SPIROPYRANS BASED ON NITROGEN HETEROCYCLES

QUINOLINE AND PHENANTHRIDINE DERIVATIVES

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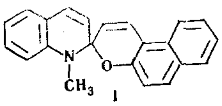
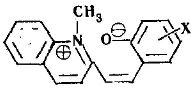
The corresponding merocyanins (II and III), which are not capable of intramolecular cyclization to form spiropyrans, were obtained by the condensation of quaternary salts of 2- and 4-methylquinoline with o-hydroxyaryl aldehydes. In contrast to II and III, the products of the condensation of 5,6-dimethylphenanthridinium salts with o-hydroxyaryl aldehydes (IV and V) exist, under the usual conditions, in the spiropyran form, while the derivative of 5-nitrosalicylaldehyde can be isolated in both the cyclic and merocyanin forms. These differences are associated with the magnitude of the positive charge on the carbon atom which participates in closing the pyran ring.

Ever since photochromic and thermochromic properties were observed for the spiropyrans of several heterocyclic compounds, repeated attempts have been made to synthesize such compounds from heterocycles which contain a pyridine ring. However, merocyanin dyes based on quaternary salts of α- and γ-picoline and o-hydroxyaryl aldehydes [1, 2], in contrast to acridine derivatives [3], turned out to be incapable of intramolecular cyclization. There are contradictory points of view regarding quinaldine and lepidine derivatives. Schiele [4], in explaining the failures of a number of investigators [2, 3, 5] with respect to the synthesis of quinoline spiropyrans, asserted that the N-methyl group rather than the C-methyl group participates in the condensation. Moreover, he maintained that he was able to obtain a spiropyran (I) through the o-hydroxystyryl derivative of quinoline, which was prepared by condensation of quinaldine with 2-hydroxynaphthaldehyde.

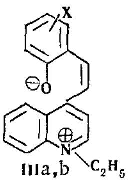


I

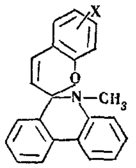
Since Schiele's conclusions completely contradict the well-known correlation of the reactivity of C- and N-methyl groups, we attempted to condense N-methylquinaldinium iodides and N-ethyllepidinium iodides with o-hydroxyaryl aldehydes in the presence of equimolar amounts of pyridine.



IIa-c

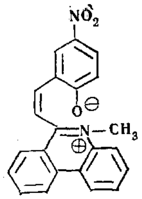


IIIa,b



IVa-c

X=a H; b 5,6 benzo; c 5-NO_2



Vc

The anhydrobases obtained (II and III) are deeply colored compounds which have negative solvatochromism due to strong polarization of the conjugated system of bonds [6]. All of the anhydrobases (II and III) were

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TABLE 1. Anhydrobases of the Quinoline Series (II and III)

Compound	X	mp, °C*	λ_{max}, nm (lg ε)		Empirical formula	Found, %			Calculated, %			Yield, %	Perchlorates, mp
			in alcohol	in dichloroethane		C	H	N	C	H	N		
IIa	H	300	330, 540, 560 (3,75; 3,26; 3,28)	330, 565 (3,48; 3,21)	$C_{18}H_{15}NO \cdot 2H_2O$	73,3	6,5	4,9	73,0	6,4	4,7	60	230—231
IIb	5,6-Benzo	230—231^{2}	345, 400, 590 (4,16; 4,06; 4,60)	350, 400, 610 (4,09; 3,90; 4,60)	$C_{22}H_{17}NO \cdot H_2O$	80,8	5,8†	4,4	81,0	5,6†	4,3	75	261—262
IIc	5-NO_2	236—237	295, 360, 510 (3,77; 3,91; 4,08)	300, 370, 565 (3,63; 3,90; 4,14)	$C_{18}H_{14}N_2O_3 \cdot 2H_2O$	63,2	5,4	8,6	63,2	5,3	8,4	80	221—223
IIId	H	221—222	450, 550 (3,43; 3,76)	295, 600 (3,93; 3,85)	$C_{19}H_{17}NO \cdot 3H_2O$	77,0	7,6	4,4	76,8	7,8	4,3	80	242—243
IIIe	5,6-Benzo	120—121 (dec.)	390, 640 (3,79; 4,60)	350, 420, 650 (3,64; 3,60; 4,60)	$C_{23}H_{19}NO \cdot H_2O$	81,1	6,4	4,2	80,8	6,2	4,1	65	212—214

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* Recrystallization solvents: IIa, alcohol—piperidine (15:1); IIb, dimethylformamide; IIc, alcohol—triethylamine—water (20:1:0.5); IIIa, propanol; IIIb, alcohol—pyridine (10:0.5).

