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A New Method for the Synthesis of 3-Alkoxybenzanthrones as Luminophore Dyes for Polymers

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ABSTRACT

A new method for the synthesis of 3-alkoxybenzanthrones is reported. The appropriate phase transfer catalysis conditions (a type of two-phase system, solvent, solid phase, catalyst) were selected. Three 3-alkoxybenzanthrones were synthesized in high yields and purity under these conditions. Their absorption and fluorescent spectra were determined and the energy of the first excited state calculated. The utility of the dyes for the mass-colouration of polystyrene was also demonstrated. Copyright © 1996 Elsevier Science Ltd

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INTRODUCTION

Benzanthrone and its derivatives have valuable properties and some of them are used for the mass-colouration of polymers. Among them, 3-alkoxybenzanthrones are well-known as luminophores, because of their intense yellow–orange fluorescence. They exhibit bright fluorescence both in solution and in the crystalline state, and have high light-fastness in various formulations. 3-Alkoxybenzanthrones are also used for daylight fluorescing pigments and for the dyeing of polymers.[1]

3-Alkoxybenzanthrones have been obtained by reaction between 3-halogenobenzanthrones and the corresponding alcohol in the presence of solid sodium or potassium hydroxide.[1,2] This reaction is normally carried out at 150°C under 10–12 atm for 16 h. Disadvantages of the method are not only the reaction conditions, namely high temperatures, pressure, special equipment and long term of the process, but the fact that the desired products are

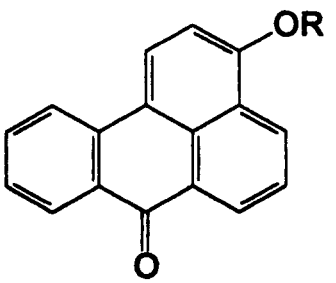
obtained in low purity, containing impurities which affect their fluorescence. For this reason, various methods for the purification of 3-alkoxybenzanthrones, especially the 3-methoxy derivative, have been developed.[3] The target product thus obtained had the desired purity (m.p. 174°C), but the yield was only 46% relative to the starting material.

For the last 10–15 years the method of phase transfer catalysis (PTC) has been developed and has attained importance in organic synthesis in view of its simplicity, easy implementation and both economical and ecological advantages.[4] In previous papers we have reported the successful application of PTC in the synthesis of triazine,[5] aromatic sulphonyl- and acylazide,[6] and sulphonimide[7] derivatives.

No information has been reported on the synthesis of benzanthrone derivatives under such conditions and in this present study, we investigate the possibility of obtaining 3-alkoxybenzanthrones under favourable reaction conditions, and in high yield and purity.

RESULTS AND DISCUSSION

The 3-alkoxybenzanthrone derivatives whose synthesis was the object of our investigations are represented by the general formula **I**:



I

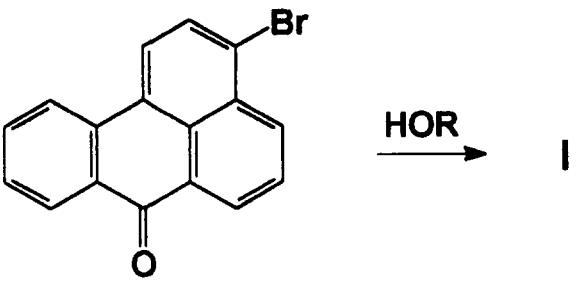
$R = -CH_3$ **1** $R = -CH_2CH_3$ **2**

$R = -CH_2CH = CH_2$ **3**

Synthesis of dyes

The route employed in the synthesis of dyes (**1–3**) was as follows (Scheme 1).

3-Bromobenzanthrone (**B**), synthesized as previously described,[8] was reacted with the corresponding alcohol (**ROH**) under PTC conditions. All reactions were carried out in a solid/liquid two-phase system at 50°C.



