THE AZO COUPLING OF 1-ARYL QUATERNARY SALTS OF LEPIDINE AND QUINALDINE AND SOME PROPERTIES OF THE REACTION PRODUCTS

O. M. Stashkevich, G. T. Pilyugin, and
V. V. Stashkevich

UDC 547.831.2'79:542.959'943

A series of formazans has been obtained by the coupling of 1-aryllepidinium and 1-arylquinaldinium salts with diazonium salts. The formazans have been converted by oxidation into tetrazolium salts and by the action of acids into benzotriazines. The absorption spectra in the visible region have been measured in neutral, alkaline, and acid media.

The azo coupling of 1-alkylquinaldiuium salts forms mixtures of mono- and bisazo derivatives [1], while that of lepidinium salt forms the monoazo derivatives exclusively [2]. In contrast to this, 1-phenylquinaldinium and 1-phenyllepidinium give bisazo derivatives related to formazans [3-5]. It appeared of interest to study the question of how general the formazan-producing reaction is from the side both of the diazonium salts and of the 1-arylquinaldinium and 1-aryllepidinium salts and also to study some transformations and optical properties of the reaction products.

A series of quaternary quinaldinium and lepidinium salts containing both electron-donating and electron-accepting substituents in the quinoline nucleus and in the phenyl radical attached to the heterocyclic nitrogen atom was introduced into the reaction with diazonium salts. It was found that the direction of the azo coupling reaction does not depend on the nature of the substituents in the quaternary salt. The reaction took place with the formation of the formazans I-XXV (Tables 1 and 2). The introduction of strong electron-donating substituents such as two methoxy groups into the molecule of the quaternary salt lowered the activity of the methyl group, which led to a decrease in the yields of the formazans XIV and XX-XXII. The direction of the azo coupling reaction scarcely depends on the diazonium salts used, either. The diazonium salts from aniline, the isomeric toluidines, alkoxyanilines, naphthylamines, nitroanilines, halogenoanilines, m- and p-aminobenzoic acids, etc., reacted with the formation of formazans.

The azo coupling was carried out in pyridine with a molar ratio of the quaternary salt to diazonium compound of 1 : 2. In an ethanolic medium in the presence of mineral alkali, a large amount of by-products was formed which decreased the yield and interfered with the purification of the formazan. Attempts to isolate monoazo derivatives from the reaction mixture were unsuccessful. When the diazonium salt was gradually added to a pyridine solution of the quaternary salt, only the formazan was detected even in the first portions of dye formed.

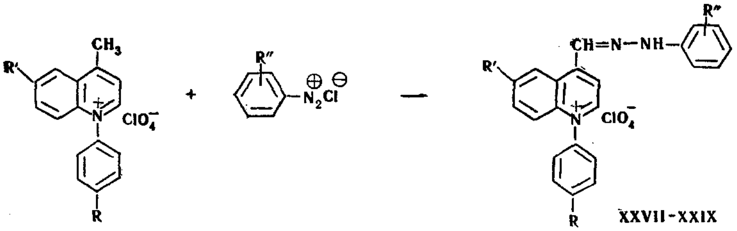
In some cases, by changing the coupling conditions, it was possible to change the direction of the reaction. Thus, p-nitrobenzenediazonium salts form formazans with the quaternary quinoline derivatives in pyridine. However, if a solution of 1-phenyllepidinium perchlorate and a p-nitrobenzenediazonium salt (molar ratio 1:1) in glacial acetic acid is treated with powdered sodium carbonate, the solution rapidly deposits only the monoazo compound XXVI, which is similar to the compound obtained by the condensation of the same quaternary salt with sodium p-nitrobenzene-anti-diazoate [6]. The formazan is not formed at a ratio of 1:2, either. In this case, the excess of diazonium salt is converted into p,p'-dinitrodiazoaminobenzene, which is difficult to separate from the monoazo compound and was identified from its spectrum

---

Chernovits State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 8, pp. 1104-1111, August, 1970. Original article submitted February 9, 1969.

(λ_{max} 424 nm) and also by chromatography in a thin layer of Al_2O_3. The reaction probably stops at the monocoupling stage because of the low solubility of the XXVI, which forms a precipitate.

