STUDIES IN THE FIELD OF SYNTHETIC DYES

LI. Synthesis of Formazans Based on N-Arylquinaldinium Salts and Their Conversion into Tetrazolium Salts*

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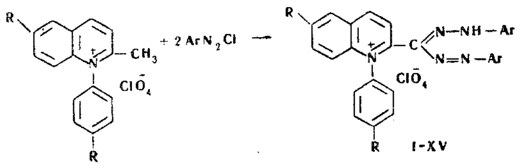
The coupling of 1-arylquinaldinium salts with diazonium salts has given a number of formazans of symmetrical structure with a 1-arylquinoline residue attached to the formazyl carbon atom. Unsymmetrical formazans have been synthesized by coupling the phenylhydrazone of 2-formyl-1-phenylquinolinium perchlorate with diazonium salts. The oxidation of the formazans has given tetrazolium salts.

Bisazo compounds with structures of the formazan type have been studied in fairly great detail [2]. However, very little has been published in the literature on formazans with quinoline nuclei attached to the formazyl carbon atom [3–5].

It has been reported previously [6] that 1-phenylquinaldinium perchlorate readily reacts with diazotized aniline and p-nitroaniline.

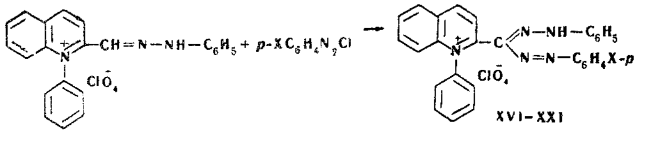
Developing these investigations, we have performed the coupling of 1-phenyl- and 1-(p-tolyl)-6-methylquinaldinium perchlorate with a number of diazonium salts. The coupling led to the formation of the formazans I–XV (see Table 1) in the following way:



I-XV

R = H, CH_3; Ar = C_6H_5, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-$C_2H_5OC_6H_4$, p-ClC_6H_4, p-BrC_6H_4, p-$NO_2C_6H_4$, α- and β-$C_{10}H_7$.

The structure of the products obtained was shown by the stepwise synthesis of the formazan I by the reaction of the phenylhydrazone of 2-formyl-1-phenylquinaldinium perchlorate [7] with benzene diazonium chloride. The unsymmetrical formazans **XVI–XXI** were synthesized analogously (see Table 1):

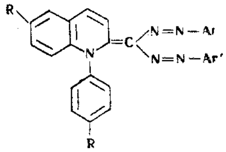


XVI-XXI

X = CH_3, CH_3O, C_2H_5O, Cl, Br, NO_2.

The absorption maxima of the unsymmetrical formazans are obtained additively from those of the corresponding symmetrical compounds. In all cases, the introduction of a substituent into the para position of the phenyl nucleus of the azo residues leads to a bathochromic effect relative to the unsubstituted compound [6].

It is an interesting fact that the formazans **XVIII**, **XIV**, and **XXI** readily lose the anion under the action of alkali or in the air and are converted into the corresponding bases:



R = CH_3, Ar = Ar′ = p-$NO_2C_6H_4$ (λ_{max} 590 nm); R = CH_3, Ar = Ar′ = α-$C_{10}H_7$ (λ_{max} 560 nm); R = H, Ar = C_6H_5, Ar′ = p-$NO_2C_6H_4$ (λ_{max} 549 nm).

After storage for a short time, these formazans give, on a thin-layer chromatogram (Al_2O_3), two spots with absorption maxima corresponding to the salt and base forms. This is apparently connected with a pronounced weakening of the quinoline nucleus, which favors the conversion of these formazans into the nonsalt state with a deepening of the color by 132, 76, and 89 nm, respectively. In an acid medium the initial color is restored.

The formazans are capable of many reactions, of which the most interesting is oxidation with the formation of tetrazolium salts, which are widely used as redox indicators in histochemistry [8]. The nitric acid oxidation of the formazans [9] I, III, **XIV**, and **XVII** gave the diperchlorates of the corresponding tetrazolium salts (Table 2), which formed light yellow microcrystalline powders.

The UV spectrum of the tetrazolium salt **XXII** is characterized by two absorption bands, at 227 nm (log ε 4.08) and 272 nm (log ε 3.89).

The action of an ethanolic solution of ascorbic acid on the tetrazolium salts reduces them to the initial formazans, which is shown by the identity of the absorption spectra in the visible region. The tetrazolium salts have been tested as indicators of redox processes in plants.

