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Synthesis of Some Unsaturated 9-Phenylxanthene Dyes

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ABSTRACT

The synthesis of some unsaturated 9-phenylxanthene dyes under phase transfer catalysis conditions is reported. The most favourable reaction conditions (a type of two-phase system, solvent, catalyst) were selected. Two 9-phenylxanthene dyes were synthesized in good yields under these conditions. The ability of the dyes for copolymerization with vinyl monomers such as styrene and methyl methacrylate was also demonstrated. The content of the chemically bound dye in the polymer chain was estimated.

Keywords: Unsaturated, 9-Phenylxanthene, Copolymerization.

INTRODUCTION

Ecological problems that have arisen in the last years from the application of different organic products, including dyes and pigments, have necessitated investigations directed to the synthesis of more tolerant materials by means of their polymeric modification [1, 2]. This could be achieved by incorporation of reactive functional groups in the compound structure, which would then be able to participate in polymerization, or polycondensation processes.

In previous studies [3–5], we have reported the syntheses of different polymerizing azo-, anthraquinone, benzanthrone and naphtalimide dyes, and thence derived coloured copolymers.

Because of their intense fluorescence, 9-phenylxanthene derivatives are well known as luminophores. They are widely used for colouring polymers, leather, paper, food, inks, stains, crayons, and in drugs, cosmetics, pharmaceuticals

and laser techniques [1]. However, these dyes have been applied on different materials only to a small extent because of their poor light-fastness properties.

We now investigate the possibility of obtaining unsaturated 9-phenylxanthene dyes. This would give the opportunity of obtaining chemically coloured fluorescing polymers by their participation in the polymerization processes. On the other hand, the use of such polymers could lead to ecologically more acceptable application of these dyes for colouring food stuffs and cosmetics, and also for obtaining laser technique materials with increased light-fastness.

Among 9-phenylxanthene derivatives, Fluorescein and Eosin are the most recognised and, for this reason, we used them as model compounds. The subject of the present work was both the synthesis of their unsaturated derivatives and the synthesis of their copolymers.

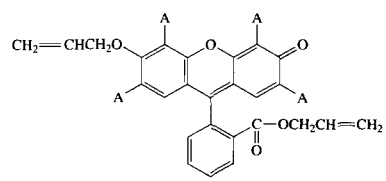
RESULTS AND DISCUSSION

The synthesis of different, allyl, ether and ether-esters of the Fluorescein has been reported with a view to studying the influence of substituents on their heat and hydrolytic stability [6]. No reports have been made on the synthesis and application of Eosin derivatives and the other compounds of the same chemical class.

The allyl ether-ester of the Fluorescein has been synthesized by interaction with allyl bromide in boiling acetone. Substantial disadvantages of this method are the long term of the process (2–12 h), and also that the desired product is obtained in a relatively low yield (43%).

Having in mind the advantages of phase transfer catalysis (PTC) [7] and our experience in the synthesis of different organic products under such conditions [8–10] it was of interest to investigate the possibility of obtaining allyl derivatives of both Fluorescein and Eosin, under favourable reaction conditions, and in high yields.

The compounds whose synthesis was the object of our investigations are represented by the general formula **I**:

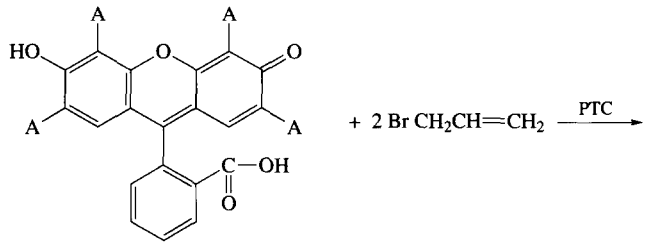


I

where: A = −H or A = −Br
1 2

Synthesis of dyes

The route employed in the synthesis of dyes **I(1,2)** was as follows (Scheme 1).



