PREPARATION OF SPIROPYRANS FROM 3-FORMYLSALICYLIC ACID DERIVATIVES

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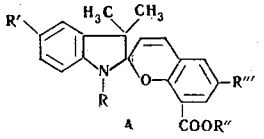
A study of the photochromic properties of 1,3,3-trimethylspiro[(2'H-1'-benzopyran)-2,2'-indolines] containing a carboxyl group in the 8 position or of its derivatives is of great interest since it makes it possible to elucidate the degree of generality of the facts of the presence of "reverse photochromism" in spiropyrans containing a carboxyl group [4] and the presence of normal photochromism in spiropyrans which have two electron-accepting substituents (such as nitro and carbalkoxy groups) in the pyran portion of the molecule [1-4]. We have established that the corresponding spiropyrans of general formula A (Table 1) are formed by the reaction of 3-formylsalicylic acid [1,5], 5-nitro-3-formylsalicylic acid [6], and its methyl [1] and ethyl ester with 5-substituted 1,3,3-trimethyl-2-methyleneindolines as well as with 1-phenyl-3,3-dimethyl-2-methyleneindoline. These compounds are crystalline substances, solutions of which in organic solvents have photochromic properties. I-VII have "reverse photochromism" in that they form intensely colored, red-violet solutions which are decolorized on illumination with an incandescent lamp. VIII-XIX manifest photochromism of the usual type, forming colorless solutions which become blue-violet in nonpolar solvents and red-violet in polar solvents. The solutions gradually return to their original state when irradiation is discontinued.

EXPERIMENTAL

Ethyl 5-Nitro-3-formylsalicylate. This was obtained in 53% yield by esterification of 5-nitro-3-formylsalicylic acid in an alcohol solution containing HCl and had mp 103-104° (from alcohol). Found %: C 50.0; H 3.7; N 6.1. $C_{10}H_9NO_6$. Calc. %: C 50.2; H 3.3; N 5.9.

TABLE 1.



A

Compound	R	R′	R″	R‴	Mp, °C	Empirical formula	Found, %			Calculated, %			Yield, %
							C	H	N	C	H	N	
I	CH_3	H	H	H	211—211,5	$C_{20}H_{19}NO_3$	74,7	5,9	4,1	74,5	5,9	4,4	78,4
II	CH_3	H	H	NO_2	234—235	$C_{20}H_{18}N_2O_5$	65,2	5,1	7,8	65,6	5,0	7,6	75,0
III	C_6H_5	H	H	NO_2	205—206	$C_{25}H_{20}N_2O_5$	70,0	4,8	6,5	70,1	4,7	6,5	70,1
IV	CH_3	F	H	H	216—217	$C_{20}H_{18}FNO_3$	70,6	5,4	4,4	70,8	5,3	4,1	73,8
V	CH_3	F	H	NO_2	240—241	$C_{20}H_{17}FN_2O_5$	62,4	4,5	—	62,5	4,5	—	71,4
VI	CH_3	Cl	H	NO_2	222—223	$C_{20}H_{17}ClN_2O_5$	60,4	4,4	6,8	59,9	4,3	7,0	65,7
VII	CH_3	Br	H	NO_2	271—272	$C_{20}H_{17}BrN_2O_5$	54,3	4,1	6,5	54,0	3,9	6,3	67,3
VIII	C_6H_5	H	CH_3	NO_2	139—140	$C_{26}H_{22}N_2O_5$	70,4	5,3	6,3	70,6	5,0	6,3	59,5
IX	CH_3	H	C_2H_5	NO_2	161—162	$C_{22}H_{22}N_2O_5$	67,4	5,6	7,2	67,1	5,6	7,1	63,2
X	C_6H_5	H	C_2H_5	NO_2	135—134	$C_{27}H_{24}N_2O_5$	71,2	5,2	6,6	71,0	5,3	6,1	55,0
XI	CH_3	F	CH_3	NO_2	192—193	$C_{21}H_{19}FN_2O_5$	63,7	5,0	6,9	63,3	4,8	7,0	52,7
XII	CH_3	F	C_2H_5	NO_2	156—157	$C_{22}H_{21}FN_2O_5$	64,3	5,2	—	64,1	5,1	—	48,5
XIII	CH_3	Cl	CH_3	NO_2	230—231	$C_{21}H_{19}ClN_2O_5$	61,2	4,9	6,6	60,8	4,6	6,8	41,3
XIV	CH_3	Cl	C_2H_5	NO_2	196—196,5	$C_{22}H_{21}ClN_2O_5$	61,9	5,3	6,2	61,6	4,9	6,5	40,2
XV	CH_3	Br	CH_3	NO_2	223—224	$C_{21}H_{19}BrN_2O_5$	54,8	4,3	6,3	54,9	4,2	6,1	40,6
XVI	CH_3	Br	C_2H_5	NO_2	196—197	$C_{22}H_{21}BrN_2O_5$	55,9	4,3	6,1	55,8	4,5	5,9	39,8
XVII	CH_3	CH_3	CH_3	NO_2	198—199	$C_{22}H_{22}N_2O_5$	67,2	5,7	6,9	67,0	5,6	7,1	35,1
XVIII	CH_3	CH_3	C_2H_5	NO_2	164—165	$C_{23}H_{24}N_2O_5$	67,9	6,2	6,8	67,6	5,9	6,9	30,7
XIX	CH_3	NO_2	CH_3	NO_2	239—240	$C_{21}H_{19}N_3O_7$	59,2	4,5	9,7	59,3	4,5	9,9	43,4

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