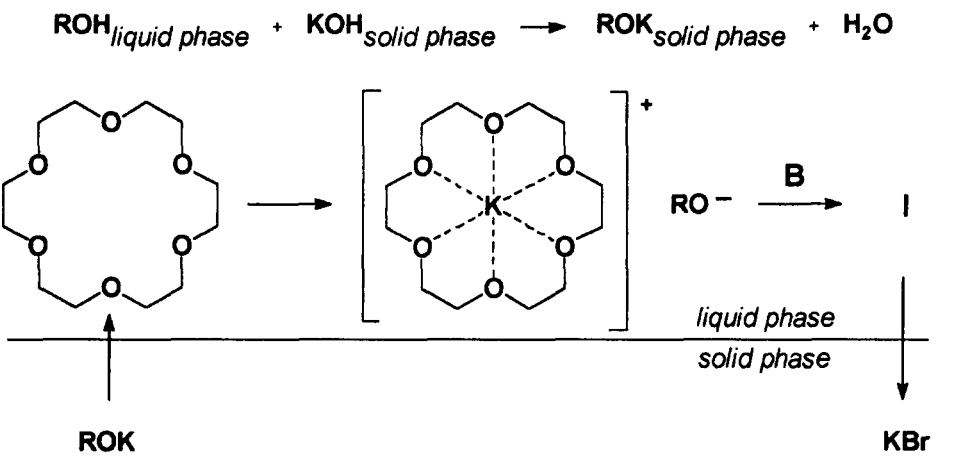
Scheme 1.

Selection of the two-phase system type

The optimal choice of the two-phase system type was very important for the results of the synthesis. This choice was governed by the solubility of the 3-bromobenzanthrone in different organic solvents. Its solubility in conventional water-immiscible organic solvents used for a liquid/liquid two-phase system, such as benzene, dichloromethane and 1,2-dichloromethane, is not sufficient. 3-Bromobenzanthrone has good solubility only in DMF,[9] which is, however, a water-miscible organic solvent. This necessitated the reaction to be carried out in a solid/liquid two-phase system.

Both finely ground potassium and sodium hydroxides were examined as solid phases. 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 benzyltriethylammonium chloride, tetrabutylammonium bromide, tetrabutylammonium hydrosulphate, hexadecyltrimethylammonium bromide and Aliquat 336 under these conditions was too low. This is because DMF has a good solvating activity to cations, which leads to blocking of the ammonium cation of the catalyst. On the other hand, DMF has not so strong an ability to solvate neutral compounds such as 18-crown-6, but solvates very well the cation complex formed between the crown compound and the metallic cation of the solid hydroxide.[10] This resulted in increased nucleophilic activity of the **ROH**. We therefore decided to use 18-crown-6 and finely ground potassium hydroxide as a solid phase, because 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^+.[11] It can be shown that 3-bromobenzanthrone reacted with the naked alkoxy anion in a homogeneous medium (Scheme 2).

This presented the opportunity to carry out the reaction at moderate temperature under normal pressure, where the mole ratio **KOH/ROH**/3-bromobenzanthrone was 4/2/1 with the participation of 5 mol% of



Scheme 2.

18-crown-6 to **ROH**. After 4 h, the reagents were converted almost quantitatively into crude 3-alkoxybenzanthrones (**1–3**). The pure products **I** (TLC control) were obtained after recrystallization from benzene.

The results obtained are shown in Table 1, where they are compared to those obtained by traditional methods.

As seen from Table 1, a comparison of the results reported therein with those previously cited shows the advantages of the new method. The yields of pure products **I** are more than 40% higher and both the reaction temperature and reaction time are significantly reduced under normal pressure.

Spectrophotometric investigations

The absorption spectra of the dyes **I** (**1–3**) in methanol were recorded and the data are presented in Table 2. The dyes had a very strong yellow–orange fluorescence.

Their fluorescence λ_{max} and the energy of the first excited state were calculated.[12]

Polymerization of styrene

Our investigations on the polymerization of styrene in the presence of dyes **1** and **3** have been previously reported.[13] It was also of interest to evaluate whether dye **2** was suitable for the mass-colouration of polystyrene during the synthesis.