† Deuterated sample of IIb: Found %: D 15.8; calc. %: D 17.6. The deuterated and normal samples were identical with respect to melting point and physical properties.

isolated as the hydrates, as indicated by the data of elementary analysis and the IR spectra (Table 1). The isolation of the hydrated froms of merocyanins was noted previously in [7].

The condensation of the N-deuteromethylquinaldinium salt with 2-hydroxynaphthaldehyde was carried out in parallel with the condensations described above. The percentage of deuterium in the merocyanin obtained corresponded to the initial amount of deuterium. Thus, the condensation of quaternary quinaldine and lepidine salts proceeds unambiguously at the C-methyl group.* Nevertheless, a spiro compound of the quinoline series could not be obtained by any of the known methods.

The inability of o-hydroxystyryl derivatives of pyridine and quinoline to form spiropyrans is apparently due to the small magnitude of the positive charge on the α- and γ-carbon atoms. In the case of acridine, however, for which $C_{(9)}$ is more positively charged [9], the spiropyran ring is readily closed [3]. A still higher positive charge is localized on $C_{(6)}$ of phenanthridine [10], in connection with which a rather high stability of spiropyrans of the phenanthridine series might be assumed. In fact, we were able to synthesize the first representatives of this series (IVa-c) by the condensation of 5,6-dimethylphenanthridinium methylsulfate with salicylaldehyde, 5-nitrosalicylaldehyde, and 2-hydroxynaphthaldehyde by heating in alcohol with piperidine. In the presence of two or more moles of piperidine the reaction proceeds quite rapidly, and IVa and IVb are isolated immediately in the colorless spiran form, while the nitrosalicylaldehyde derivative is isolated in the merocyanin form (Vc) as red-brown crystals. In contrast to IVa and IVb, Vc is insoluble in slightly polar solvents, but a bluish-green solution, from which almost colorless crystals of the spiropyran form (IVc) are isolated on cooling, is formed gradually on refluxing a suspension of it in chlorobenzene, xylene, or toluene. Compound IVc can be recrystallized from nonpolar solvents. When IVc is refluxed in alcohol, in which it is virtually insoluble, the merocyanin form (Vc) is again formed. To the best of our knowledge, this is the first instance where both the spiropyran and merocyanin forms can be isolated in chemically pure form under the usual conditions.

Compounds IVa and IVb are thermochromic: a green (IVa) or blue (IVb) color, which disappears on cooling, develops when they are heated in hydroquinone dimethyl ether. On dissolving in acetic acid, they form yellow salts of the open forms, from which they are again isolated as spirans on neutralization. Thus the o-hydroxyarylvinyl derivatives of the phenanthridine series, like acridine derivatives and in contrast to the merocyanins of pyridine and quinoline, are capable of intramolecular cyclization to form stable spiropyrans.

EXPERIMENTAL

5,6-Dimethylphenanthridinium Methylsulfate. This was obtained in 90% yield by refluxing a toluene solution of 0.1 mole of phenanthridine with 0.2 mole of dimethyl sulfate for 2 h. It was isolated as light-yellow needles and was readily crystallized

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* After the completion of this portion of the investigation, Schiele reported the erroneousness of his earlier conclusions [8].

from alcohol (1:30) to give a product with mp 23[illegible]-238 deg (dec., heating from 215 deg). Found %: N 4.6; S 10.2. $C_{16}H_{17}NO_4S$. Calc. %: N 4.4; S 10.0.