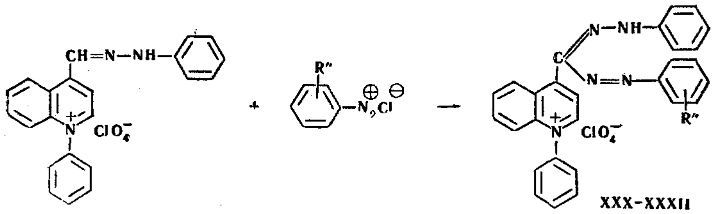
In contrast to other diazonium salts, o-hydroxybenzene and o-carboxybenzenediazonium salts form with 1-aryllepidinium salts in pyridine solution the monoazo derivatives XXVII-XXIX in the following way:


XXVII-XXIX

XXVII R=R′=H, R″=o-OH; XXVIII R=R′=H, R″=o-COOH; XXIX R=R′=Br, R″=o-COOH

The reaction of these diazonium compounds with salts of 2-methylbenzothiazole has been found to take place similarly [7].

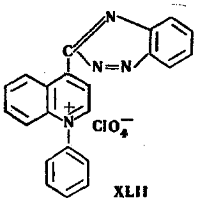
When it is impossible to obtain the formazan in one stage, the method of coupling aldehyde arylhydrazones with diazonium salts is used [8]. The coupling of 4-formyl-1-phenylquinolinium perchlorate [9] with diazonium salts gave the unsymmetrical formazans XXX-XXXII in the following way:


XXX-XXXII

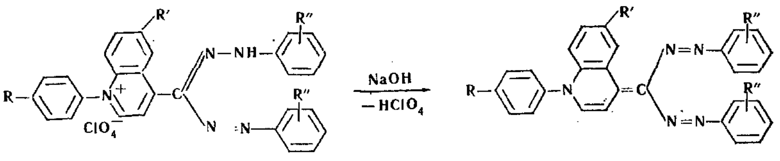
XXX R″= o-COOH; XXXI R″= p-COOH; XXXII R″=p-SO$_3$H

Like other formazans, the formazans that we obtained are smoothly oxidized by conc.HNO_3 to the colorless tetrazolium salts XXXIII-XLI (Table 3). Reduction converts the tetrazolium salts into the initial formazans.

On being heated with conc. H_2SO_4, the formazans decomposed with the formation of the benzotriazines [10]. The acid cleavage of the formazan XXXII gave the benzotriazine XLII.

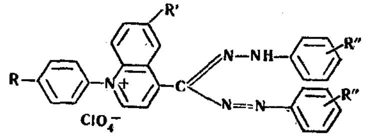

XLII

The formazans obtained were colored compounds the spectra of which in the visible region had a single broad absorption band. When an ethanolic solution of a formazan was made alkaline, the color changed because of the formation of the bisazo dye [5] in the following way:



The formazans dissolve in conc. H_2SO_4, giving deeply colored blue, green, or violet solutions. In the course of time, these solutions become decolorized. This pronounced change in color may be connected with the formation of halochromic doubly charged ions:

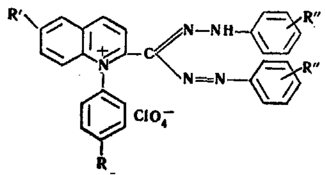
TABLE 1. Formazans Obtained from Lepidinium Salts