TABLE 1
Reaction Conditions, Melting Points and Yields of 3-Alkoxybenzanthrones **I**

Dye **I** no.	Reaction time (h)		Reaction temperature (°C)		Melting point[b] (°C)		Yield[d] (%)	
	Ref. data	New data	Ref. data	New data	Ref. data	New data	Ref. data	New data
1	16	4	150[a]	50	174	177–8	46	88
2	16	4	150[a]	50	172[c]	135–6	—	80
3	16	4	150	50	151–3	151–3	48	85

[a] The reactions were carried out under pressure.[1,2]
[b] Melting points of 3-alkoxybenzanthrones **I** after recrystallization.[3,4]
[c] Melting point of crude 3-ethoxybenzanthrone **2**.[2]
[d] Yields of 3-alkoxybenzanthrones **I** after recrystallization.[3,4]

Experiments on the bulk polymerization of styrene in the presence of 0.1 wt% of dye **2** and 0.1 wt% of dibenzoylperoxide (DBP) at 80°C were carried out. A transparent brightly coloured polymer with an intense orange fluorescence was obtained. No effect of the dye on the polymerization process (yield of the polymer obtained) and neither batho- nor hypsochromic shifts in the colour were observed.

On the basis of these results we conclude that dye **2** could be suitable for the mass-colouration of polystyrene.

EXPERIMENTAL

All melting points are uncorrected. UV/vis spectra were recorded on a Hewlett Packard 8452 A spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL JNM-PS-100 spectrometer. TLC analyses were made on silica gel plates (Fluka F_{60}254), using the solvent system hexane/benzene/chloroform 3/2/1 as eluant. 18-Crown-6 was pure (Fluka, >98%). Styrene (Nephtochim – BG) was redistilled under vacuum in nitrogen atmosphere and dried with

TABLE 2
Absorption, Fluorescence and Energy Data of 3-Alkoxybenzanthrones **I**

Dye **I** no.	λ^{abs}_{max} (nm)	λ^{fl}_{max} (nm)	E_{si} (μJ/mol)
1	428	535	225.6
2	434	542	230.4
3	432	540	240

Na_2SO_4. Nitrogen was pure (99.99%) and dry. Methanol was of spectroscopic grade (Fluka).

Synthesis

3-Bromobenzanthrone was prepared as previously described.[4]

The target products **I** (**1–3**) were synthesized by the following general procedure. A solution of 3-bromobenzanthrone (0.01 mol) in 40 ml DMF, 0.02 mol of the corresponding alcohol **ROH**, 0.001 mol of 18-crown-6 and 0.04 mol of finely ground potassium hydroxide were mixed and the resulting mixture was stirred at 50°C. After 4 h, the reaction mixture was cooled to room temperature and then poured into 100 ml of acidified water (pH 2) before filtration of the desired product **I**. The latter was dried to give pure 3-alkoxybenzanthrone **I** (**1–3**) after recrystallization from benzene.

3-Methoxybenzanthrone **1**

Bright yellow–orange crystals, $R = 0.16$, m.p. 177–178°C.

^{1}H NMR ($CDCl_3$, 100 MHz) ppm: 3.94 (s, 3H, OCH_3); 6.74 (d, 1H, J_o 8 Hz, 2-H); 7.18÷8.74 (m, 8H, arom.).

3-Ethoxybenzanthrone **2**

Bright yellow–orange crystals, $R = 0.17$, m.p. 135–136°C.

^{1}H NMR ($CDCl_3$, 100 MHz) ppm: 1.38 (t, 3H, CH_3); 3.90 (q, 2H, OCH_2); 6.42 (d, 1H, J_o 8 Hz, 2-H); 7.18÷8.60 (m, 8H, arom.).

3-Allyloxybenzanthrone **3**

Bright yellow–orange crystals, $R = 0.15$, m.p. 151–153°C.

^{1}H NMR ($CDCl_3$, 100 MHz) ppm: 4.50 (d, 2H, OCH_2); 5.16÷5.52 (m, 2H, CH_2); 5.80÷6.36 (m, 1H, CH); 6.48 (d, 1H, J_o 8 Hz, 2-H); 7.16÷8.62 (m, 8H, arom.).

Polymerization

Styrene (10 g), 0.01 g of dye **2** and 0.01 g of DBP were mixed in an ampoule flushed with dry and pure N_2, then sealed and heated at 80°C in a thermostat for 8 h. The coloured transparent polymer thus obtained was precipitated once from toluene by methanol and dried in vacuum at 30°C.

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