N-Deuteromethylquinaldinium Iodide. This was obtained in quantitative yield by heating equimolecular amounts of quinaldine and CD_3I at 80 deg for 2 h in a sealed tube and had mp 192 deg (from alcohol).*

The quaternary salts of quinaldine and lepidine were condensed with o-hydroxyaryl aldehydes by refluxing an alcoholic solution of the reagents with an equimolecular amount of piperidine for 15-30 min. The resulting precipitates were refluxed in water with triethylamine for 1 h.

5'-Methylspiro[2H-1-benzopyran-2,6'-(5',6'-dihydrophenanthridine)] (IVa). Salicylaldehyde [0.8 ml (7.35 mmole)] and 2 ml (20 mmole) of piperidine were added with stirring to a hot solution of 2.35 g (7.35 mmole) of 5,6-dimethylphenanthridinium methylsulfate in 160 ml of alcohol. The solution became dark-red, and a light-colored precipitate formed after a few minutes. The mixture was refluxed for 30 min, cooled, and the resulting precipitate was filtered and washed with alcohol to give 2.08 g (91%) of IVa. Two crystallizations from benzene (1:20) yielded 1.52 g of a product with mp 212.5-213.5 deg (dec., heating from 198 deg) in the form of fine, colorless, strongly electrifiable needles with R_f 0.9 (chloroform, activity II Al_2O_3). λ_{max}, nm (log ε), in dioxane: 240, 267, and 320 (4.72, 4.28, and 3.89). Found %: C 84.2; H 5.5; N 4.7. $C_{22}H_{17}NO$. Calc. %: C 84.3; H 5.5; N 4.5.

5'-Methylspiro[3H-naphtho]2,1-b[pyran-3,6'-(5',6'-dihydrophenanthridine)] (IVb). This was similarly obtained in 85-90% yield by the condensation of 5,6-dimethylphenanthridinium methylsulfate with 2-hydroxynaphthaldehyde. The fine, colorless crystals were insoluble in alcohol, acetone, and ether and slightly soluble in benzene; they were crystallized from toluene (1:110), chloroform, and chlorobenzene (hot solutions in these solvents were blue) and had mp 262-264 deg (dec., heating from 240 deg). λ_{max}, nm (log ε), in dioxane: 250, 303, 316, and 340 (4.91, 3.93, 4.03, and 3.98). Found %: C 86.7; H 5.8; N 3.9. $C_{26}H_{19}NO$. Calc. %: C 86.4; H 5.3; N 3.9.

6-Nitro-5'-methylspiro[2H-1-benzopyran-2,6'-(5',6'-dihydrophenanthridine)] and the Merocyanin (IVc and Vc). The condensation with 5-nitrosalicylaldehyde was carried out in analogy with the previously described procedure. A total of 15-20% of the alcohol was vacuum-distilled from the dark-red reaction mass, and the mixture was allowed to stand for a day. The precipitated brownish-red needles of Vc were filtered and washed with alcohol and ether to give 61% of product. Vc was insoluble in hexane, ether, CCl_4, and benzene and slightly soluble in acetone (violet solution); at room temperature the solubility in alcohol was 20 mg per 100 ml. It melted with decomposition at 200-205 deg when it was heated from 195 deg. λ_{max}, nm (log ε), in alcohol: 255, 300, 390, and 490 (3.86, 3.46, 3.22, and 3.18). Found %: C 74.1; H 5.1; N 7.7. $C_{22}H_{16}N_2O_3$. Calc. %: C 74.1; H 4.5; N 7.9.

Heating of Vc in a 15-fold amount of boiling chlorobenzene or xylene gave a bluish-green solution, from which 70 % of yellowish crystals of IVc were isolated on cooling. IVc decomposed at 195-199 deg when heated from 185 deg. λ_{max}, nm (log ε), in dioxane: 230, 265, and 330 (4.77, 4.53, and 4.24). Found %: C 74.4; H 5.0; N 7.87. $C_{22}H_{16}N_2O_3$. Calc. %: C 74.1; H 4.5; N 7.9.

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* I. A. Sinitsyna participated in the synthesis of N-deuteromethylquinaldinium iodide and in its condensation with 2-hydroxynaphthaldehyde.