EXPERIMENTAL

Symmetrical formazans (I)–(XV). With stirring, the diazonium salt prepared by the usual method from 6.4 mM of the appropriate amine was added in drops to a solution of 1 g (3.1 mM) of a 1-phenylquinaldinium perchlorate in 10 ml of quinoline or a mixture of water and pyridine (1:1) cooled to 0° C.

After 5–7 hr, the reaction mixture was treated with ether whereupon the crude formazan precipitated in the form of a powder. The pure formazan was obtained after repeated washing of the powder with hot water to eliminate unchanged quaternary salt and crystallization from ethanol or acetic or formic acid.

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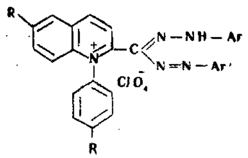
*For communication L, see [1].

Table 1



Compound	R	Ar	Ar′	Mp, °C	λ_{max}, nm	Empirical formula	Found, %		Calculated, %		Yield, %
							N	Cl	N	Cl	
I*	H	C_6H_5	C_6H_5	234	458	$C_{28}H_{22}ClN_5O_4$	13.40	6.45 6.37	13.26	6.71	84
II	H	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	246—247	472	$C_{30}H_{26}ClN_5O_4$	12.76 12.68	6.74 6.81	12.59	6.37	72
III	H	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	216—217	502	$C_{30}H_{26}ClN_5O_6$	12.08 11.93	6.36 6.19	11.91	6.03	61
IV	H	p-$C_2H_5OC_6H_4$	p-$C_2H_5OC_6H_4$	171—172	506	$C_{32}H_{30}ClN_5O_6$	11.36 11.40	—	11.37	—	68
V	H	p-BrC_6H_4	p-BrC_6H_4	218—219	470	$C_{28}H_{20}Br_2ClN_5O_4$	10.29 10.39	—	10.21	—	77
VI	H	p-ClC_6H_4	p-ClC_6H_4	217—218	470	$C_{28}H_{20}Cl_3N_5O_4$	11.90 11.97	17.40 17.60	11.73	17.85	63
VII	CH_3	C_6H_5	C_6H_5	155—157	458	$C_{30}H_{26}ClN_5O_4$	12.45 12.71	6.52 6.80	12.6	6.39	98
VIII	CH_3	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	223—224	472	$C_{32}H_{30}ClN_5O_4$	11.89 11.87	6.48 6.34	11.99	6.08	78
IX	CH_3	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	168—170	506	$C_{32}H_{30}ClN_5O_6$	11.19 11.31	5.64 5.96	11.37	5.76	93
X	CH_3	p-$C_2H_5OC_6H_4$	p-$C_2H_5OC_6H_4$	140—141	506	$C_{34}H_{34}ClN_5O_6$	10.98 10.87	5.96 5.83	10.87	5.51	86
XI	CH_3	p-ClC_6H_4	p-ClC_6H_4	209—211	468	$C_{30}H_{24}Cl_3N_5O_4$	11.09 11.41	17.55 17.40	11.20	17.02	92
XII	CH_3	p-BrC_6H_4	p-BrC_6H_4	207—208	468	$C_{30}H_{24}Br_2ClN_5O_4$	9.72 9.62	—	9.38	—	88
XIII	CH_3	p-$NO_2C_6H_4$	p-$NO_2C_6H_4$	202—203	458	$C_{30}H_{24}ClN_7O_8$	15.01 14.98	5.94 5.88	15.18	5.50	93
XIV	CH_3	α-$C_{10}H_7$	α-$C_{10}H_7$	155—157	484	$C_{38}H_{30}ClN_5O_4$	10.96 10.95	5.70 5.68	10.67	5.41	85
XV	CH_3	β-$C_{10}H_7$	β-$C_{10}H_7$	189—191	490	$C_{38}H_{30}ClN_5O_4$	10.64 10.40	5.67 5.85	10.67	5.41	90
XVI	H	C_6H_5	p-$CH_3C_6H_4$	190—191	471	$C_{29}H_{24}ClN_5O_4$	13.18 13.05	—	12.92	—	92
XVII	H	C_6H_5	p-$CH_3OC_6H_4$	174—175	482	$C_{29}H_{24}ClN_5O_5$	12.30 12.46	—	12.55	—	84
XVIII	H	C_6H_5	p-$C_2H_5OC_6H_4$	158—159	482	$C_{30}H_{26}ClN_5O_5$	12.08 11.97	—	12.07	—	84
XIX	H	C_6H_5	p-ClC_6H_4	214—215.5	465	$C_{28}H_{21}Cl_2N_5O_4$	12.67 12.67	12.88 12.97	12.45	12.63	87
XX	H	C_6H_5	p-BrC_6H_4	217—218.5	465	$C_{28}H_{21}BrClN_5O_4$	11.60 11.71	—	11.54	—	77
XXI	H	C_6H_5	p-$NO_2C_6H_4$	188—189	460	$C_{28}H_{21}ClN_6O_6$	14.71 14.79	—	14.67	—	88

