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4-Alkoxynaphthaldehydes and their application in synthesis of styryl pyrylium dyes with broad absorption band in visible spectrum.

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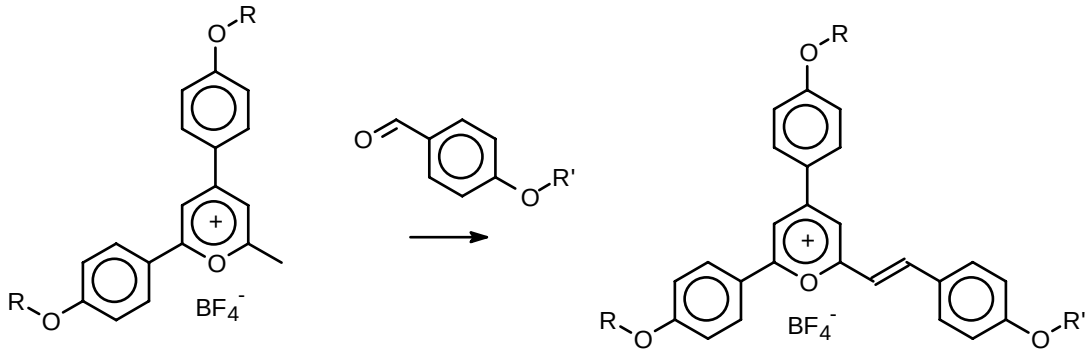
Abstract: 2,4-Di(4-propoxyphenyl)-6-(4-propoxynaphthyl)pyrylium tetrafluoborate - styryl pyrylium dye with broad absorption bands at 400-500nm and 500-630nm was synthesized. Method for obtaining intermediate 4-propoxynaphthaldehyde was improved.

Owing to cessation of manufacturing of the whole range of dyes traditionally used in the chemical photographic industry a problem of their substitution arose. The most severe problem appeared to be substitution of dye No. 5121 in antihalation layers of technical photo plates.

In the course of our researches we turned our attention to styryl pyrylium dyes which were obtained through condensation of aromatic aldehydes with pyrylium salts tetrafluoborates bearing active methyl group (scheme 1) [1, 2, 3, 4, 5].



I

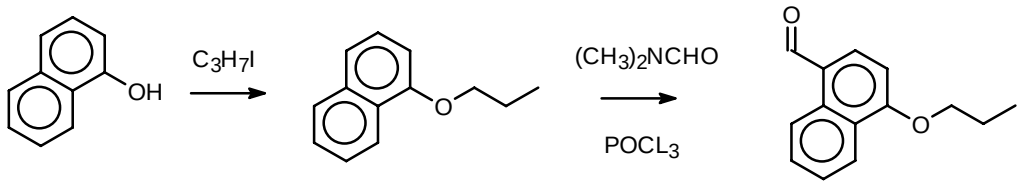
Scheme 1. Synthesis of 2,4-di(4-alkoxyphenyl)-6-(4-alkoxyphenyl)pyrylium tetrafluoborates (I).

It turned out, that dyes of this class are suitable for substitution of dye No. 5121. Thereat, they overlapped a range 400-560 nm. However, for practical needs we wanted to have a dye with a broader absorption band.

Broadening of the band was achieved by application of 4-alkoxynaphthaldehyde as carbonyl coupler. The best method of its obtaining is admission of formyl group to 1-alkoxynaphthalene in the course of Vilsmeier reaction. If in case of 1-methoxynaphthalene the process was described [6], for other substitutions we had to develop it. Reaction takes place at addition of phosphorus oxychloride to a mixture of ether and dimethyl formamide at temperature 90-100°C with yielding of 80-90%.

Dye (III) was selected out of obtained compounds which met specified requirements better than the others, and overlapped a range 400-660 nm.

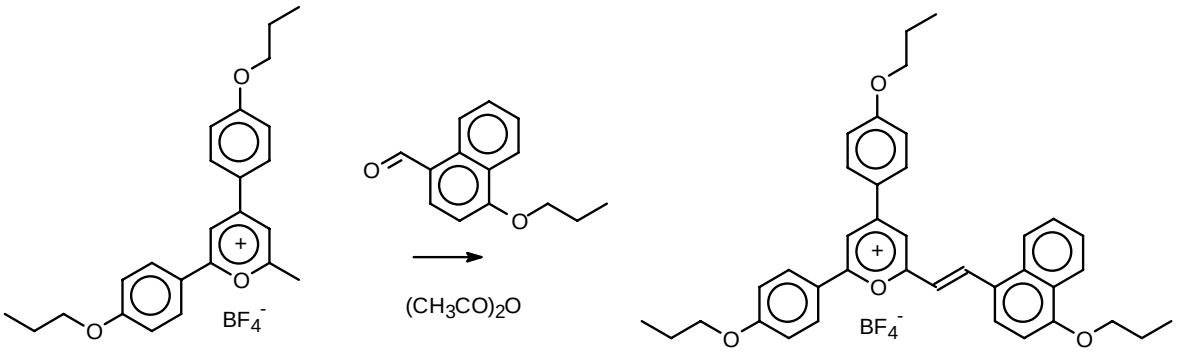
Synthesis of dye (III) was conducted through condensation of 2-methyl-4,6-di-(4-propoxyphenyl)pyrylium tetrafluoborate with 1-propoxynaphtaldehyde (II). The compound II was obtained by formylation of 1-propoxynaphthalene, and its synthesis starting from 1-naphthol according to scheme 2.



