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REACTION OF VINYLOGS OF A FISCHER BASE WITH SALICYLALDEHYDES

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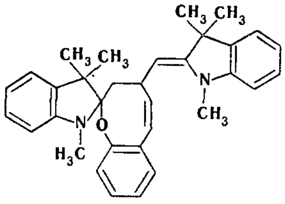
The reaction of vinylogs of the Fischer base, viz., 1,3,3-trimethyl-2-(3-methyl-2-buten-1-ylidene)indoline, 1,3,3-trimethyl-2-(2-penten-1-ylidene)indoline, 1,3,3-trimethyl-2-(3-phenyl-2-propen-1-ylidene)indoline, and 1,3,3-trimethyl-2-(2-buten-1-ylidene)indoline, with salicylaldehydes commences with displacement by the aromatic o-hydroxy aldehyde of the vinyl part of the dienamine molecule, as a result of which the usual spirobenzopyran is formed. In the case of the first two dienamines the reaction stops at this stage, whereas in the latter two a second molecule of dienamine adds to the initially formed spirobenzopyran at the double bond of the pyran ring to give "dicondensed" spirochromans.

At the present time a rather good deal of study has been devoted to spiropyrans of the indoline series, numerous representatives of which have valuable thermo- and photochromic properties [1]. It was recently reported [2] that fundamentally new indoline spirans that contain an eight-membered oxocin ring, viz., spirooxocins, had been synthesized. Babeshko and co-workers studied the condensation of a Fischer base with o-hydroxycinnamaldehydes and arrived at the conclusion that the products of this reaction are "dicondensed" spirooxocins with general formula I. Nothing regarding the photochromic properties of the compounds obtained was stated in the paper, although it is known that such "dicondensed" products in series of indoline spirobenzopyrans do not have these properties [1, p. 254].



I

We made an attempt to achieve the synthesis of "monocondensed" spirooxocins starting from vinylogs of a Fischer base (I), which were recently obtained by French chemists by condensation of a Fischer base with saturated aliphatic aldehydes [3]. It was assumed that the reaction of dienamines IIa-c with salicylaldehydes would proceed with the formation of indoline spirans that contain an eight-membered oxocin ring. However, our study showed that "dicondensed" spirochromans V rather than spirooxocins are formed in this case (Scheme and Table 1)

The reaction of vinylogs of the Fischer base with salicylaldehydes evidently commences with displacement by the aromatic o-hydroxy aldehyde of the vinyl part of the dieneamine molecule in the form of the corresponding saturated aliphatic aldehyde; the usual spirobenzopyran (III) is formed in this case. Similar reactions involving replacement of one aldehyde by another have been described in the literature. For example, it is known that 3,5-dinitrosalicylaldehyde displaces salicylaldehyde from the molecule of the corresponding spiropyran [1, p. 257].

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TABLE 1. Spirochromans Va-c

Compound	R	X	mp, °C	Found, %				Empirical formula	Calculated, %			
				C, %	H, %	N, %	M*		C, %	H, %	N, %	M*
Va	CH_3	H	191—192	83,9	7,8	5,8	490	$C_{34}H_{38}N_2O$	83,3	7,8	5,7	490
Vb	CH_3	NO_2	181—182	76,4	6,9	7,8	535	$C_{34}H_{37}N_3O_3$	76,3	6,9	7,9	535
Vc	C_6H_5	NO_2	171—172	78,5	6,6	7,1	597	$C_{39}H_{39}N_3O_3$	78,4	6,5	7,1	597

*Found from the mass spectrum obtained with a Varian MAT-112 spectrometer.