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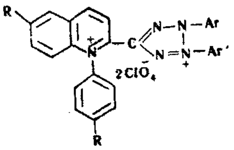
*Obtained previously [6].

Table 2



Compound	R	Ar	Ar′	Mp, °C	Empirical formula	Found, %		Calculated, %		Yield, %
						N	Cl	N	Cl	
XXII	H	C_6H_5	C_6H_5	242—243	$C_{28}H_{21}Cl_2N_5O_8$	11.31 11.29	11.42 11.49	11.18	11.34	60.9
XXIII	H	C_6H_5	p-$CH_3OC_6H_4$	204—205	$C_{29}H_{23}Cl_2N_5O_9$	10.55 10.79	10.90 10.97	10.67	10.82	50
XXIV	H	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	184—185	$C_{30}H_{25}Cl_2N_5O_{10}$	10.35 10.42	10.48 10.50	10.21	10.34	66
XXV	CH_3	α-$C_{10}H_7$	α-$C_{10}H_7$	229—230	$C_{38}H_{29}Cl_2N_5O_8$	9.35 9.41	9.50 9.62	9.28	9.41	30

Stepwise synthesis of the formazan I. A solution of 0.84 g (2 mM) of the phenylhydrazone of 2-formyl-1-phenylquinolinium perchlorate in 20 ml of pyridine cooled to 0° C was coupled with a solution of the benzenediazonium chloride obtained from 0.2 g (2.2 mM) of aniline, 0.14 g of $NaNO_2$, and 0.5 ml of hydrochloric acid (d 1.19). After a day, the reaction mixture was treated with water and the resin that deposited was carefully washed with water and crystallized first from ethanol and then from aqueous acetone (1:10). Dark red crystals with mp 234–235° C were obtained (λ_{max} 458 nm). Yield 0.56 g (54%). Found, %: N 13.60, 13.39. Calculated for $C_{28}H_{22}ClN_5O_4$, %: N 13.26. A mixture with the substance obtained previously [6] gave no depression of the melting point.

The unsymmetrical formazans (XVI–XXI). The diazonium salt prepared in the usual way from 2.5 mM of the appropriate amine was added to a solution of 1 g (2.5 mM) of the phenylhydrazone of a 2-formyl-1-phenylquinolinium perchlorate in 10 ml of pyridine cooled to 0° C. After the coupling reaction was complete, the reaction product separated in the form of an oil, which was converted by the addition of 42% $HClO_4$ into a crystalline mass. After washing with hot water and recrystallization from ethanol, compounds **XVI–XXI** were obtained in the form of lustrous brick-red crystals.

The tetrazolium salt XXII. A solution of 1.32 g of the formazan I in 150 ml of HNO_3 (d 1.38) was heated with constant stirring until the evolution of oxides of nitrogen had ceased and the solution had become decolorized. The reaction was considerably accelerated by the addition of 2–3 drops of ethanol. The colorless solution was filtered, diluted with water, and treated with 42% $HClO_4$. The flocculent precipitate was crystallized from ethanol with the addition of a few drops of HNO_3.

Compounds **XXIII–XXV** were obtained similarly.

(Phenylazo)-(1-phenyl-1,2-dihydroquinol-2-ylidene)-(4'-nitrophenylazo)methane. A solution of 1 g (3.7 mM) of **XXI** in 10 ml of ethanol was treated with a 10% solution of NaOH, whereupon the color of the solution changed from red to violet. The substance precipitated in the form of a deep blue powder with mp 159° C (from ethanol). λ_{max} 549 nm (ethanol). When the solution was acidified, it had λ_{max} 460 nm, which corresponds to the absorption maximum of the initial formazan. Found, %: N 17.39, 17.36. Calculated for $C_{28}H_{20}N_6O_2$, %: N 17.79.

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