INVESTIGATIONS IN THE FIELD OF SYNTHETIC DYES

LXXIII. Synthesis and Absorption Spectra of the Arylhydrazones of 1-Aryl-2-formylquinolinium Perchlorates*

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The reaction of 6-methyl-1-(p-tolyl)-, 6-methoxy-1-(p-methoxyphenyl)- and 6-bromo-1-(p-bromophenyl)quinaldinium perchlorates with diazoamino compounds and with sodium anti-p-nitrobenzenediazoate, as a result of which arylhydrazones of 1-aryl-2-formylquinolinium perchlorates are obtained, has been studied. It has been shown that the UV spectra of the initial quaternary salts and arylhydrazones are similar to one another, but in the arylhydrazones the absorption maxima are shifted somewhat in the long-wave direction.

Aldehydes of 1-arylquinoline compounds have not been described in the literature. However, their arylhydrazones can be obtained by indirect routes [1, 2]. Interest in hydrazones of different structures is due to the fact that they are the starting materials for the synthesis of formazanes and tetrazolium salts, which have found use as complex-forming agents [3–7], plant growth accelerators [8], and redox indicators in biological investigations [9–12].

The activity of the methyl group in aryl halide derivatives of quinaldine and lepidine is shown in the relative ease of their reaction with diazonium salts [13], diazoates, and diazoamino compounds [14]. Developing work in this direction, by the reaction of 6-methyl-1-(p-tolyl)-, 6-methoxy-1-(p-methoxyphenyl)-, and 6-bromo-1-(p-bromophenyl)quinaldinium perchlorates with a number of symmetrical diazoamino compounds (triazenes) and sodium anti-p-nitrobenzenediazoate, we have obtained a series of arylhydrazones of 1-aryl-2-formylquinolinium perchlorates **I–XVII** (see table). The initial quaternary salts, 6-methyl-1-p-tolyl- and 6-methoxy-1-(p-methoxyphenyl)quinaldinium perchlorates, were obtained by a previously described method [15, 16] but with some variations permitting the yields to be improved. So far as concerns the 6-bromo-1-(p-bromophenyl)quinaldinium perchlorate, it was previously unknown and was obtained by the cyclization of p, p'-dibromodiphenylamine with butyl vinyl ether in an acid medium. The UV spectrum of the salt (in ethanol) is characterized by two absorption bands with maxima at 243 and 317 nm and a curve with a shape similar to those of other aryl halide derivatives of quinaldine [17]. 6-Bromo-1-(p-bromophenyl)quinaldinium perchlorate undergoes the usual cyanine condensations with the formation of styryl dyes and a symmetrical trimethylcyanine with absorption maxima at 570 and 632 nm, respectively.

The arylhydrazones **I–XVII** are red, well-crystallizing substances readily soluble in pyridine, acetone, and ethanol, and insoluble in water and ether. With sodium anti-p-nitrobenzenediazoate the nonsaltlike ethylene azo dyes **XVIII** and **XIX** are obtained in the form of blue-black powders whose ethanolic solutions are blue. The acidification of such a solution leads to the heightening of the color, which is connected with the formation of a saltlike arylhydrazone.

In the UV region, the arylhydrazones showed two absorption bands at 250–280 and 320–340 nm which are analogous to the absorption bands of the initial quaternary salts (240 and 320 nm) [17] but shifted somewhat in the long-wave direction. The shapes of the curves, their maxima and their intensities have great similarity with one another, which shows the common structure of the whole group of compounds. In the visible region, all the arylhydrazones have a single absorption band in the 480–520 nm region. The introduction of electron-donating substituents (CH_3, OCH_3) into the phenyl nucleus of the hydrazone residue gave a bathochromic effect in all cases in comparison with the unsubstituted compounds, while a substituent in the para position caused a greater shift than one in the ortho position. The deepening of the coloration, it must be assumed, is connected with an increase in the electron density in the chain of conjugation. Electron-accepting substituents (Cl, NO_2) decrease the electron density in the chain of conjugation and therefore cause a hypsochromic displacement as compared with the unsubstituted compounds. Introduction of electron-donating substituents into the quinoline nucleus (R = CH_3, OCH_3) has practically no effect on the absorption maximum (**I** and **VII**, **II**, **VIII**, etc.); in contrast to this, an electron-accepting bromine atom (R = Br) causes a bathochromic shift of the absorption maximum relative to the unsubstituted compounds [14] by 10 nm.

