STUDIES IN THE FIELD OF SYNTHETIC DYES

LXVII. Reaction of 1-Phenyllepidinium Perchlorate with Diazoamino Compounds*

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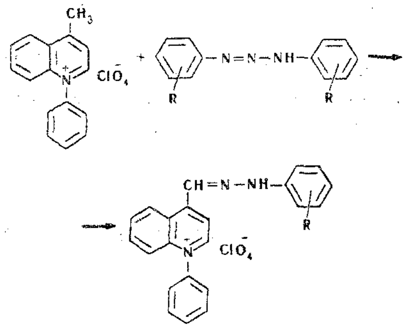
Substituted arylhydrazones of 4-formyl-1-phenylquinolinium perchlorate have been obtained by the reaction of 1-phenyllepidinium perchlorate with a number of symmetrical diazoamino compounds.

Depending on the conditions, the reaction with diazo compounds of heterocyclic compounds containing a reactive methyl group may take place with the replacement of one or two hydrogen atoms by arylazo residues. They do not react with diazonium salts of quinaldine and lepidine [1], and their alkyl halide derivatives give mono- [2–4] or a mixture of mono- and bisazo compounds [5, 6] while their N-aryl derivatives and quaternary salts of their N-oxides form formazans [7–9]. In contrast to this, the less active diazoamino compounds give only monoazo derivatives [10, 11]. Only diazoaminobenzene has so far been used in reactions with quaternary salts of heterocyclic bases.

In order to broaden the possibilities of the synthesis of monoazo derivatives, we have studied the reaction between 1-phenyllepidinium perchlorate and a number of symmetrical diazoamino compounds (triazenes) with electron-donating and electron-accepting substituents in their nuclei.

It was found that 1-phenyllepidinium perchlorate readily reacts with triazenes on heating in ethanolic solution with the formation of arylhydrazones of 4-formyl-1-phenylquinolinium perchlorate **I–VIII** (see table):

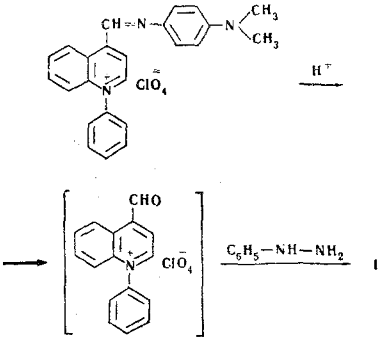


I–VIII

I R = H, II R = o-CH_3, III R = n-CH_3, IV R = o-OCH_3, V R = p-OCH_3, VI R = p-OC_2H_5, VII R = p-Cl, VIII R = p-Br

Electron-donating substituents in the triazene (CH_3, OCH_3, OC_2H_5) accelerate this reaction, while electron-accepting substituents (Cl, Br) retard it and p,p'-dinitrodiazoaminobenzene does not react either in ethanol or in amyl alcohol even on prolonged heating.

The hydrazone structure of the compounds obtained was confirmed through independent synthesis by the following route [12]:



The compounds obtained were readily soluble in acetone, nitrobenzene, nitromethane, dioxane, chloroform, dimethylformamide, acetic acid, and, on heating, in ethanol; they were sparingly soluble in benzene and in cold ethanol, and were practically insoluble in ether and water. Solutions of these compounds in various solvents are red with different tinges. With concentrated H_2SO_4 they give halochromic compounds which are red-brown or, in the case of compounds **IV**, **VII**, and **VIII**, green. On dilution with water, the original color of the dye is restored. These substances are capable of dyeing cotton fabric or fiber red and violet without a mordant.

The arylhydrazones **I–VIII** have a deeper color than the corresponding bisazo derivatives [8]. Electron-accepting substituents (Cl, Br) in the aryl nucleus of the hydrazone residue displace the absorption maximum hypsochromically and electron-donating substituents (CH_3, OCH_3, OC_2H_5) displace it bathochromically as compared with the unsubstituted I. Compounds **I–VIII** change color on the addition of alkali and can be used as acid-base indicators. Making an alcoholic solution alkaline leads to a deepening of the color in the case of electron-donating substituents (**VII**, **VIII**) and to a lightening of the color in the case of strongly electron-donating substances (**V**, **VI**).

EXPERIMENTAL

1-Phenyllepidinium perchlorate. This was obtained with a yield of 24.6% by a modification of our previous method [8]. With stirring, solutions of 34 g (0.2 mole) of diphenylamine in 36 ml of acetone and of 7.7 g (0.25 mole) of 97% paraformaldehyde in 70 ml of water were added over 2 hr to a mixture of 75 ml of 57% $HClO_4$, 50 ml of nitrobenzene, and 100 ml of acetone heated to the boil. After the addition of the solutions, the reaction mixture was heated for 2 hr and then 500 ml of water was added and it was heated for another 2 hr. The isola-

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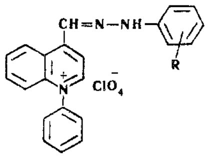
*For communication LXVI, see [13].