Compound	R	R'	R''	mp, °C (solvent)	λ_{max}, nm (lg ε)			Empirical formula	N, %		Yield %
					ethanol	ethanol NaOH	conc. H_2SO_4		found	calculated	
I	H	H	o-OC_3H_7(i)	189—190* (acetone—ethanol)	497 (4,57)	442	—	$C_{34}H_{34}ClN_5O_6$	10,9	10,8	95
II	H	H	p-OC_3H_7	123—124 (acetone—ethanol)	522 (4,57)	488	—	$C_{34}H_{34}ClN_5O_6$	11,0	10,8	94
III	H	H	3,4-Benzo	204—205* (isobutanol)	500 (4,43)	534	—	$C_{36}H_{26}ClN_5O_4$	11,2	11,2	94
IV	H	H	m-COOH	232—233 (water—acetic acid)	470 (4,31)	512	—	$C_{30}H_{22}ClN_5O_8$	11,2	11,4	52
V	H	H	o-NO_2	146—148* (ethanol)	466 (4,04)	546	656	$C_{28}H_{20}ClN_7O_8$	16.2	15,9	92
VI	H	H	p-NO_2	150—152 (ethanol)	466 (3,99)	622	556	$C_{28}H_{20}ClN_7O_8$	15,6	15,9	75
VII	CH_3	CH_3	H	193—194 (acetone—water)	466 (4,25)	520	—	$C_{30}H_{26}ClN_5O_4$	12,8	12,6	62
VIII	CH_3	CH_3	p-Cl	187—188* ethanol	472 (4,35)	520	648	$C_{30}H_{24}Cl_3N_5O_4$	11,5	11,2	59
IX	CH_3	CH_3	p-NO_2	202—203 (ethanol)	460 (4,06)	636	546	$C_{30}H_{24}ClN_7O_8$	15,0	15,3	86
X	Br	Br	p-CH_3	215—216 (acetone—ethanol)	495 (4,38)	514	—	$C_{30}H_{24}Br_2ClN_5O_4$	10,1	9,8	91
XI	Br	Br	p-OCH_3	226—228* (acetone—ethanol)	528 (4,33)	504	—	$C_{30}H_{24}Br_2ClN_5O_6$	9,7	9,4	90
XII	Br	Br	p-Cl	215—216* ethanol	480 (4,34)	518	660	$C_{28}H_{18}Br_2Cl_3N_5O_4$	9,3	9,3	87
XIII	Br	Br	p-NO_2	223—224 (acetone—acetic acid)	464 (3,99)	626	522	$C_{28}H_{18}Br_2ClN_7O_8$	12,9	12,6	61
XIV	OCH_3	OCH_3	p-Cl	218—219* (ethanol)	442 (3,77)	524	—	$C_{30}H_{24}Cl_3N_5O_6$	11,0	10,7	34
XV	H	5,6-Benzo	p-Cl	206—208* (ethanol)	448 (4,04)	520	—	$C_{32}H_{22}Cl_3N_5O_4$	11,0	10,8	60
XVI	OCH_3	5,6-Benzo	p-Cl	199—200 (ethanol)	445 (3,89)	516	—	$C_{33}H_{24}Cl_2N_5O_5$	10,2	10,3	47

*With decomposition.

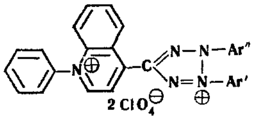
TABLE 2. Formazans Obtained from Quinaldinium Salts

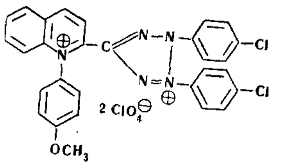
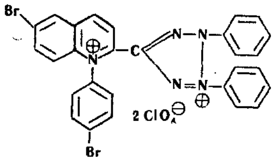


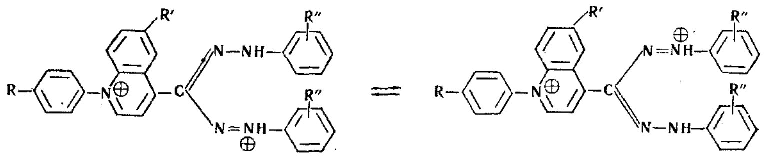
Compound	R	R'	R''	mp, °C (solvent)	λ_{max}, nm (log ε)			Empirical formula	N, %		Yield, %
					ethanol	ethanol + NaOH	conc. H_2SO_4		found	calc.	
XVII	OCH_3	H	H	174–175 (ethanol)	458 (3,26)	498	620	$C_{29}H_{24}ClN_5O_5$	12,6	12,5	66
XVIII	OCH_3	H	*n*-Cl	235–236* (ethanol)	462 (3,26)	501	650	$C_{29}H_{22}Cl_3N_5O_5$	11,1	11,2	76
XIX	OCH_3	H	*n*-NO_2	186–188 (acetone–water)	453 (3,23)	584	590	$C_{29}H_{22}ClN_7O_9$	15,2	15,1	69
XX	OCH_3	OCH_3	H	145–146 (ethanol–water)	457 (3,56)	499	599	$C_{30}H_{26}ClN_5O_6$	12,1	11,9	31
XXI	OCH_3	OCH_3	*n*-Cl	154–156 (ethanol)	462 (3,42)	506	654	$C_{30}H_{24}Cl_3N_5O_6$	10,8	10,6	38
XXII	OCH_3	OCH_3	*n*-NO_2	186–187,5 (formic acid)	451 (3,37)	590	582	$C_{30}H_{24}ClN_7O_{10}$	14,8	14,5	46
XXIII	Br	Br	H	195–196* (acetic acid–water)	485 (3,20)	472	626	$C_{28}H_{20}Br_2ClN_5O_4$	10,5	10,2	85
XXIV	Br	Br	*n*-Cl	218–220* (acetic acid)	481 (3,21)	498	658	$C_{28}H_{18}Br_2Cl_3N_5O_4$	9,5	9,3	82
XXV	Br	Br	*n*-NO_2	241–242* (acetic acid)	468 (—)	584	546	$C_{28}H_{18}Br_2ClN_7O_8$	12,7	12,6	80