TABLE 2. PMR Spectra of Spirochromans Va-c in Deuteroacetone

Compound	δ, ppm										J, Hz			
	A ring		B ring		R	Hx	Ha, b	Hm	5'-H	7'-H	J_{xy}	J_{am} (trans)	J_{bm} (cis)	J_{Ry}
	3-CH_3	1-CH_3	3-CH_3	1-CH_3										
Va	1,27 1,28	2,87	1,59 1,61	3,15	1,66	5,42	~2,4	4,02	—	—	11,7	13,0	6,0	1,2
Va*	1,28 1,31	2,86	1,61 1,63	3,11	1,68	5,36	2,42 2,19	3,88	—	—	11,8	13,0	5,8	1,2
Vb	1,29 1,32	2,92	1,59 1,62	3,16	1,72	5,45	~2,5	4,17	~8,00		11,6	12,8	6,1	1,0
Vc †	1,26 1,26	2,74	1,55 1,62	2,91	—	5,32	~2,4	4,45	8,47	8,05	11,8	11,5	6,2	—

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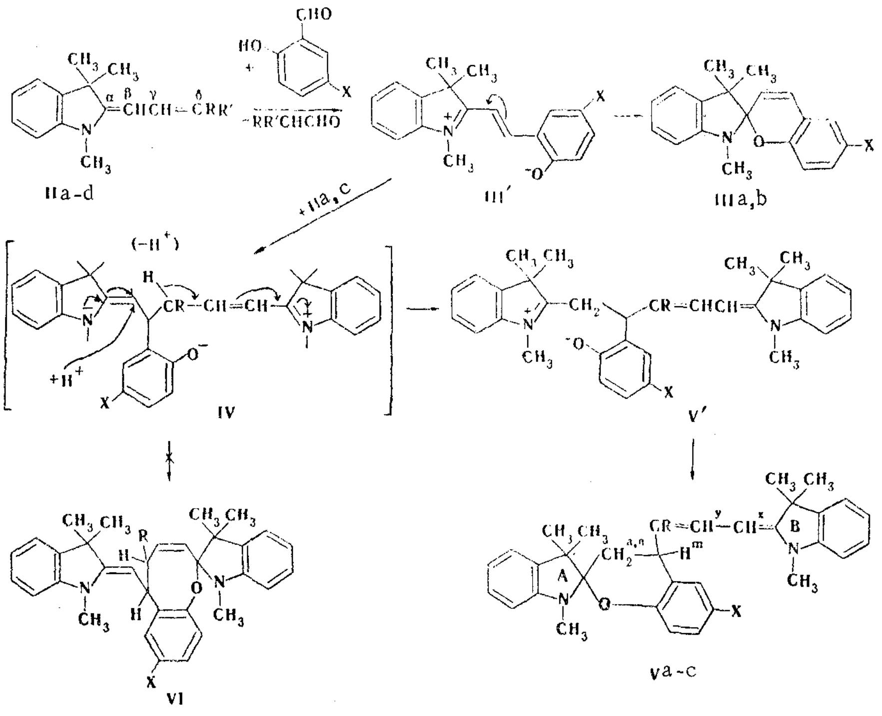
*In $CDCl_3$ J_{ab} = 13.7 Hz.

†5'-H (d, J_{meta} = 2.1 Hz, 7'-H (q, J_{ortho} = 8.7 Hz, J_{meta} = 2.1 Hz).

In the case of dienamines IIb, d, which contain one ethyl group or two methyl groups as substituents attached to the δ-carbon atom, respectively, the reaction stops at the step involving the formation of spirobenzopyran III. In the case of dienamines IIa, c with one methyl or one phenyl group the reaction proceeds further. In this case a second molecule of the vinylog of the Fischer base adds to the open form of chromene III (III') to give intermediate IV, which evidently easily undergoes rearrangement to "dicondensed" spirochroman V. A similar rearrangement was observed by Maas and Zwanenburg during a study of the addition of Michler's ethylene [sic] to indoline spirobenzopyrans [4]. In the same research the authors demonstrated convincingly by means of deuterium labeling that the proton migration that occurs at this site is realized intermolecularly with the participation of the solvent. Intermediate IV could via ring formation produce a spirooxocin derivative (VI); however, the formation of spirooxocins VI does not occur in this reaction, evidently as a consequence of the higher thermodynamic stability of spirobenzopyrans V as compared with spirooxocins VI.