EXPERIMENTAL

6-Methyl-1-(p-tolyl)quinaldinium perchlorate. To a solution of 24 g of p, p'-ditolylamine in 70 ml of toluene were added 23 ml of HCl (d 1.19) and, in drops, with stirring, over 1 hr, 47 ml of butyl vinyl ether, without a pronounced rise in temperature being allowed. The reaction mixture was stirred for 2 hr, after which it was heated in the boiling water bath for 2 hr with stirring; then the volatile components were distilled off with steam, the residue was treated with 200 ml of hot water, and the resinous mass was filtered off. The filtrate, after being boiled with a small amount of activated carbon, was treated with an excess of 42% $HClO_4$ which led to the formation of a voluminous white precipitate of the quaternary salt. Yield 22 g (52%), mp 194–195° C (from water) [15].

6-Methoxy-1-(p-methoxyphenyl)quinaldinium perchlorate. A mixture of 5 g of p, p'-dimethoxydiphenylamine, 5 ml of HCl (d 1.19),

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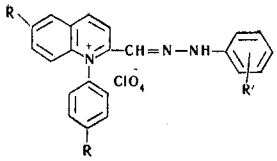
*For part LXXII, see [19].



Compound	R	R'	Mp, °C (decomp.)	Empirical formula	N, % found	N, % calc.	λ_{max}, nm (lg ε)	Reaction time, min	Yield %
I	CH_3	p-CH_3	247—248	$C_{25}H_{24}ClN_3O_4$	9.27 8.96	9.02	276, 327, 488 (3.40) (2.98) (3.76)	60	53
II		o-CH_3	254—256	$C_{25}H_{24}ClN_3O_4$	8.91 9.02	9.02	266, 327, 474 (3.34) (2.88) (3.42)	60	60
III		p-OCH_3	250—251	$C_{25}H_{24}ClN_3O_5$	8.93 8.58	8.72	278, 326, 504 (3.27) (2.91) (3.59)	20	73
IV		o-OCH_3	248—249	$C_{25}H_{24}ClN_3O_5$	8.55 8.68	8.72	266, 335, 494 (3.29) (2.86) (3.58)	20	83
V		p-Cl	261—262,5	$C_{24}H_{21}Cl_2N_3O_4$	8.62 8.53	8.64	271, 321, 474 (3.35) (2.92) (3.54)	90	40
VI	OCH_3	H	246,5—247	$C_{24}H_{22}ClN_3O_6$	8.62 8.81	8.68	271, 343, 478 (3.24) (2.86) (3.00)	60	30
VII		p-CH_3	238—239	$C_{25}H_{24}ClN_3O_6$	8.41 8.37	8.51	278, 343, 490 (3.20) (2.81) (3.10)	50	62
VIII		o-CH_3	239—240	$C_{25}H_{24}ClN_3O_6$	8.78 8.68	8.51	274, 346, 478 (3.14) (2.82) (2.76)	20	50
IX		p-OCH_3	215—216	$C_{25}H_{24}ClN_3O_7$	8.12 8.24	8.17	280, 321, 506 (3.13) (2.81) (2.98)	30	62
X		o-OCH_3	247—248	$C_{25}H_{24}ClN_3O_7$	8.37 8.39	8.17	266, 335, 494 (3.11) (2.78) (3.38)	15	60
XI		p-Cl	217—218	$C_{24}H_{21}Cl_2N_3O_6$	8.37 8.07	8.16	267, 343, 476 (3.14) (2.84) (3.32)	240	30
XII	Br	H	237—238	$C_{22}H_{16}Br_2ClN_3O_4$	7.46 7.47	7.22	271, 326, 488 (3.11) (2.63) (2.92)	2	80
XIII		p-CH_3	239—240	$C_{23}H_{18}Br_2ClN_3O_4$	7.07 7.11	7.05	271, 331, 499 (3.10) (2.64) (3.22)	2	70
XIV		o-CH_3	259—259,5	$C_{23}H_{18}Br_2ClN_3O_4$	7.07 7.36	7.05	278, 327, 490 (3.58) (2.04) (2.89)	2	60
XV		p-OCH_3	241—242	$C_{23}H_{18}Br_2ClN_3O_5$	6.82 6.68	6.86	279, 331, 521 (3.33) (2.96) (3.24)	2	60
XVI		o-OCH_3	277—278	$C_{23}H_{18}Br_2ClN_3O_5$	6.67 6.69	6.86	250, 330, 509 (3.32) (2.73) (2.89)	2	50
XVII		p-Cl	243,5—244	$C_{22}H_{15}Br_2Cl_2N_3O_4$	6.80 6.66	6.81	268, 328, 487 (3.42) (2.10) (3.25)	5	40

