N,N'-DIARYL-4,4'-DIPYRIDINIUM DIBROMIDES

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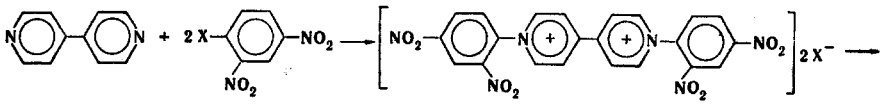
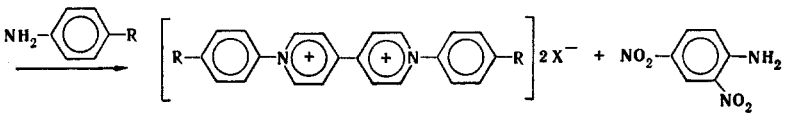
We have observed that N,N'-diaryl-4,4'-dipyridinium dibromides (I) are electrochemichromes, regardless of the electronic nature of substituents R. Compositions based on them have improved operating characteristics (the response voltage is less than 1.2 V, and the lifetime is more than 10^5 "recording–erasing" cycles) as compared with the known dichlorides (II). This makes it possible to use salts I as the working substances in electrochromic devices for the display of information.



III



I a-g II

I X = Br; a R = H; b R = CH_3; c R = OCH_3; d R = Cl; e R = Br; f R = $COOCH_3$; g R = NO_2;

II X = Cl

However, whereas, according to the data in [1], heating to 100°C in water is sufficient for the recyclization of dichloride III (X = Cl) to II, in the case of the dibromides the reaction under these conditions was possible only in the case of preparation of I with electron-donor R groups. However, if R is an electron-acceptor substituent, more severe recyclization conditions — heating at 110-115°C in polar organic solvents such as dimethylformamide — are required. It is also possible to carry out the reaction at temperature that do not exceed 100°C, but catalytic amounts of pyridine must be added. The bromide ion in Ia-h can be replaced by perchlorate or tetrafluoroborate ion.

A 6.6-g (0.01 mole) sample of dibromide III (X = Br), obtained by arylation of 4,4'-dipyridyl with 2,4-dinitrobromobenzene, was added in portions at 80°C to a solution of 0.04 mole of p-substituted anilines in 40 ml of dimethylformamide, 4 ml of pyridine was added dropwise, and the mixture was heated at 100°C for 1 h. Salts I were precipitated by the addition of acetone. The salts were obtained in 60-80% yields [compound and melting point (from water) given]: Ia 342°, Ib 350°, Ic 320°, Id 370°, Ie 380°, If 280°, and Ig 310°C. The results of elementary analysis were in agreement with the calculated values.

LITERATURE CITED

1. J. G. Allen, British Patent No. 1399595 (1971); Ref. Zh. Khim., 3N246 (1976).

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