was added 0.63 ml (7 mmole) of nitric acid (d 1.35). The reaction mixture was stirred for 5 min and diluted with water. The violet precipitate was filtered off, washed with water, and dried to give 1.9 g (82%) of compound VIII, mp 172-173° (from alcohol). Found, %: C 57.4, H 4.6, Br 17.2, N 2.9. $C_{22}H_{20}BrNO_5$. Calculated, %: C 57.6, H 4.4, Br 17.4, N 3.0.

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SYNTHESIS OF 3-METHYLPYRIDO[3,2,1-j,k]CARBAZOLIUM SALTS AND DERIVED CYANINE DYES

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When carbazole is heated with formaldehyde and acetone (or with methyl vinyl ketone) in the presence of mineral acid, 3-methylpyrido[3,2-j,k]carbazolium salts form. These react with p-dimethylaminobenzaldehyde, triethyl orthoformate, Michler's ketone, 1-ethylquinolinium iodide, or 1,3,3-trimethyl-2-formylmethyleneindolinium iodide to give the respective cyanine dyes. Deviations of the unsymmetrical dyes and Hückel molecular orbital calculations show that the Brooker basicity of the pyrido[3,2,1-j,k]carbazolium series is lower than that of the 1-phenylquinolinium series.

It has previously been shown that diphenylamine and other secondary aromatic amines undergo heterocyclization with the condensation products of formaldehyde with acetone, to form N-aryl(alkyl)-substituted lepidinium salts [1, 2]. It was of interest to extend this reaction to heterocycles containing a diarylamine segment, in order to obtain condensed systems with a nitrogen bridge atom and cyanine dyes with those terminal groups. The present communication presents a study of cyclization with the above-mentioned carbonyl components in the presence of mineral acid, of the heterocyclic analog of diphenylamine, viz., carbazole; pyrido[3,2,1-j,k]carbazolium salts (Ia, b) were obtained. Formation of analogous salts has been noted only in the patent literature [3-5]. Salt Ic (X = I) was separated in very low yield (3.6%) in the condensation of carbazole with methyl vinyl ketone in ethanol solution in the presence of zinc chloride, orthonitrophenol, and sulfuric acid. In patents [3-5] no physical constants are given either for salt Ic or for cyanine dyes prepared from it, although valuable sensitizing properties of the latter in silver halide emulsions are noted.

We were able to increase the yield of pyrido[3,2,1-j,k]carbazolium salt severalfold by changing the solvent and condensing agent, and by using the more available formaldehyde and acetone instead of methyl vinyl ketone. In view of the fact that carbazole undergoes polycondensation with formaldehyde to give resin [6], we modified the condensation procedure previously used for diphenylamine [2]. To obtain salts Ia, b formaldehyde was first condensed with acetone, and the resulting mixture of 4-hydroxybutanone and 3-butenone was reacted with carbazole in the presence of mineral acid and nitrobenzene (the latter is required for oxidation of the intermediate product). The reaction was also carried out under the same condi-

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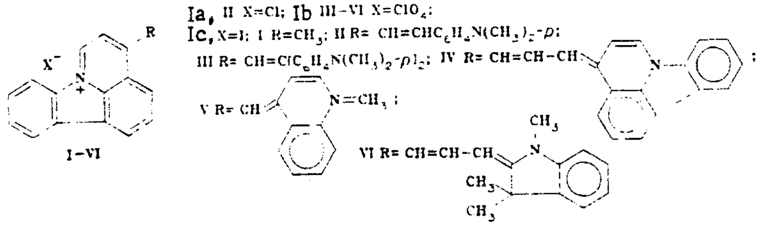
TABLE 1. 3-Methylpyrido[3,2,1-j,k]carbazolium Salts and Derived Cyanine Dyes

Compound	mp, °C (dec.)	UV spectrum, λ_{max}, nm (log ε)	Yield, %		Empirical formula	Calculated, %		Yield, %
			Cl	N		Cl	N	
Ia	271—273	224 (4.15), 248 (4,05), 297 (3.54)	13,8	5,4	$C_{16}H_{12}ClN$	14,1	5,5	16 (A), 24 (B)
Ib	360	224 (4.28), 247 (4,15), 295 (3,62)	11,2	4,6	$C_{16}H_{12}ClNO_4$	11,2	4,4	41 (A), 46 (B)
II	380	650 (3.62)	9,2	7,3	$C_{25}H_{21}ClN_2$	9,2	7,3	69
III	178—180	604 (2.86)	6.3	7.3	$C_{33}H_{30}ClN_3O_4$	6.2	7.4	25
IV	201—203	725 (4.05)	6.6	5.2	$C_{33}H_{21}ClN_2O_4$	6.5	5,1	40
V	234—236	590 (3.46)	7,7	6,0	$C_{26}H_{19}ClN_2O_4$	7.7	6,1	61
VI	218—220	625 (4,87)	7,2	5,4	$C_{29}H_{25}ClN_2O_4$	7,1	5,6	90

tions with 3-butenone instead of formaldehyde and acetone mixture, but this gave only an insignificant increase (by 5-8%) in yield of salt I.