10 ml of dioxane, and 5 ml of butyl vinyl ether was heated in a sealed tube in the boiling water bath for 7–8 hr. The reaction mixture was treated in a similar manner to the preceding experiment. After treatment of the filtrate with saturated $NaClO_4$ solution, the quaternary salt deposited in the form of light yellow crystals, mp 175–176° C (from ethanol) [16], yield 3.62 g (42%).

6-Bromo-1-(p-bromophenyl)quinaldinium perchlorate. This was obtained in a similar manner to the preceding compound from 5 g of p,p'-dibromodiphenylamine [18], 10 ml of dioxane, 5 ml of HCl (d 1.19), and 5 ml of butyl vinyl ether. Heating was continued for 16–17 hr. After steam distillation, filtration, and treatment with 42% $HClO_4$, yellowish crystals were obtained. Yield 2.9 g (40%), mp 267–268° C (decomp.), from aqueous ethanol. Found, %: C 39.62, 39.71; H 2.86, 2.75; N 3.02, 3.10. Calculated for $C_{16}H_{12}Br_2ClO_4$, %: C 39.38; H 2.46; N 2.87.

2-Formyl-6-methyl-1-(p-tolyl)quinolinium p-tolylhydrazone perchlorate (I). A mixture of 1 g of 6-methyl-1-(p-tolyl)quinaldinium perchlorate, 0.64 g of p,p'-diazoaminotoluene, and 10 ml of ethanol was boiled for 1 hr. During the heating, the solution acquired a cherry-red color and crystals began to deposit from it; after cooling these were filtered off and dried. Recrystallization from ethanol yielded claret-red needles of I. Compounds II–XVII were obtained similarly.

6-Methoxy-1-(p-methoxyphenyl)-2-(p-nitrophenylazomethylene)-1,2-dihydroquinoline (XVIII). A solution of 0.5 g of 6-methoxy-1-(p-methoxyphenyl)quinaldinium perchlorate in 5 ml of ethanol was mixed with a hot solution of 0.24 g of sodium anti-p-nitrobenzenediazoate in 5 ml of ethanol. A violet coloration rapidly appeared, and after 3–4 hr a dark blue powder deposited. After crystallization from aqueous pyridine (1 : 1), compound **XVIII** was obtained in the form of blue needles with a metallic luster. Yield 40%, mp 227–228° C (decomp.). Found, %: N 10.66, 10.80. Calculated for $C_{24}H_{21}N_4O_4$, %: N 10.59. λ_{max} 582 nm (log ε 3.32) (on acidification of the nonsaltlike dye, λ_{max} 470 nm).

6-Bromo-1-(p-bromophenyl)-2-(p-nitrophenylazomethylene)-1,2-dihydroquinoline (XIX) was obtained similarly. Yield 32%, mp 217–218° C (decomp.). Found, %: N 10.72, 10.50. Calculated for $C_{22}H_{14}Br_2N_4O_2$, %: N 10.64. λ_{max} 550 nm (log ε 2.08) (on acidification of the dye, λ_{max} 475 nm).

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