II

Scheme 2. Synthesis of 4-propoxynaphthaldehyde (II) [7].

Condensation of II and 2-methyl-4,6-di(4-propoxyphenyl)pyrylium tetrafluoroborate gives desired styryl pyrylium dye (scheme 3).



III

Scheme 3. Synthesis of 2,4-di(4-propoxyphenyl)-6-(4-propoxynaphthyl)-pyrylium tetrafluoborate (III) [8].

Absorption spectra of standard dyes mixture for photo plates antihalation layers and proposed dye III are shown below.

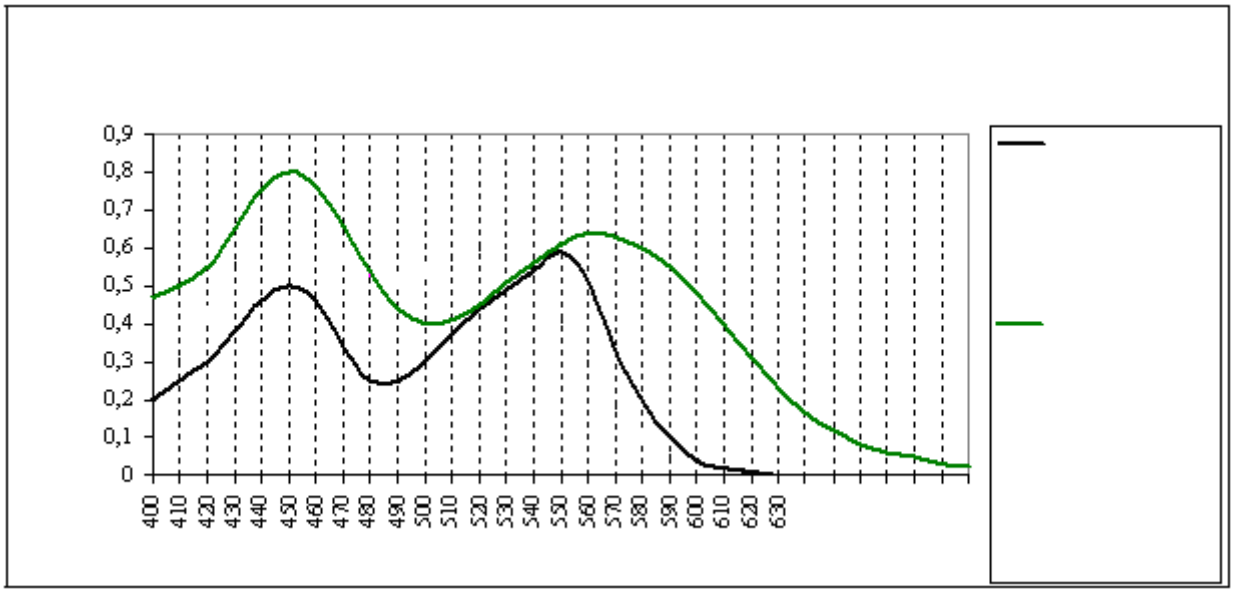


Figure 1. Absorption spectra of standard antihalation dyes mixture (dye No. 5121 and parafuxine) – black line, and proposed pyrylium dye III – green line.

References

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7. 4-Propoxynaphthaldehyde, yield 83 %, m.p. 64-65°C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 1,15 (t, 3H, $\underline{CH_3}CH_2CH_2O$-, J = 7.5 Hz); 2.00 (m, 2H, $CH_3\underline{CH_2}CH_2O$-); 4.20 (t, 2H, $CH_3CH_2\underline{CH_2}O$-, J = 6.45 Hz); 6.90 (d, 1H, CH(8), J = 8.1 Hz); 7,57 (dd, 1H, CH(6), J_1 = 7.2 Hz, J_2 = 6.9); 7.70 (dd, 1H, CH(7), J_1 = 7.2 Hz, J_2 = 6.9); 7.90 (d, 1H, CH(5), J = 8.7 Hz); 8.37 (d, 1H, CH(3), J = 8.1 Hz); 9.30 (d, 1H, CH(2), J = 8.1 Hz); 10.22 (s, 1H –CHO). Found, %: C 78.42; H 6.69. $C_{14}H_{14}O_2$. Calculated, %: C 78.50; H 6.54.

8. 2,4-Di(4-propoxyphenyl)-6-(4-propoxynaphthyl)-pyrylium tetrafluoborate, yield 73 %, m. p. 135-136°C; λ_{max} = 450±2 nm (ε 2.6×10^4), 565±2 nm (ε 2.3×10^4). Found, %: C 70.85; H 6.11. $C_{38}H_{39}BF_4O_4$. Calculated, %: C 70.59; H 6.04. Solubility 0.0051 g/ml in 75% ethanol - 25% water mixture.