The structure of the heterocyclization products was confirmed by IR spectra and ^1H and ^{13}C NMR spectra. Salts I can be considered as analogs of fluoranthene (benz[a]acenaphthylene) with nitrogen at one of the nodal positions. In the region of the aromatic ring valence vibrations (1600-1500 cm^{-1}) the IR spectra of Ia, b are characterized by five intense bands. In the region of C—H extraplanar deformational vibrations, both salts have intense bands of two, three, and four neighboring hydrogen atoms (see Experimental).

The PMR spectrum of salt Ib contains a singlet at 3.29 ppm that corresponds to the reactive 3-CH_3 group (the structurally analogous N-phenyllepidinium salt has a CH_3 peak at 3.34 ppm [7]). The 1-H proton, which is closest to the quaternary nitrogen, gives a doublet far downfield at 9.69 ppm, J = 5.86 Hz. The paramagnetic shift of this proton signal relative to the shift for the N-phenyllepidinium salt (δ 9.06 ppm [17]) is apparently due to the appreciable ring currents of the adjacent benzene nucleus. The doublet of the 2-H proton (δ 8.28 ppm) that is bonded by spin-spin coupling could be identified against the background of the complex multiplet of the 5-, 7-, and 10-H protons. In this case the aromatic proton spectrum was calculated by means of the PANIC program, which gave good agreement between calculated and experimental spectra for the δ and J values shown in the Experimental section. Analysis of the J constants of salt Ib gives evidence that this system is entirely free of anomalies. As in the case of fluoranthene [8], the J constants of protons ortho to one another lie in the 7.5-7.9 Hz range, except for I_{45} = 9.0 Hz.



In the ^{13}C {H} NMR spectrum of salt Ib the carbons in positions 1, 11a, and 10a that are bonded to nitrogen give signals at 138.7, 140.6, and 164.4 ppm, respectively. This assignment is based on comparison with the ^{13}C NMR spectrum of 1-phenyl-4-methylquinolinium perchlorate, in which the signals of the analogous carbons $C_{(2)}$, $C_{(8a)}$, and $C_{(1)}$ lie at 148.7, 141.7, and 163.6 ppm.

Salts Ia-c react readily with p-dimethylaminobenzaldehyde, triethyl orthoformate, and 1-methylquinolinium iodide, and 1,3,3-trimethyl-2-formylmethyleneindoline to form, respectively, the styryl (II), trimethyncyanine (IV, VI), and monomethyne cyanine (V) dyes (Table 1). Moreover, condensation with Michler's ketone gives the β-dimethylaminophenyl substituted styryl dye (III). The reaction with Michler's ketone indicates the increased reactivity of the γ-methyl of the I salts over that of the analogous group in the N-alkyl substituted lepidinium salts [9, 10]. It is of interest that the absorption intensity of dye III is an order of magnitude less than that of its analog II; this indicates significant steric effects in the cation of III. The wavelength deviations of the absorption maxima of the unsymmetrical dyes II and VI, calculated according to Kiprianov [11] and Brooker [12] on the basis of the respective symmetrical dyes [13, 14], are, respectively, 17.5 and 10 nm, whereas for the N-phenylquinoline analogs they are 86 [15] and 13.5 nm [15], respectively. This indicates that according to the Kiprianov–Brooker system the basicity of pyrido[3,2,1-j,k]carbazolium is lower than that of N-phenylquinolinium. This result agrees with the electron donor capability calculations Φ_0 for the respective positions in the 1-phenylquinolinium and pyrido[3,2,1-j,k]carbazolium nuclei in the symmetrical carbocyanines (42 and 36°, respectively).

EXPERIMENTAL

Electron absorption spectra of the synthesized compounds were obtained with an SF-18 spectrophotometer in methanol solution. IR spectra were recorded with a UR-20 spectrophotometer in KBr tablets. NMR spectra of solutions in CF_3COOD were measured with a Brucker WP-100 SY spectrometer (100 MHz). Compound purity was verified by TLC on Silufol-254 plates.

3-Methylpyrido[3,2,1-j,k]carbazolium Chloride (Ia). (A). A mixture of 8.8 g (0.05 mole) of carbazole, 50 ml of butanol, 100 ml of nitrobenzene, and 25 ml (0.25 mole) of concentrated HCl was heated to 100°. To it was added in small portions over 1 h a solution obtained by heating a mixture of 50 ml of butanol, 50 ml of acetone, 1.5 g (0.05 mole) of paraformaldehyde, and 0.1 ml of 35% hydrochloric acid for 6 h at 100°. The reaction mixture was heated another 7 h and cooled, and the precipitate was filtered off. Butanol and nitrobenzene were steam-distilled out of the filtrate. The resulting precipitate was crystallized from ethanol.

(B). Chloride Ia was obtained in 24% yield by the above procedure, by replacing paraformaldehyde and acetone by 14 g (0.2 mole) of methyl vinyl ketone, which was added in mixture with 50 ml of butanol over 1 h. IR spectrum: 1648 s, 1635 s, 1601 s, 1524 s, 1502 s, 836 s, 805, 752, 774 cm^{-1}.