Scheme 1

Fluorescein, and Eosin, were synthesized as previously described [11], and were reacted with allyl bromide under PTC conditions to give dyes **I(1,2)**.

Selection of the favourable phase transfer catalysis conditions
The correct choice of the two-phase system was very important for the results of the synthesis. This choice was governed by the solubility of Fluorescein and Eosin in different organic solvents. Their solubility in both conventional water-immiscible and water-miscible organic solvents used for a liquid/liquid two-phase system and solid/liquid one respectively, is satisfactory. This necessitated the reactions to be examined in both types of PTC systems.

Initially, the reactions were carried out in a benzene/aq. sodium hydroxide two-phase system due to adequate solubility of both Fluorescein and Eosin in benzene. The influence of different factors on the progress of the reactions, namely the type of the phase transfer catalyst, the phase concentration, the mole ratio of the reactants, and the reaction temperature was examined.

It was experimentally established that the best results of the synthesis were obtained with the use of tetrabutylammonium bromide (TBAB) as phase transfer catalyst, when the mole ratio Fluorescein/allyl bromide was 1/2 at 50°C. By the use of 30% aq. sodium hydroxide, the pure allyl ether-ester of the Fluorescein **1** was obtained after 2 h in 60% yield from the organic phase after washing the latter with water and drying over anhydrous sodium sulfate before evaporating the organic solvent in vacuum. Better results were obtained when 12.5% aq. sodium hydroxide was used as the aquerous phase. Under these conditions the yield of dye **1** increased to 74%. This could be explained by the improved exchange of the ions in a diluted water phase and probably the enhanced transfer of the generated ion pairs in the organic phase.

Under the same circumstances (12.5% aq. sodium hydroxide) the allyl ether-ester of Eosin **2** was obtained in a yield of 55%.

With a view to improving the synthesis results, the reactions were examined also in a solid/liquid two-phase system.

Because of the good solubility of both Fluorescein and Eosin in acetonitrile, the latter was used as an organic phase. The choice of a solid phase depended on the efficiency of the employed phase transfer catalyst. Our experiments on investigating different catalysts showed that the efficiency of ammonium salts such as TBAB under these conditions was too low. The best results were obtained with the use of 18-crown-6 as a phase transfer catalyst, when finely ground potassium hydroxide was used as a solid phase. It is known that the ion diameter of K^+ is better suited to the effective cavity volume of the 18-membered crown ether ring and is therefore bound more strongly than Na^+[12].

By variation of the reaction conditions, it was established that the target products **I(1,2)** were obtained in highest yields in boiling acetonitrile (200 ml per 0.01 mol of Fluorescein or Eosin, respectively) and mole ratio KOH/allyl bromide/Fluorescein(Eosin) = 2.5/2/1 with participation of 10 mol% of 18-crown-6 with regard to Fluorescein (Eosin). Thus, the pure allyl ether-esters of Fluorescein **1** and Eosin **2** (TLC controlled) were obtained in yields of 80 and 65%, respectively, for 2 h, after filtration and evaporation of acetonitrile in vacuum.

The experiments conducted in both liquid/liquid and solid/liquid two-phase systems showed that the use of excess allyl bromide, as well as the prolongation of the reaction time, did not lead to a perceptible rise in the yields of the desired products **I(1,2)**. Furthermore, lower reactivity of the Eosin was observed, which could be explained by steric factors.

In conclusion it should be noted that higher yields of dyes **I(1,2)** were obtained in a solid/liquid two-phase system. This is most probably due to the better solubility of the ionic pair formed between the cation complex of the crown ether and the anion of Fluorescein, or Eosin in acetonitrile, than in benzene.

The syntheses were monitored by TLC on silica gel and the dyes **I(1,2)** were characterized and identified by melting points, R_f values, UV/Vis and ^{1}H-NMR spectra.

The yields of dyes **I(1,2)** obtained in a solid/liquid two-phase system and their characteristics are shown in Table 1.