The yield of bisindoline spirochroman Vc (R = C_6H_5) is lower by a factor of four than that of Vb (R = CH_3). Considering the fact that IIb, d do not form "dicondensed" products at all, it may be concluded that the greater the steric hindrances at the δ-carbon atom of the vinylog of the Fischer base, the greater the difficulty involved in its addition to spirobenzopyran III. A similar observation was also made by Zwanenburg and Maas. Thus Michler's ethylene [sic] reacts with salicylaldehydes to give only bis products [5], while its derivative, viz., 1,1-bis(4-dimethylaminophenyl)propene, does not react with salicylaldehyde at all, and with more reactive nitro-substituted salicylaldehydes it gives only monocondensation products [6].

The assumption that the formation of a "dicondensed" product is the result of a reaction between the open form of the chromene and a second molecule of the methylene base has also been expressed by Bertelson [1, p. 256]. Recently in a number of studies the direct syntheses of bis products from chromenes and various bases have been realized [4-8]. To confirm the scheme of the formation of "dicondensed" V in the reaction that we studied we carried out the reaction of spiropyran IIIa, obtained by the method in [9], with dieneamine IIa. The product of this reaction proved to be identical to spirochroman Va.



II a $R=CH_3$, $R'=H$; b $R=C_2H_5$, $R'=H$; c $R=C_6H_5$, $R'=H$; d $R=R'=CH_3$; III a $X=H$; b $X=NO_2$; V a $R=CH_3$, $X=H$; b $R=CH_3$, $X=NO_2$; c $R=C_6H_5$, $X=NO_2$

The structure of V was established on the basis of the PMR spectra* (Table 2) and the results of elementary analysis. Signals of nonequivalent gem-methyl groups of the A ring and also in the form of two singlets of the gem-methyl groups of the B ring. A similar fact of the nonequivalence of the latter two methyl groups in bis products was also noted in [10], in which Bogaert and co-workers expressed the assumption that this phenomenon was due to the different orientation of the gem-methyl groups with respect to the pyran ring. In addition, the spectra of Va, b contains the signal of a methyl group ($R = CH_3$) in the side chain in the form of a doublet as a consequence of the further reaction, apparently, with the H^y proton. A doublet of the H^x proton is observed in a region close to the region of the β-H protons in dienamines II [3]. Like the λ-H signal in II [3], the H^y signal lies in the aromatic proton region.

The presence in the spectra of "dicondensed" products of an ABX system constitutes evidence in favor of structure V, which contains a CH_2—CH fragment, and constitutes evidence against alternative structure VI, which does not have such a fragment. Nonequivalence of the protons of the methylene group of the chroman ring was noted previously in an analysis of the PMR spectra of "dicondensed" products from 1,1-diphenylethylene [7], a Fischer base [11], and 9-methylene-10-methylacridan [12] with salicylaldehyde. We were also able to observe nonequivalence of the H^a and H^b protons in the PMR spectrum of Va in deuterochloroform. However, in solutions of Va-c in deuteroacetone, the chemical shifts of these protons are very close. We were therefore unable to assign the nonequivalent protons of the CH_2 group and distinguish the J_{gem} value.

EXPERIMENTAL

The PMR spectra of solutions of Va-c in deuteroacetone were recorded with a Varian CFT-20 high-resolution NMR spectrometer (80 MHz). The PMR spectrum of Va in deuterochloroform was recorded with a Varian XL-100A-12 spectrometer (100 MHz). The chemical shifts were measured on the δ scale relative to tetramethylsilane as the internal standard.

The vinylogs of the Fischer base, viz., 1,3,3-trimethyl-2-(2-buten-1-ylidene)indoline (IIa), 1,3,3-trimethyl-2-(2-penten-1-ylidene)indoline (IIb), 1,3,3-trimethyl-(3-phenyl-2-propen-1-ylidene)indoline (IIc), and 1,3,3-trimethyl-2-(3-methyl-2-buten-1-ylidene)indoline (IId), were obtained by the method in [3] by condensation of the Fischer base with, re-

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*The authors thank L. N. Kurkovskaya for her assistance in interpreting the PMR spectra.

spectively, propionaldehyde, butyraldehyde, and isobutyraldehyde. Compounds IIb, d were used in the subsequent syntheses without isolation. Dienamine IIa had bp 135°C (1 mm) [bp 135°C (1 mm) [3]]. Dienamine IIc had mp 106-107°C (mp 107°C [3]).

