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The dyeing of cotton with hetero bi-functional reactive dyes containing both a monochlorotriazinyl and a chloroacetylamino reactive group

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Abstract

Water-soluble reactive dyes incorporating both a chloroacetylamino group and a monochlorotriazinyl group have been prepared. Under the alkaline application conditions employed, little or no additional fixation, via the desired nucleophilic displacement of chloride from the chloroacetylamino group, by cellulosate, was observed. The principal reaction was amide hydrolysis. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Cotton; Reactive dyes; Exhaust dyeing; Monochlorotriazine; Chloroacetylamino

1. Introduction

Reactive dyes react chemically with certain fibres to form a covalent bond. The first reactive dyes for cellulose, Procion M dyes, were introduced in 1956 by ICI [1]. These dyes contain a highly reactive dichlorotriazinyl group, which reacts with cellulose in the presence of alkali at room temperature. In subsequent years, ICI and Ciba marketed dyes containing the lower reactivity (hot dyeing) monochlorotriazinyl (MCT) reactive group, whilst Hoechst marketed Remazol (warm-dyeing) dyes bearing the sulphatoethylsulphonyl 'vinyl sulphonyl' (VS) reactive group. Both of these reactive groups are still used widely today, approximately 40 years after their first exploitation in reactive dyes for cotton. During the alkali fixation stage, competitive hydrolysis of the reactive dye also occurs. This unfixed, hydrolysed dye must be removed via a thorough wash-off process in order that the dyed cotton exhibits high wet fastness properties. In order to maximise the amount of dye fixation in exhaust dyeing, particularly at long liquor ratios, ICI introduced the Procion H-E range of dyes in the early 1970s. These dyes, which contain two monochlorotriazinyl (bis MCT) reactive groups, are generally of the type shown in Structure 1, where X represents an arylene linking group.

The presence of the two monochlorotriazinyl reactive groups often results in high substantivity dyes which deliver increased fixation efficiency, resulting in improved economy and less coloured effluent. Research, by dyestuff companies over the

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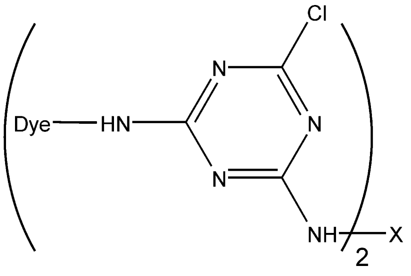
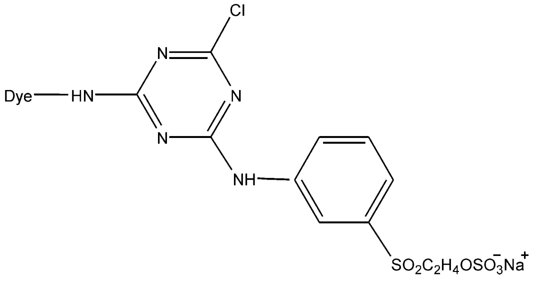


Structure 1.

last 30 years, aimed at improving the fixation yield of reactive dyes on cotton, has focused both on the use of alternative reactive groups (such as monofluorotriazines and difluorochloropyrimidines) and on the use of combinations of different reactive groups [2]. In the latter category, Sumitomo introduced the Sumifix Supra range of hetero bifunctional reactive dyes in the early 1980s. These dyes contain both the monochlorotriazinyl and vinyl sulphonyl reactive groups, the latter being attached to the monochlorotriazine entity as a 'second leg' substituent (see Structure 2).

The combination of both warm and hot dyeing (60 °C, vinyl sulphone and 80 °C, monochlorotriazine, respectively) reactive groups within the same molecule allows higher fixation to be obtained with very good 'temperature range' properties, i.e. a similar colour yield is obtained when dyeing at temperatures between 60 and 80 °C.

Following the commercially successful introduction of Sumifix Supra dyes, it has become increasingly common for dyestuff manufacturers to 'mix and match' different warm dyeing reactive groups, e.g. the use of monofluorotriazinyl and alkylvinyl sulphonyl reactive groups in Cibacron C and Levafix CA dyes.



Structure 2.