---

*With decomposition.

TABLE 3. The Tetrazolium Salts 

Compound	Ar′	Ar″	mp, °C	Empirical formula	Found, % N	Found, % Cl	Calculated, % N	Calculated, % Cl	Yield, %
XXXIII	C_6H_5	C_6H_5	203—204	$C_{28}H_{21}Cl_2N_5O_8$	11,0	11,6	11,2	11,4	40
XXXIV	p-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	249—250	$C_{30}H_{25}Cl_2N_5O_8$	11,0	11,2	10,7	10,8	69
XXXV	p-$CH_3OC_6H_4$	*p*-$CH_3OC_6H_4$	179—180	$C_{30}H_{25}Cl_2N_5O_{10}$	10,2	10,5	10,2	10,3	70
XXXVI	p-ClC_6H_4	*p*-ClC_6H_4	198—199	$C_{28}H_{19}Cl_4N_5O_8$	10,1	20,1	10,1	20,4	61
XXXVII	C_6H_5	*o*-$HOOCC_6H_4$	228—229	$C_{29}H_{21}Cl_2N_5O_{10}$	10,3	10,2	10,4	10,6	55
XXXVIII	C_6H_5	*p*-$HOOCC_6H_4$	248—249	$C_{29}H_{21}Cl_2N_5O_{10}$	10,6	10,4	10,4	10,6	41
XXXIX	C_6H_5	*p*-$HO_3SC_6H_4$	247—248	$C_{28}H_{21}Cl_2N_5O_{11}S$	10,0	9,9	9,9	10,1	23
XL			205—206	$C_{29}H_{21}Cl_4N_5O_9$	9,5	19,7	9,6	19,6	41
XLI			202—203	$C_{28}H_{19}Br_2Cl_2N_5O_8$	9,0	—	8,9	—	37



On dilution with water, the halochromic compounds are destroyed.

EXPERIMENTAL

The quaternary quinaldinium and lepidinium salts were obtained as described in the literature [4,11-13].

The Formazans I-XXV. With vigorous stirring, a diazonium salt solution prepared in the usual way from 4 mmoles of the appropriate amine was added dropwise to a solution of 2 mmoles of a quaternary salt in 8-10 ml of pyridine cooled to -5 to 0°C. As the diazonium salt was added, the reaction mixture became red. The mixture was kept at 0°C for 2 hr and then at room temperature for 24 hr. To isolate the formazan, the reaction mixture was diluted with water and was then treated with an excess of $HClO_4$ (42%). The precipitate that deposited was filtered off, carefully washed with hot water, and crystallized.

4-Nitrophenylazomethylene-1-phenyl-1,4-dihydroquinoline (XXVI). Solutions of 1 g (3.13 mmoles) of 1-phenyllepidinium perchlorate in 20 ml of glacial acetic acid and of p-nitrobenzenediazonium chloride prepared from 0.43 g (3.13 mmoles) of p-nitroaniline, 2 ml of conc.HCl, and 0.3 g of $NaNO_2$ in 3 ml of water were mixed at 0°C. With stirring and cooling, the resulting solution was treated with powdered carbonate in order to neutralize the acid. The initially yellow solution gradually acquired a red-brown color, and on further neutralization a black-blue precipitate was formed. The yield of crude dye was 0.8 g (69%). After crystallization from ethanol-acetone (1:1) it formed a powder with mp 176-177°C giving a red-orange coloration with conc.H_2SO_4. A mixture with a sample obtained from p-nitrobenzene-anti-diazoate [6] showed no depression of the melting point. λ_{max} 608 nm (log ε 4.59, ethanol); on acidification, λ_{max} 485 nm. Found, %: C 71.9; H 4.5; N 15.2. Calculated for $C_{22}H_{16}N_4O_2$, %: C 71.7; H 4.3; N 15.2.