1,3,3-Trimethyl-6'-nitroindoline-2-spiro-2'-[2H]chromene (IIIb). An ether solution of dienamine IIb or IId, obtained by condensation of 0.87 g (5 mmole) of the Fischer base and 5 mmole of the corresponding aliphatic aldehyde in 9 ml of ether, was added to 0.84 g (5 mmole) of 5-nitrosalicylaldehyde dissolved by heating in 10 ml of ethanol, and the mixture was allowed to stand for 25 h, after which the solution was evaporated to $\sim 1/5$ of its original volume. The precipitated crystals were removed by filtration to give, respectively, 0.94 g (58% based on 5-nitrosalicylaldehyde) and 1.3 g (81% based on 5-nitrosalicylaldehyde) of spiropyran IIIb with mp 175-176°C (from ethanol). No melting-point depression was observed for a mixture with a genuine sample. According to the data in [10], this compound has mp 179-180°C.

1,3,3-Trimethyl-4'-[4-(1,3,3-trimethylindolin-2-ylidene)-2-buten-2-yl]indoline-2-spiro-2'-chroman (Va). A) A 1.1-g (5.2 mmole) sample of freshly distilled dienamine IIa and 0.94 g (7 mmole) of salicylaldehyde in 5 ml of absolute alcohol was refluxed for 1 h, after which the reaction mixture was diluted with 20 ml of alcohol, and the resulting precipitate was removed by filtration to give 0.3 g (24% based on dienamine IIa) of chroman Va. Recrystallization from benzene—ethanol gave white needles. Evaporation of the mother liquor gave 0.84 g (58% based on dienamine IIa) of 1,3,3-trimethylindoline-2-spiro-2'-[2H]chromene (IIIa) with mp 94°C (from ethanol). No melting-point depression was observed for a mixture with a genuine sample [9].

B) A mixture of 0.5 g (1.8 mmole) of spiropyran IIIa and 0.38 g (1.8 mmole) of dienamine IIa in 15 ml of absolute alcohol was allowed to stand at room temperature for 2 weeks. The precipitate was removed by filtration to give 0.2 g (23%) of chroman Va.

1,3,3-Trimethyl-4'-[4-(1,3,3-trimethylindolin-2-ylidene)-2-buten-2-yl]-6'-nitroindoline-2-spiro-2'-chroman (Vb). A 1.67-g (10 mmole) sample of 5-nitrosalicylaldehyde dissolved by heating in 40 ml of absolute alcohol was added to 1.70 g (8 mmole) of dienamine IIa in 10 ml of absolute alcohol, and the mixture was allowed to stand at room temperature for 2 days. The resulting precipitate was removed by filtration to give 0.66 g (30% based on dienamine IIa) of chroman Vb. Recrystallization from benzene—ethanol gave light-yellow needles. Evaporation of the mother liquor gave 1.1 g (47% based on dienamine IIa) of spiropyran IIIb with mp 175-176°C (from ethanol).

1,3,3-Trimethyl-4'-[1-phenyl-3-(1,3,3-trimethylindolin-2-ylidene)-1-propen-1-yl]-6'-nitroindoline-2-spiro-2'-chroman (Vc). A mixture of 1.83 g (6.6 mmole) of dienamine IIc and 1.27 g (7.7 mmole) of 5-nitrosalicylaldehyde in 70 ml of absolute alcohol was allowed to stand at room temperature for 2 days, after which the resulting precipitate was removed by filtration and washed with hot alcohol to give 0.15 g (8% based on dienamine IIc) of chroman Vc. Recrystallization from benzene—ethanol gave yellow crystals. Evaporation of the mother liquor gave 1.8 g (84% based on dienamine IIc) of spiropyran IIIb with mp 175-176°C (from ethanol).

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