4 hr. After the volatile components have been vacuum distilled, the residue is dissolved by small portions in hot hydrochloric acid, which is then cooled, and twice the volume of alcohol added. On rubbing the walls of the vessel colorless material is precipitated; this is filtered off, washed with alcohol, and dried, giving 2.9 g (65%) of II. The base prepared from II by the action of triethylamine melts at 246-247°.

β-(8-Quinolyl)-α-alanine dihydrochloride (III). Prepared similarly to II.

β-(2-Phenyl-4-carboxy-6-quinolyl)-α-alanine dihydrochloride (V), dihydrate. Prepared similarly to II.

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INVESTIGATIONS OF SYNTHETIC DYES. XLV. STYRYLS FROM N-ARYLQUINALDINE SALTS

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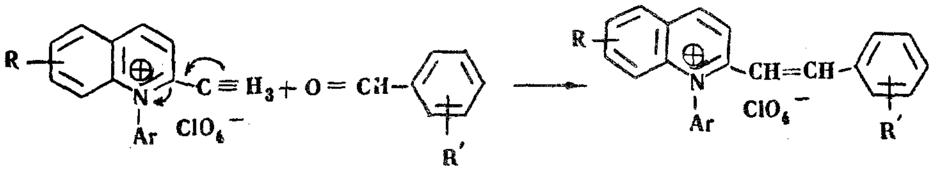
Condensation of N-arylquinaldine salts with benzaldehyde and its o- and p-derivatives gives a series of styryl compounds. The absorption maxima of the hydroxystyryls are bathochromically shifted by 12-34 mμ, as compared with the unsubstituted analogs. Transformation of hydroxystyryl salts to the bases is linked with deepening of the color by 90-130 mμ.

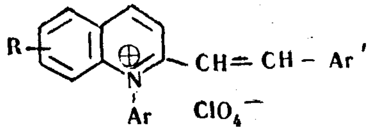
The relative mobility of the methyl hydrogens of N-halogenarylates of quinaldine, due to conjugation of the group with a cationic center, causes onium salts to condense rather readily with aromatic aldehydes. Continuing research along these lines, we used benzaldehyde and its o- and p-hydroxy derivatives for the condensation. The starting salts were synthesized by cyclizing the corresponding secondary aromatic amines with acetaldehyde in acid medium using methods previously developed [1, 2].



The spectra of the dyes prepared (table) were observed in acid and alkaline 96% alcohol.

Compounds I-XIII are comparatively highly colored, and have low molecular extinctions. Their absorption bands lie in a narrow range of long wavelengths, and the change in structure of the quinoline ring affects their light absorption to only an insignificant extent. A hydroxy group in the o position of the N-phenyl ring (I and II, V and VI) causes a small hypsochromic displacement of the absorption maximum, while an acetoxy group causes a smaller effect in the same direction (I and III, V and VII). The effect of these same groups in the p position of phenyl is somewhat weaker, and the absorption maxima of compounds V and VIII almost coincide. These facts correspond to the action of the OH