As can be seen from Table 1, comparison of the yield of the allyl ether-ester of Fluorescein **1** to the previously cited one shows the advantages of the new method. The yield of the dye **1** is approximately two times higher, while the reaction time is significantly reduced.

TABLE 1
Characteristics and Yields of Dyes **I(1,2)**

Dye I no.	*Melting point (°C)*	R_f	$\lambda^{abs}{}_{max}(nm)$	*Yield (%)*
1	153–5[a]	0.65	458	80[b]
2	198–200	0.75	542	65

[a]The melting point of dye **1** was the same as that previously cited [11].
[b]Dye **1** was obtained in a yield two times higher than that reported in Ref. 11.

Polymerization of the dyes

Copolymerization of dyes **I(1,2)** with vinyl monomers such as methyl methacrylate and styrene in the presence of the radical initiator dibenzoylperoxide (DBP) was investigated. Experiments on the bulk polymerization were carried out in the presence of three different concentrations (0.025 wt%, 0.05 wt% and 0.1 wt%) of the respective dye **I(1,2)** with regard to the vinyl monomer. Under all experiments, after 8 h, coloured solid transparent polymers with an intense fluorescence were obtained. It was found that even the lowest concentration of the dyes (0.025 wt%) in the initial monomer mixture was enough to obtain brightly coloured polymers with clearly observable fluorescence.

The absorption spectra of the coloured polymers were recorded (Table 1) after repeatedly (five- to six-fold) reprecipitation from chloroform by ethanol in order to remove the unreacted dye. The observed absorptions (λ_{max}) were the same as those of the corresponding chromophores, without any noticeable batho- or hypsochromic shift. Such an effect was not observed either in the absorption spectra of dyes **I(1,2)** when they were heated only in the presence of DBP under the polymerization conditions. This is an indication that no changes occurred in the basic chromophores, neither during the process, nor as a result of their inclusion in the polymer chain. On this basis, we decided to use the method of the standard curve for spectrophotometric determination of the content of a chemically bound dye in the polymer chain. It was estimated that the percentage of dye **1** in the reprecipitated polymers was 65–75%, while that of dye **2** was lower (45–50%). Most probably, the lower percentage of dye **2** is due to its poor reactivity in the copolymerization process and/or to the fact that a part of the dye reacts with the formation of oligomers that are removed during the precipitation. The reason for such behaviour could be both the largest steric volume of the bromine substituents and their electron acceptable properties, both of which influence the reactivity of the polymerizing groups. More detailed investigations dealing with the kinetics of the dyes binding to the polymer chain, as well as the influence of the dyes on the properties of the polymer, namely the molecular mass, the polydispersity and photostability, will be a subject of future reports.

EXPERIMENTAL

Melting points are uncorrected. UV/Vis spectra were recorded on a Hewlett Packard 8452 A spectrophotometer in DMF. ^{1}H NMR spectra were recorded on a JEOL JNM-PS-100 spectrometer. TLC analyses were performed on silica gel plates (Fluka F_{60}254), using benzene/methanol (9/1) as eluant.

18-Crown-6 and TBAB were pure (Fluka, >98%). Benzene and acetonitrile were p.a. (Fluka). Methanol and DMF were of chromatographic spectrophotometric grade (Fluka). DBP was pure (C. Erba, 99.9%). Styrene (Nephtochim–BG) and methyl methacrylate (Agrochim–BG) were redistilled under vacuum in a nitrogen atmosphere and dried over sodium sulfate.

Synthesis

Fluorescein and Eosin were prepared as previously described [11].

The target dyes **I(1,2)** were synthesized by the following general procedure:

Allyl bromide (0.02 mol) was added dropwise to a mixture of 0.01 mol of Fluorescein (or Eosin) in 200 ml acetonitrile, 0.001 mol of 18-crown-6 and 0.025 mol of finely ground potassium hydroxide at room temperature. The resulting mixture was stirred under reflux for 2 h. The organic phase was filtered and the organic solvent evaporated in vacuum to give the target dye.