However, very much less attention seems to have been paid to the combination of different reactive groups which will enhance fixation efficiency under hot dyeing (80 °C) conditions. The chloroacetyl(amino) group appeared to be one such potential hot dyeing reactive group for cellulose, which could be used alongside a conventional monochlorotriazinyl group. It had first been exploited as a reactive group for wool by Bayer when it was used in Supramine Orange R [3] in 1937. A patent [4] indicated that the high wet fastness of this and related dyes could be attributed to the formation of a covalent bond with the wool. Subsequently, several other patents claimed dyes for wool which incorporated a chloroacetylamino group [5–7]. The chloroacetylamino group has also been claimed as reactive group as is for cellulose [8,9] in the 1950s and 1960s but has never been exploited in a commercial dyestuff. Since the chloroacetylamino group might be expected to exhibit a similar (low) level of reactivity to that of the monochlorotriazinyl group, and its use in hetero bi-functional dyes appeared to be novel, dyes incorporating both groups have been synthesised and their technical properties assessed. The chloroacetylamino group possesses some other potential attractions. It is of low Mv (92.5) and thus does not 'dilute' the chromophoric strength of the dye too drastically. It can also be readily incorporated, synthetically, into dye molecules.

2. Experimental

2.1. Materials

Proton NMR spectra were taken with a Bruker DPX 300 instrument equipped with a proton/carbon, *z*-gradient, dual probe with an automatic sample changer. The solvent used was deuterium oxide >99.9 at.% D, with tetramethyl silane being used as an internal standard.

Mass spectra were obtained by using two different techniques viz. FAB (fast atom bombardment) and MALDI (matrix assisted laser desorption ionisation).

Elemental analyses for carbon, hydrogen, nitrogen and sulphur were carried out on a Carlo Erba 1108 elemental analyser. Chlorine analysis was by automatic argenometric titration, following oxygen flask decomposition.

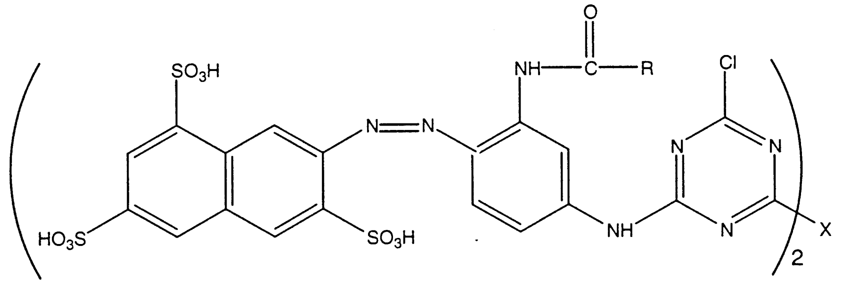
Thin layer chromatography was performed on aluminium plates coated with silica gel, 60 F_{254} (Merck). The eluent system used was iso-butanol: *n*-propanol:ethyl acetate:water (2:4:1:3), unless otherwise stated. The developed plates were visualised under both short and long wavelength ultraviolet light.

Procion Yellow H-E4R (C.I. Reactive Yellow 84, Structure 3), Procion Yellow MX-3R (C.I. Reactive Orange 86) and Procion Yellow P-3R (C.I. Reactive Orange 12, Structure 4) were available commercially. Samples of 3-aminoacetanilide, 2-aminonaphthalene-3,6,8-trisulphonic acid and benzidine-2,2′-disulphonic acid were provided by Zeneca/BASF/DyStar.

The strength of any given dyestuff sample was estimated from the ratio of its actual relative molecular mass (Mv) to its effective molecular mass (estimated by titanous chloride titration), each water-soluble dyestuff usually being contaminated with varying amounts of non-coloured (mainly inorganic) material [10].

2.2. Synthesis of N-(3-aminophenyl)chloroacetamide

Chloroacetic anhydride (2.25 g, 0.01 mol) was added, in small portions, to a stirred solution of meta phenylenediamine (1.08 g, 0.01 mol) in water (20 ml) and hydrochloric acid (36%, 30 ml) at 0–3 °C and pH $<$ 1. Sodium carbonate solution (10% w/v) was added at such a rate as to maintain the pH at $\sim$1. After completion of the addition, the reaction mixture was stirred for 1 h. The product, *N*-(3-aminophenyl)chloroacetamide, was filtered off and dried under vacuum overnight at room temperature. Weight 1.84 g. Mass spectrum $(M+H)^+$ 185, Mv ($C_8H_9N_2OCl$) 184. Micro analysis found: C 39.9%; H 4.95%; N 12.05%; Cl 29.3% ($C_8H_9N_2OCl \cdot HCl \cdot H_2O$ requires C 40.2%, H 5.0%, N 11.7%, Cl 29.7%). ^{1}H-NMR; δ_H (300 MHz, D_2O), 7.8 ppm (1H, singlet, aromatic C2), 7.6 ppm (1H, doublet, aromatic C6), 7.6 ppm (1H, triplet, aromatic C5), 7.3 ppm (1H, doublet, aromatic C4), 4.4 ppm (2H, singlet, $-CH_2-Cl$).



where

C.I. Reactive Yellow 84, R = NH_2, X = (Benzidine-2,2′-disulphonic acid).

Dye 1, R = CH_3, X = (Benzidine-2,2′-disulphonic acid).