TABLE



Compound	R	Ar	Ar′	λmax mμ	εmax × 10⁻⁴	λmax in alkaline soln. mμ	Yield, %	M.p., °C	Empirical formula	N, % Found	N, % Calculated
I	H	C_6H_5	C_6H_5	425			70	258—260	$C_{23}H_{18}ClNO_4$	3.18; 3,24	3.43
II	H	o-HO—C_6H_4		416	0.96	413	32	276	$C_{23}H_{18}ClNO_5$	3.06; 3.18	3.30
III	H	o-CH_3—CO—O—C_6H_4		419	0.98		86	189	$C_{25}H_{20}ClNO_6$	2,88; 2.92	3.01
IV	H	o-CH_3O—C_6H_4		429			45	216	$C_{24}H_{20}ClNO_5$	3.16; 2,24	3.20
V	5, 6-benzo	C_6H_5		436	1,26		69	244–245 (decomp.)	$C_{27}H_{20}ClNO_4$	2,89; 2.94	3.05
VI	„	o-HO—C_6H_4		427	1,3		60	253 (decomp.)	$C_{27}H_{20}ClNO_5$	2.84; 2.88	2.96
VII	„	o-CH_3—CO—O—C_6H_4		430	1,25		80	224	$C_{29}H_{22}ClNO_6$	2.60; 2,64	2.71
VIII	„	n-HO—C_6H_4		434	1.3	432	68	244–246 (decomp.)	$C_{27}H_{20}ClNO_5$	2,86; 2.90	2.96
IX	„	n-CH_3—CO—O—C_6H_4		432	1.3						
X	6-OH	α-$C_{10}H_7$		432	1,3		54	236—237	$C_{27}H_{20}ClNO_5$	2.79; 2.84	2.96
XI	7, 8-benzo	o-HO—C_6H_4		422	1,24	418	57	238	$C_{27}H_{20}ClNO_5$	2,79; 2.90	2.96
XII	„	o-CH_3—CO—O—C_6H_4		424	1,40						
XIII	„	o-CH_3O—C_6H_4		429	1,2		56	249	$C_{28}H_{22}ClNO_5$	2.76; 2.84	2.88
XIV	H	C_6H_5	p-OHC_6H_4	450 (3)	25*						
XV	H	o-HO—C_6H_4		442	26	545	78	271	$C_{23}H_{18}ClNO_6$	3.11; 3,16	3.19
XVI	H	o-CH_3O—C_6H_4		450	21	574	90	253 (decomp.)	$C_{24}H_{20}ClNO_6$	2.96; 3.11	3.09
XVII	6-OH	α-$C_{10}H_7$		455	23	565					
XVIII	5, 6-benzo	n-HO—C_6H_4		456	22	562	84	264—265	$C_{27}H_{20}ClNO_6$	2,80; 2.78	2.87
XIX	„	o-HO—C_6H_4		455	28	544	77	286 (decomp.)	$C_{27}H_{20}ClNO_6$	2,91; 2.94	2.87
XX	7, 8-benzo	o-HO—C_6H_4		456	34	550	80	277—278	$C_{27}H_{20}ClNO_6$	2.78; 2.90	2.87
XXI	„	o-CH_3O—C_6H_4		460	31	580	70	271 (decomp.)	$C_{28}H_{22}ClNO_6$	2.63; 2,59	2.78
XXII	H	o-HO—C_6H_4	o-OHC_6H_4	432	16	546	64	251 (decomp.)	$C_{23}H_{18}ClNO_6$	3,02; 3.07	3.19
XXIII	H	o-CH_3O—C_6H_4		436	7	584	88	234—235	$C_{24}H_{20}ClNO_6$	2.84; 2.89	3.09
XXIV	6-OH	α-$C_{10}H_7$		450	18	560	66	258—259	$C_{27}H_{20}ClNO_6$	2.70; 2.68	2,87
XXV	5, 6-benzo	n-HO—C_6H_4		446	12	560	72	258—260	$C_{27}H_{20}ClNO_6$	2.69; 2.80	2,87
XXVI	„	o-HO—C_6H_4		454	27	544	60	281	$C_{27}H_{20}ClNO_6$	2.71; 2,80	2.87
XXVII	7, 8-benzo	o-HO—C_6H_4		450	28	550	62	248—249	$C_{27}H_{20}ClNO_6$	2,71; 2.81	2,87
XXVIII	„	o-CH_3O—C_6H_4		450	21	584	65	219	$C_{28}H_{22}ClNO_6$	2.61; 2.68	2.78

*λmax shift compared with unsubstituted.

group as an electron donor, leading to increase in electronegativity of the quinoline, increase in molecular asymmetry, and the observed hypsochromic shift. So the increasing coloration of these compounds in alkaline solution (by 2-4 mμ) becomes understandable.

Significantly deeper are the colorings of the condensation products of salts with isomeric o- and p-hydroxybenzaldehydes. As is known, the bathochromic shift observed here is a result of conjugation of free electron pairs of the oxygen with π electrons of the conjugated chain of the molecule, leading to more complete equalization of single and double bonds. It is interesting to note that with the p-hydroxystyryls the shift of the maximum, in comparison with unsubstituted ones, is greater than for the corresponding o-hydroxystyryls, and this is actually connected with certain steric hindrances in the latter. The deepest coloration appears with hydroxystyryls in alkaline solution, due to splitting off of the elements of acid and the formation of bases, where both structures, non-polar and polar, are present in the molecule to an equal extent [4, 5]. For these dyes the absorption shift in the long wavelength region is 90-130 mμ.

EXPERIMENTAL

(1-o-Hydroxyphenyl-5, 6-benzoquinoline-2)-p-hydroxystyryl perchlorate (XIX). 0.4 g 1-o-Hydroxyphenyl-5, 6-benzoquinaldinium perchlorate, 0.2 g p-hydroxybenzaldehyde, and 3 ml pyridine were boiled gently together for 30 min. The dye was precipitated with water, washed a few times with hot water, and recrystallized from isobutanol containing a few drops of perchloric acid. M.p. 286° (decomp.), yield 0.38 g (77%). Found: N 2.91, 2.94%. Calculated for $C_{27}H_{20}ClNO_6$: N 2.87%.

The other styryls were prepared similarly.

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