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RESEARCHES ON SYNTHETIC DYES

LVI. Synthesis of Bisazo Dyes, Derivatives of N-Aryllepidine Salts*

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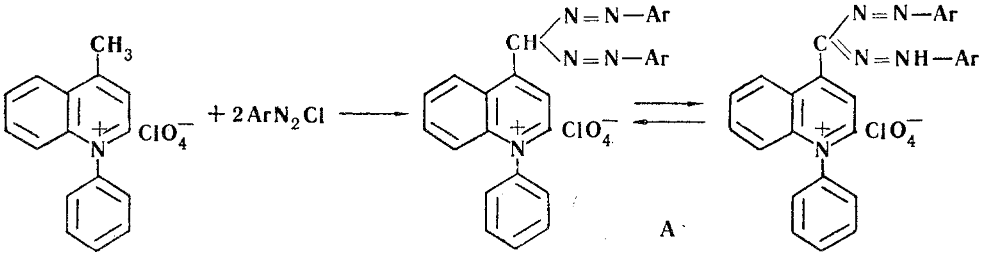
It is shown that formazan-type compounds can be synthesized by coupling diazonium salts with nitrogen containing N-aryllepidine salts. N-phenyllepidinium perchlorate is used to prepare 8 dyes of the type mentioned.

It was previously shown [1] that N-arylquinaldinium quaternary salts react at an active methyl group with diazonium salts to give bisazo dyes related to formazan compounds. It was of interest to ascertain how N-aryllepidinium quaternary salts react.

The literature information regarding reaction of diazonium salts with lepidine onium compounds is rather scanty. In strong alkali solution, lepidine N-alkyl quaternary salts and diazonium salts give monoazo dyes [2]. It has also been shown that synthesis of formazan-type compounds can be based on quaternary salts of quinaldine and lepidine N-oxides [3].

To investigate the reactivity of the methyl group, the reactions between N-phenyllepidinium perchlorate and a number of diazonium salts were studied. The equation is



Type A compounds (bisazo dyes) were obtained using diazonium salts prepared from aniline, o- and p-toluidine, o- and m-anisidine, p-phenetidine, p-chloroaniline, and p-bromoaniline.

The bisazo dyes A synthesized (see table) are red salt-like substances, giving blue or green halochromic compounds with concentrated sulfuric acid.

The bisazo dyes decomposed above their melting points, were readily soluble in pyridine, nitromethane, ethanol and butanol, slightly soluble in dioxane, but practically insoluble in ether.

The one-type nature of the absorption spectra, with only one clearly-defined absorption band, indicates a typical similarity in the structure of the dyes. It may be mentioned that introduction of substituents at positions 2 and 4 in the phenyl ring of the arylazo group results in bathochromic shift of the absorption maximum, the order for the substituents being:

$$H < p\text{-}Cl(Br) < o\text{-}CH_3 < p\text{-}CH_3 < o\text{-}OCH_3 < p\text{-}OCH_3 (p\text{-}OC_2H_5)$$

Experimental

N-Phenyllepidinium perchlorate. Prepared according to modified directions [4, 5]. A four-necked flask was fitted with mechanical stirrer, reflux condenser, and two graduated burets, then 15 ml perchloric acid (42%), 25 ml nitrobenzene, and 25 ml acetone were introduced. The mixture was stirred and boiled, and 10 g diphenylamine in 15 ml acetone and 25 ml formaldehyde solution (8%) added alternately from the two burets, 1 ml at a time. The reaction mixture was refluxed for 1 hr while stirred, 100 ml water added, and boiling continued for another 3 hr. When the reaction was finished, acetone and nitrobenzene were steam-distilled off, the aqueous layer carefully poured off from the tar

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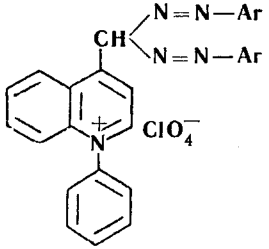
*For Part LV see [6].