Dye 1

Bright yellow-orange crystals, R_f=0.65, m.p. 153–155°C.

^{1}H NMR (Acetone-D6, 100 MHz) ppm: 4.50 (dt, 2H, –OCH_2 – ether); 4.77 (dt, 2H, –OCH_2 – ester); 5.06 and 5.12 (dd, 2H, =CH_2 – ether); 5.31 and 5.47 (dd, 2H, =CH_2 – ester); 5.66 (m, 1H, =CH – ether); 6.11 (m, 1H, =CH – ester); 6.17 (d, 1H, H-8); 6.35 (dd, 1H, H-6); 6.85 (d, 1H, H-5); 6.88 (dd, 1H, H-3); 6.92 (d, 1H, H-4); 7.10 (d, 1H, H-1); 7.50 and 8.27 (dd, 2H, 9-phenyl ring); 7.83 (dt, 2H, 9-phenyl ring).

Dye 2

Bright redish-orange crystals, R_f=0.75, m.p. 198–200°C.

^{1}H NMR (Acetone-D6, 100 MHz) ppm: 4.50 (dt, 2H, –OCH_2 – ether); 4.79 (dt,2H, –OCH_2 – ester); 5.06 and 5.13 (dd, 2H, =CH_2 –ether); 5.30 and 5.45 (dd, 2H, =CH_2 – ester); 5.67 (m, 1H, =CH – ether); 6.10 (m, 1H, =CH – ester); 7.10 (s, 2H, H-4 and H-5); 7.51 and 8.23 (dd, 2H, 9-phenyl ring); 7.81 (dt, 2H, 9-phenyl ring).

Polymerization

Styrene (10 g), 0.01 g of dye 1 or 2 and 0.01 g of DBP were mixed in an ampoule flushed with dry and pure nitrogen, then sealed and heated at 80°C

in a thermostat for 8 h. The coloured transparent polymer thus obtained was repeatedly precipitated from chloroform by ethanol and dried to constant weight at 30°C in vacuum.

The methyl methacrylate polymerization in the presence of dyes **I(1,2)** was carried out in the same way at 60°C.

REFERENCES

1. Zollinger, H., *Color Chemistry*, VCH, D-6940 Weinheim, 1987, pp. 279, 311, 326.
2. Barashkov, N. and Gunder, O., *Fluorescent Polymers*, Khimia, Moskwa,1987, p. 23 (in Russian).
3. Konstantinova, T., Draganov, A. and Konstantinov, Hr., *Die. Angew. Makromol. Chemie*, 1975, **43**, 29.
4. Konstantinova, T., *Dyes and Pigments*, 1998, **10**, 63.
5. Konstantinova, T., Meallier, P. and Grabchev, I., *Dyes and Pigments*, 1993, **22**, 191.
6. Hurd, Ch. and Schmerling, L., *J. Am. Chem. Soc.*, 1937, **59**, 112.
7. Dehmlow, E. V. and Dehmlow, E. S., *Phase Transfer Catalysis*, VCH Verlagsgesellschaft, Weinheim, 1983, p. 13.
8. Bojinov, V. and Konstantinova, T., *Dyes and Pigments*, 1996, **32**, 151.
9. Konstantinova, T. and Bojinov, V., In *Chemical Industry and Environment*, Vol. 3, N. Pellicer and M. Rigola. Arts Grafiques, SC, Girona, 1993, p. 293.
10. Bojinov, V. and Batchvarova, R., *Biotechnol. and Biothecnol. Eq.*, 1996, **10**, 27.
11. Wolfson, N. C. (ed.), *Preparativnaya Organicheskaya Khimia*, Chapter XXXIX Khimia, Moskwa, 1964, p. 793 (in Russian).
12. Veber, E., In *Phase Transfer Catalysis—Properties and Application; Crown Compounds—Properties and Practice*. MERCK–Schuchardt, 1987, p. 44.