o-Hydroxyphenylhydrazone of 4-Formyl-1-phenylquinolinium Perchlorate (XXVII). A solution of 0.68 g (6.28 mmoles) of o-aminophenol in 15 ml of methanol and 1 ml of conc.HCl was cooled to 0°C, diazotized with a solution of 0.5 g of $NaNO_2$ in 5 ml of water, and, with cooling to 0°C, it was mixed with a solution of 1 g (3.13 mmoles) of 1-phenyllepidinium perchlorate in 30 ml of pyridine. No formation of a dye was observed. Consequently, the reaction mixture was treated with 30 g of finely crushed ice and 10 g of sodium carbonate. After some time, the solution became violet. After it had stood at 0°C for 70 hours, the mixture was diluted with water and treated with 42% $HClO_4$ until it gave an acid reaction to Congo red; it was then filtered, and the precipitate was washed until it was completely free from sodium and pyridinium perchlorates. The yield of crude dye was 0.9 g (65%). After two crystallizations from ethanol it formed green needles with mp 259-261°C (decomp.), giving a cherry red coloration in conc.H_2SO_4. λ_{max} 532 nm (log ε 4.61, ethanol); alkaline solution, λ_{max} 546 nm. Found, %: Cl 8.0; N 9.7. Calculated for $C_{22}H_{18}Cl\cdot N_3O_5$, %: Cl 8.1; N 9.6.

o-Carboxyphenylhydrazone of 4-Formyl-1-phenylquinolinium Perchlorate (XXVIII). This was obtained in a similar manner to compounds I-XXV from 1 g (3.13 mmoles) of 1-phenyllepidinium perchlorate in 5 ml of pyridine and the diazonium salt from 0.45 g (3.13 mmoles) of anthranilic acid. The yield of crude dye was 1.15 g (79%). Dark red crystals with a greenish tinge having mp 258-259°C (decomp.) were obtained after two crystallizations from acetic acid. λ_{max} 496 nm (log ε 4.65, ethanol); in alkaline solution, λ_{max} 526 nm. Found, %: Cl 7.8; N 9.1. Calculated for $C_{23}H_{18}ClN_3O_6$, %: Cl 7.6; N 9.1.

o-Carboxyphenylhydrazone of 6-Bromo-(p-bromophenyl)-4-formylquinolinium Perchlorate (XXIX). This was obtained from 0.96 g (2 mmoles) of 6-bromo-1-bromophenyllepidinium perchlorate in 25 ml of pyridine and the diazonium salt from 0.55 g (4 mmoles) of anthranilic acid. Violet-red microcrystalline powder with mp 205-206°C (decomp, from ethanol–acetone), giving a cherry-red halochromism in conc. H_2SO_4. Yield 1.15 g (92%), λ_{max} 500 nm (log ε 4.62, ethanol); in alkaline solution, λ_{max} 520 nm. Found, %: Br + Cl 31.4; N 6.9. Calculated for $C_{23}H_{16}Br_2ClN_3O_6$, %: Br + Cl 31.1; N 6.7.

1-Phenyl-3-(1'-phenylquinolin-4'-yl)-5-(p-sulfophenyl)formazan Perchlorate (XXXII). A solution of a p-sulfobenzenediazonium salt obtained from 0.84 g (4.7 mmoles) of sulfanilic acid was added dropwise to a solution of 2 g (4.7 mmoles) of the phenylhydrazone of 4-formyl-1-phenylquinolinium perchlorate in 30 ml of pyridine cooled to -10°C. The mixture was kept at 0°C for 2-3 hr and was then diluted with water and treated with an excess of 42% $HClO_4$. The precipitate that deposited was filtered off, washed with water, and crystallized from ethanol. Red microcrystalline powder with mp 169-170°C. Yield 1.45 g (44%). λ_{max} 469 nm (log ε 4.41, ethanol). Found, %: Cl 5.6; N 11.6. Calculated for $C_{28}H_{22}ClN_5O_7S$, %: Cl 5.8; N 11.5.