Bisazo Dyes, N-Phenyllepidinium Perchlorate Derivatives



Compound No.	Ar	Mp (solvent)	Color with conc. H_2SO_4	λ_{max}, mμ (EtOH)	lg ε	Formula	Element	Found, %	Calculated, %	Yield, %
I	C_6H_5	201—202* (acetone water)	Blue	468	3.84	$C_{28}H_{22}ClN_5O_4$	N Cl	13.25; 13.24 6.95; 7.14	13.27 6.73	87.7
II	o-$CH_3C_6H_4$	192—193* (iso-BuOH)	Bluish-green	470	3.64	$C_{30}H_{26}ClN_5O_4$	N Cl	12.76; 12.90 6.13; 6.51	12.60 6.39	91.9
III	p-$CH_3C_6H_4$	209.5—210 (acetone-water)	Green	484	3.82	$C_{30}H_{26}ClN_5O_4$	N Cl	12.72; 12.68 6.74	12.60 6.39	71.2
IV	o-$CH_3OC_6H_4$	207.5—208* (EtOH-iso-BuOH)	Blue	495	4.08	$C_{30}H_{26}ClN_5O_6$	N Cl	12.27; 12.09 6.53; 6.32	11.91 6.06	92.7
V	p-$CH_3OC_6H_4$	155—156 (EtOH)	Green	520	3.60	$C_{30}H_{26}ClN_5O_6$	N Cl	11.89; 11.91 6.49; 6.11	11.91 6.39	96.3
VI	p-$C_2H_5OC_6H_4$	139—140 (EtOH)	Green	520	3.92	$C_{32}H_{30}ClN_5O_6$	N Cl	11.40; 11.42 6.28; 6.14	11.37 5.76	96.0
VII	p-ClC_6H_4	183—184* (EtOH)	Blue	468	3.58	$C_{28}H_{20}Cl_3N_5O_4$	N Cl	11.42; 11.53 17.37; 18.19	11.73 17.85	85.5
VIII	p-BrC_6H_4	210.5—211* (iso-BuOH)	Blue	470	4.12	$C_{28}H_{20}Br_2ClN_5O_4$	N Br+Cl	10.35; 10.43 28.38; 28.55	10.21 28.50	81.4

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* Decomp.

through a filtering device, and the tar repeatedly boiled with water till the quaternary salt was completely extracted. The aqueous extracts were evaporated to small volume, and, on cooling, deposited needle-shaped crystals. Two recrystallizations from water gave needle-shaped crystals mp 173°-174° C [4, 5], yield 4 g (21.3%).

Coupling N-phenyllepidinium perchlorate with p-tolylidizonium chloride. A solution of 1 g (3.1 mmole) N-phenyllepidinium perchlorate in 6 ml pyridine was cooled to 0° C, stirred, and a solution of p-tolyldiazonium chloride, prepared from 0.67 g (6.2 mmole) p-toluidine, added dropwise. The reaction mixture became intensely red, it was left at room temperature for 24 hr, treated with excess perchloric acid (42%). After 2 hr standing, the precipitate was filtered off, then washed on the filter first with cold water, then with hot. The dye was dried, and carefully washed with ether. Yield of III 1.24 g (71.2%). After recrystallizing from BuOH and then from aqueous Me_2CO, a dark red finely divided crystalline powder was obtained, mp 209.5°-210° C.

Compounds II, IV-VIII were prepared similarly. Compound I was prepared as described in [1]. The spectra of ethanol solutions of the dyes were observed with a self-registering SF-2M spectrophotometer.

REFERENCES

1. G. T. Pilyugin and S. V. Shinkorenko, ZhOKh, 28, 1313, 1958.
2. E. Koenigs and H. Bueren, J. pr. Chem., 146, 119, 1936.
3. L. S. Efros and I. M. Mishina, ZhOKh, 32, 2217, 1962.
4. G. T. Pilyugin and B. M. Gutsulyak, ZhOKh, 29, 3076, 1959.
5. B. I. Ardashev and B. A. Tertov, ZhOKh, 29, 3050, 1959.
6. G. T. Pilyugin, Ya. O. Gorichok, B. M. Gutsulyak, and S. I. Gorichok, KhGS [Chemistry of Heterocyclic Compounds], 896, 1965.

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