SYNTHESIS OF NEW SPIROPYRANS BASED ON 2,3-CYCLOALKENOBENZOPYRYLIUM SALTS

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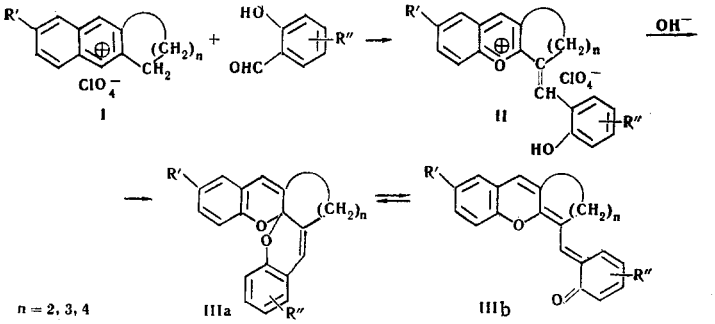
A method is described for the synthesis of spiropyrans from 2,3-cycloalkenobenzopyrylium salts and hydroxyaldehydes with subsequent treatment of the α-styryl derivatives with ammonia in ether.

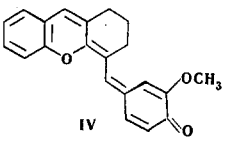
Compounds of the spiropyran type display photo-, thermo-, and solvatochroism properties which make them of considerable interest [1-4]. In this communication we describe the synthesis of a number of new spiropyrans based on 2,3-cycloalkenobenzopyrylium salts (I) via the scheme



Styryl derivatives of the II type were isolated and identified in all cases (Table 1).

It should be noted that transition from styryl derivatives II to spiropyrans III is possible only in the case of benzopyrylium salts. In the case of styryl derivatives obtained on the basis of 2-methyl-4,6-diphenylpyrylium salts the pyrylium ring is opened even by the action of weak bases, and compound III cannot be obtained. These results are in agreement with the observations in [5].

Compounds of the III type exist in the form of slightly colored spiropyran forms (IIIa) in the solid state and in solutions of nonpolar solvents. Conversion to the intensely colored valence-tautomeric IIIb form occurs in polar media under UV irradiation and heating. Evidence of this is the intense color of solutions of compound IV as well as compounds 1-3 (Table 1).



We are currently carrying out spectral and photochemical investigations of the compounds obtained.

EXPERIMENTAL

2,3-Cycloalkenobenzopyrylium Perchlorates (I). These were obtained by reaction of salicylaldehyde with the appropriate cyclic ketones via the method in [6].

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TABLE 1. α-Styryl-2,3-cycloalkenobenzopyrylium Perchlorates (II)

Compound	mp	Empirical formula	Found, %				Calc., %				Yield, %
			C	H	Hal.	N	C	H	Hal.	N	
α-(4-Dimethylaminobenzylidene)-2,3-cyclohexenobenzopyrylium perchlorate	200—201	$C_{22}H_{22}O_5ClN$	63,86	5,41	8,26	3,40	63,53	5,34	8,53	3,37	80
α-(4-Diethylaminobenzylidene)-2,3-cyclohexenobenzopyrylium perchlorate	178—179	$C_{24}H_{26}O_5ClN$	64,69	6,19	7,80	3,11	64,92	5,91	7,99	3,16	75
α-(4-Dimethylaminobenzylidene)-2,3-cycloheptenobenzopyrylium perchlorate	202—203	$C_{23}H_{24}O_5ClN$	64,23	5,67	8,39	3,22	64,30	5,59	8,26	3,26	70
α-(2-Hydroxybenzylidene)-2,3-cyclopentenobenzopyrylium perchlorate	206—207	$C_{19}H_{15}O_6Cl$	61,31	4,20	9,31	—	61,04	4,01	9,48	—	45
α-(2,4-Dihydroxybenzylidene)-2,3-cyclopentenobenzopyrylium perchlorate	195—196	$C_{19}H_{15}O_7Cl$	58,33	3,89	8,81	—	58,45	3,85	9,10	—	40
α-(2,4-Dihydroxybenzylidene)-2,3-cyclohexenobenzopyrylium perchlorate	170—171	$C_{20}H_{17}O_7Cl$	59,27	4,07	8,95	—	59,40	4,21	8,77	—	55
α-[(2-Hydroxy-5,6-benzo)-benzylidene]-2,3-cyclohexenobenzopyrylium perchlorate	156—157	$C_{24}H_{19}O_6Cl$	65,61	4,29	8,21	—	65,73	4,33	8,02	—	60
α-(3-Hydroxybenzylidene)-2,3-cyclohexenobenzopyrylium perchlorate	207—208	$C_{20}H_{17}O_6Cl$	61,76	4,20	9,25	—	61,81	4,38	9,14	—	58
α-(3-Methoxy-4-hydroxybenzylidene)-2,3-cyclohexenobenzopyrylium perchlorate	190—191	$C_{21}H_{19}O_7Cl$	60,10	4,38	8,59	—	60,42	4,54	8,46	—	51
α-(2-Hydroxybenzylidene)-2,3-cycloheptenobenzopyrylium perchlorate	230—231	$C_{21}H_{19}O_6Cl$	62,42	4,61	8,95	—	62,63	4,72	8,82	—	555
α-[(2-Hydroxy-5,6-benzo)-benzylidene]-2,3-cycloheptenobromobenzopyrylium perchlorate	210—211	$C_{25}H_{20}O_6ClBr$	56,32	3,66	21,89	—	56,50	3,76	21,75	—	49

*From acetic acid.

TABLE 2. Anhydro Bases of α-Styryl Derivatives of 2,3-Cycloalkenobenzopyrylium Salts

Compound	mp*	Empirical formula	Found, %			Calc., %			Yield, %
			C	H	Br	C	H	Br	
IIIa, $n=2$, R′=R″=H	219—220	$C_{19}H_{14}O_2$	83,21	4,94	—	83,21	5,11	—	18
IIIa, $n=2$, R′=H, R″=OH	213—214	$C_{19}H_{14}O_3$	78,32	5,10	—	78,54	4,83	—	20
IIIa, $n=3$, R′=R″=H	156—157	$C_{20}H_{16}O_3$	83,18	5,82	—	83,30	5,60	—	31
IIIa, $n=3$, R′=H, R″=OH	139—140	$C_{20}H_{16}O_3$	79,05	5,58	—	78,95	5,31	—	39
IIIa, $n=3$, R′=H, R″=C_4H_4	98—99	$C_{20}H_{18}O_2$	85,41	5,64	—	85,17	5,38	—	33
α-(3-Anhydrohydroxybenzylidene)-1,3,4-tetrahydroxanthilium	149—150	$C_{20}H_{16}O_2$	83,00	5,82	—	83,30	5,60	—	41
	138—139	$C_{21}H_{18}O_3$	79,30	5,79	—	79,25	5,66	—	43
IIIa, $n=4$, R′=R″=H	203—204	$C_{21}H_{18}O_2$	84,10	5,90	—	83,95	6,00	—	39
IIIa, $n=4$, R=Br, R″=C_4H_4	169—170	$C_{25}H_{19}O_2Br$	69,77	4,69	18,41	69,65	4,41	18,55	19

*From benzene–alcohol (5:1).

2-Salicylal-2,3-cycloalkenobenzopyrylium Perchlorates (II). These were synthesized by refluxing I with 5 to 10% excess aldehyde in acetic acid for 30 min (Table 1).

Spiropyrans. These were obtained by treatment of a suspension of the appropriate styryl derivatives in absolute ether with dry ammonia (Table 2).

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