The following were obtained similarly: XXX – dark red crystals with mp 153-154°C (from acetone), yield 45%, λ_{max} 465 nm (log ε 4.31, ethanol). Found, %: Cl 6.2; N 12.4. Calculated for $C_{29}H_{22}ClN_5O_6$, %: Cl 6.2; N 12.2. XXXI – brick-red crystals with mp 177-178°C, yield 37%, λ_{max} 460 nm (log ε 4.48, ethanol). Found, %: Cl 6.4; N 12.1. Calculated for $C_{29}H_{22}ClN_5O_6$, %: Cl 6.2; N 12.2.

2,3-Diphenyl-5-(1'-phenylquinolin-4'-yl)tetrazolium Diperchlorate (XXXIII). A mixture of 2.65 g (5 mmoles) of 1,5-diphenyl-3-(1'-phenylquinolin-4'-yl)formazan perchlorate [4] and 300 ml of HNO_3 (d 1.40) was heated at the boil and stirred until it had become completely decolorized and the solid matter had passed into solution. After the end of the reaction, the solution had acquired a straw-yellow color. It was cooled and filtered, and the tetrazolium salt was precipitated with 42% $HClO_4$. Yield 1.25 g (40%). After two crystallizations from a mixture of ethanol and water (2:1) it formed a yellow-orange microcrystalline powder with mp 203-204°C. The salt is readily soluble in ethanol and sparingly soluble in water.

Compounds XXXIV-XLI were obtained similarly.

3-(1'-Phenylquinolin-4'-yl)benzotriazine Perchlorate (XLII). A solution of 1.8 g of the formazan XXXII in 20 ml of glacial acetic acid and 30 ml of conc.H_2SO_4 was heated in the water bath until the blue color had changed to brown. Then the mixture was poured into cold water and treated with 5 ml of 42% $HClO_4$. The precipitate that deposited was crystallized from acetone. Yellow-green powder with mp 180-181°C. Yield 10%. Found, %: N 12.8. Calculated for $C_{22}H_{15}ClN_4O_4$, %: N 12.9.

LITERATURE CITED

1. W. König, Ber., 56, 1543 (1923); 57, 891 (1924).
2. E. Koenigs and H. Bueren, J. Pr. Chem., 146, 119 (1936).
3. G. T. Pilyugin and S. V. Shinkorenko, ZhOKh, 28, 1313 (1958).

4. G. T. Pilyugin, S. V. Shinkorenko, O. M. Stashkevich, and V. V. Stashkevich, KhGS [Chemistry of Heterocyclic Compounds], 2, 406 (1966).
5. G. T. Pilyugin, S. V. Shinkorenko, and V. V. Stashkevich, KhGS [Chemistry of Heterocyclic Compounds], 4, 311 (1968).
6. O. M. Stashkevich, G. T. Pilyugin, S. V. Shinkorenko, and V. V. Stashkevich, KhGS [Chemistry of Heterocyclic Compounds], 4, 152 (1968).
7. H. Wahl and M. T. Lebris, Bull. Soc. Chim. France, 589 (1954).
8. A. N. Nineham, Chem. Rev., 55, 355 (1955).
9. G. T. Pilyugin, O. M. Stashkevich, S. V. Shinkorenko, and V. V. Stashkevich, KhGS [Chemistry of Heterocyclic Compounds], 4, 316 (1968).
10. E. Bamberger and E. Wheelwright, Ber., 25, 320 (1892); 26, 2788 (1893).
11. O. M. Stashkevich and G. T. Pilyugin, Ukr. Khim. Zh. 33, 614 (1967).
12. G. T. Pilyugin, T. S. Zueva, V. V. Stashkevich, S. V. Shinkorenko, and O. M. Stashkevich, ZhOKh, 38, 1392 (1968).
13. G. T. Pilyugin, Ya. O. Gorichok, B. M. Gutsulyak, and S. I. Gorichok, KhGS [Chemistry of Heterocyclic Compounds], 1, 889 (1965).