3-Methylpyrido[3,2,1-j,k]carbazolium perchlorate (Ib) was obtained by procedures (A) and (B) by replacing hydrochloric acid with 21 ml of 42% perchloric acid. The mixture was heated for 8 h at 100°. The reaction product was crystallized from ethanol. IR spectrum: 1651 s, 1638 s, 1603 s, 1517 s, 1498 v.s (1100 v.s), 842, 813, 746, 772 cm^{-1}, ^1H PMR spectrum: 9.69 (1H, d, J_{12} = 5.86 Hz, 1-H); 8.80-7.80 (8H, m, arom.), 3.29 (3H, s, CH_3); 8.75 (6-H); 8.56 (4-H); 8.34 (7-H); 8.28 (5-H); 8.28 (2-H); 8.25 (10-H); 7.85 (8-H); 7.84 m.d (9-H); $J_{45} = 9.0$, $J_{56} = 7.1$, $J_{78} = 7.0$, $J_{79} = 1.5$, $J_{89} = 7.0$, $J_{8,10} = 1.5$, $J_{9,10} = 7.0$ Hz; ^{13}C {H} NMR (25.1 MHz): 20.2 (CH_3); 138.7, 140.6, 164.4, 124-136 ppm (remaining 12 carbons).

3-(p-Dimethylaminophenylethenyl)pyrido[3,2,1-j,k]carbazolium Chloride (II). A mixture of 1.6 g (6 mmole) of salt Ia, 1.05 g (7 mmole) of p-dimethylaminobenzaldehyde, and 15 ml of acetic anhydride was boiled for 30 min. After cooling, 100 ml of ether was added, and the precipitate was filtered off and crystallized from acetone.

3-(Bis-2,2-(p-dimethylaminophenyl)ethenylpyrido[3,2,1-j,k]carbazolium Perchlorate (III). A mixture of 1.9 g (6 mmole) of salt Ib, 2.7 g (10 mmole) of Michler's ketone, and 10 ml of acetic anhydride was boiled for 1 h, then left for 24 h at 20°. The precipitated excess Michler's ketone was filtered off, the precipitate was washed several times with hot ethanol, and the filtrate was evaporated to dryness. The residue was washed with ether and crystallized from ethanol.

3-[3-(Pyrido[3,2,1-j,k]carbazole-3(11H)-ylidene)-1-propenyl]pyrido[3,2,1-j,k]carbazolium Perchlorate (IV). A mixture of 1.9 g (6 mmole) of salt Ib, 6 ml (40 mmole) of triethyl orthoformate, and 20 ml of anhydrous pyridine was boiled for 15 min. The dye was precipitated with ether and crystallized from ethanol.

3-[(1-Methylquinolylidene-4)methylene]pyrido[3,2,1-j,k]carbazolium Perchlorate (V). A mixture of 1.9 g (6 mmole) of salt Ib, 2 g (7 mmole) of 1-methylquinolinium iodide, 1 g (16 mmole) of potassium hydroxide, and 4 ml of anhydrous pyridine was boiled for 15 min. Then the mixture was treated with 1.6 g (14 mmole) of sodium perchlorate and left for 24 h. The precipitate was filtered off, washed with water, and crystallized from ethanol.

3-[3-(1,3,3-Trimethylindolinylidene-2)propenyl]pyrido[3,2,1-j,k]carbazolium Perchlorate (VI). A mixture of 1.6 g (5 mmole) of salt Ib, 1 g (5 mmole) of 1,3,3-trimethyl-2-formylmethyleneindoline, and 5 ml of acetic anhydride was boiled for 30 min. The reaction mixture was left for 24 h, and the precipitate was separated, washed with ether, and crystallized from ethanol.

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PROTIC ACID-INDUCED INTRAMOLECULAR REACTIONS OF 2-CYCLOPROPYLAZOBENZENES

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541.124

Treatment of 2-cyclopropylazobenzenes with concentrated sulfuric acid affords the intramolecular N- and C-alkylation products. Treatment of azobenzenes with trifluoroacetic acid results in quantitative rearrangement to arylindazoles via the intermediate formation of acid-stable indazolium ions. It is suggested that the formation of indazolium ions in trifluoroacetic acid results from the synchronous opening of the cyclopropane ring and stabilization of the developing carbocation by an internal nucleophile (the azo-group).

We have previously shown [1] that 2-cyclopropylazobenzene (I) on treatment with concentrated sulfuric acid is converted into the N-arylaminoindole (III) and the azoalcohols (IV) and (V), the percentages and ratios of which remain constant with time. We were able to show that the aminoindole (III) is formed, not from the arylcyclopropane (I), but from its isomerization product, ortho-propenylazobenzene (II). *(See scheme on top of next page.)

The key step in the conversion of compound (I) is the formation of the bemzyl carbocation (A). Azobenzenes containing in the orthoposition a substituent which is capable under the reaction conditions of giving rise to the corresponding carbocation are known to be able to undergo intramolecular reactions to give the indazoles [2, 3].*

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*It should be pointed out that the synthesis of indazoles from the appropriate orthosubstituted azobenzenes is of limited usefulness as a result of the relative inaccessibility of the starting materials.

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