Compound	R	Mp (decomp), °C (solvent)	λ_{max}, nm: ethanol ($\varepsilon \times 10^{-4}$)	λ_{max}, nm: ethanol + NaOH	Empirical formula	Element	Found, %	Calculated, %	Yield, %
I	H	248—249 (acetone—ethanol)	509 (2.50)	525	$C_{22}H_{18}ClN_3O_4$	N Cl	10.13; 10.14 8.54; 8.39	9.89 8.36	50.4
II	o-CH_3	245—246 (acetone—ethanol)	513 (2.31)	520	$C_{23}H_{20}ClN_3O_4$	N Cl	9.90; 9.97 8.11; 8.36	9.60 8.11	55.9
III	p-CH_3	261—262* (nitromethane)	526 (2.58)	524	$C_{23}H_{20}ClN_3O_4$	N Cl	9.90; 9.91 8.35; 8.24	9.60 8.11	66.2
IV	o-OCH_3	236—237 (acetone—ethanol)	530 (2.66)	522	$C_{23}H_{20}ClN_3O_5$	N Cl	9.15; 9.29 8.27; 8.14	9.26 7.83	89.9
V	p-OCH_3	171—172 (ethanol)	542 (2.16)	524	$C_{23}H_{20}ClN_3O_5$	N Cl	8.95; 9.01 7.54; 7.62	9.26 7.83	53.2
VI	p-OC_2H_5	146—147 (ethanol)	544 (2.31)	523	$C_{24}H_{22}ClN_3O_5$	N Cl	8.82; 8.86 7.37; 7.48	8.98 7.59	65.5
VII	p-Cl	252—253* (acetone—ethanol)	502 (2.76)	528	$C_{22}H_{17}Cl_2N_3O_4$	N Cl	9.35; 9.54 15.43; 15.02	9.17 15.49	67.6
VIII	p-Br	257—258 (acetone—ethanol)	504 (2.30)	534	$C_{22}H_{17}BrClN_3O_4$	N Br+Cl	8.72; 8.47 22.75; 22.96	8.35 22.9	71.8

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*Without decomposition.

tion and purification of the products was carried out in a similar manner to the previous work [8].

Phenylhydrazone of 4-formyl-1-phenylquinolinium perchlorate (I). a) A mixture of 1 g (3.1 mM) of 1-phenyllepidinium perchlorate and 0.6 g (3.1 mM) of diazoaminobenzene in 10 ml of ethanol was heated at a gentle boil for 20 min. During the heating process, the reaction mixture acquired a cherry-red color and crystals began to deposit from the solution. After cooling, filtering and washing with ether, the crude dye was obtained. Two recrystallizations from a mixture of acetone and ethanol (1:1) gave **I** in the form of a lustrous dark red microcrystalline powder.

Compounds **II–IV**, **VII**, and **VIII** were obtained similarly.

b) By heating to the boil, 1.17 g (2.5 mM) of N-(4-dimethylaminophenyl)-(1'-phenyl-4'-quinolyl)azomethine perchlorate was dissolved in a mixture of 25 ml of ethanol and 25 ml of water, with the addition of 2 ml of concentrated hydrochloric acid. A solution of 0.4 g (2.5 mM) of phenylhydrazine hydrochloride in 10 ml of water was added to the initial solution with stirring, whereupon the reaction mixture acquired a bright red color and, after cooling, lustrous dark red crystals deposited. Yield 0.75 g (71%). They were recrystallized from ethanol and acetone with the addition of a few drops of $HClO_4$. A mixture with a sample obtained from diazoaminobenzene gave no depression of the melting point. λ_{max} 509 nm (ethanol, ε 2.48 × 10^4), changing to 525 nm on the addition of alkali. Found, %: N 9.85, 9.90. Calculated for $C_{22}H_{18}ClN_3O_4$, %: N 9.89.

p-Methoxyphenylhydrazone of 4-formyl-1-phenylquinolinium perchlorate (V). A mixture of 1 g (3.1 mM) of 1-phenyllepidinium perchlorate and 0.8 g (3.1 mM) of p,p'-dimethoxydiazoaminobenzene in 5 ml of ethanol was heated for 10 min. After cooling. the reaction mixture was treated with ether, dissolved in the minimum amount of acetone, and precipitated with a large volume of water. After filtration, the precipitate was dried, washed with ether, and twice crystallized from ethanol with the addition of $HClO_4$. Compound V was obtained in the form of a violet microcrystalline powder.

Compound VI was obtained similarly.

The absorption curves were recorded on an SF-2M spectrophotometer.

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