum-chemical calculations carried out within the π-electron approximation, this band is formed by a single-configuration $S_0 \rightarrow S_1^*$ transition of the π,π* type and is associated with transfer of electron density from the oxazole rings and, to a lesser extent, from the terminal phenyl radicals to the central phenylene fragment of the molecule (Table 2). In the ground state the central benzene ring is a weak electron-density donor. A negative charged is shifted to the oxazole rings and to the terminal phenyl radicals. The polarization changes on excitation to the S_1^* state, and the central fragment becomes a π-electron acceptor.

The successive replacement of one and two oxazole rings in the POPOP molecule by 1,3,4-oxadiazole rings (Table 1, II and III) leads to a small degree of redistribution of the electron density: the terminal phenyl radical bonded directly to the oxadiazole ring acquires weakly expressed donor character even in the ground state (Table 2). Nevertheless, this does not affect the principles of the formation of the long-wave band, and the character of the spectrum does not change on passing from I to II and III. Only a short-wave shift of the absorption maxima (Table 1) caused by a decrease in the diene character of the azole heteroring is observed [5].

It must be noted that the $S_0 \rightarrow S_1^*$ transition in all of the examined cases is localized on the three central rings of the molecules with almost no involvement of the terminal phenyl radicals, as evidenced by the number of localizations (see Table 2). As a result, replacement of the outer benzene rings in the II and III molecules by thiophene (IV and V) or furan (VI and VII) rings has little effect on the character and position of the long-wave absorption band (Table 1) and is manifested only in an increase in the extinction coefficient (ε). The small bathochromic shift of this band (4-15 nm) is associated with the stronger (as compared with the phenyl ring) electron

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