Dye 2, R = CH_2Cl, X = (Benzidine-2,2′-disulphonic acid).

Structure 3.

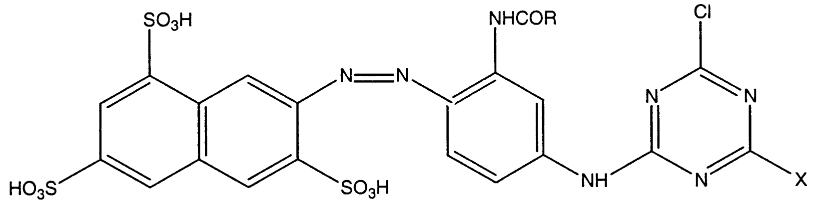
*2.3. Synthesis of dye **1** (see Structure 3)*

2-Aminonaphthalene-3,6,8-trisulphonic acid (55.9 g, strength 68.5%, 0.1 mol) was dissolved in water by adding a few drops of aqueous sodium carbonate solution (10% w/v). Sodium nitrite (6.9 g, 0.1 mol) was dissolved in the minimum amount of water and added to the cold 2-aminonaphthalene-3,6,8-trisulphonic acid solution. The resulting solution was added dropwise, with stirring, to 60 ml of hydrochloric acid (36%) at less than 5 °C. An immediate yellow precipitate (diazonium salt) resulted. The reaction mixture was stirred for an hour at 0 to 5 °C and $pH < 2$, before excess nitrous acid was destroyed by adding sulphamic acid (confirmed by the blue colour on spotting a drop of the reaction mixture onto starch iodide paper). 3-Aminoacetanilide (27.7 g, strength 54%, 0.1 mol), dissolved in dilute hydrochloric acid, was added slowly to the above diazonium salt suspension, with continuous stirring, at 4–6 °C. The pH was raised to 6–6.5 with aqueous sodium carbonate solution (10% w/v) and maintained at this value, with stirring, until completion of the coupling. The reaction mixture was filtered to remove any insoluble impurity before the product (Dyebase **1**) was salted out at pH 2.5–3.0 by slow addition of sodium chloride (approx. 110 g, to give 10% w/v), collected by filtration and dried under vacuum. Yield 42 g, 52%, strength 75%.

A sample of Dyebase **1** (8.10 g, 75% strength. i.e. 0.01 mol) was dissolved in water, with stirring, and added to a freshly prepared suspension of cyanuric chloride (1.85 g, 0.01 mol) in aqueous acetone. The pH of the reaction mixture was kept at 6–6.5, using sodium carbonate (10% w/v) solution, and below 5 °C. After the pH had stabilised at 6–6.5, the temperature was raised to 35 °C and the solution filtered to remove any insoluble impurity. To 90% of this solution of the dichlorotriazinyl dyestuff (i.e. 270 ml, 0.0089 mol), benzidine-2,2′-disulphonic acid (1.77 g, 85% strength, 0.0044 mol) dissolved in 30 ml water, was added dropwise, the temperature being maintained at 35–40 °C and at pH 6.5. After completion of the reaction, a small amount of insoluble material was filtered off and the final product salted out with sodium chloride (27.5 g). The material was dried overnight under vacuum at room temperature. Yield 12 g, 57%, strength 78%, $(M-SO_3)^-$ 1575, Mv; $(C_{54}H_{40}N_{16}O_{26}S_8Cl_2)$ 1654.

*2.4. Synthesis of dye **2** (see Structure 3)*

A similar procedure was adopted as for the synthesis of dye **1**. 2-Aminonaphthalene-3,6,8-tri-



where

C.I. Reactive Orange 86 $R = NH_2$ $X = Cl$

C.I. Reactive Orange 12 $R = NH_2$ $X = NH_2$

Dye 3, $R = CH_2Cl$ $X = NH_2$

Structure 4.

sulphonic acid (5.59 g, strength 68.5%, 0.01 mol) was diazotised and coupled with *N*-(3-aminophenyl)chloroacetamide (2.39 g, strength 77%, 0.01 mol) to yield Dyebase **2** [yield 8.2 g, 65%, strength 46%]. After the completion of the condensation of Dyebase **2** with cyanuric chloride (1.85 g, 0.01 mol), benzidine-2,2′-disulphonic acid (2.02 g, strength 85%, 0.005 mol) was added. On completion of this amination reaction, sodium chloride (42 g) was used to salt out the product. The material was dried overnight, under vacuum, at room temperature. Yield 15.0 g, 48%, strength 55%, $(M)^+$ 1722, Mv ($C_{54}H_{38}N_{16}O_{26}S_8Cl_4$) 1722.

*2.5. Synthesis of dye **3** (see Structure 4)*

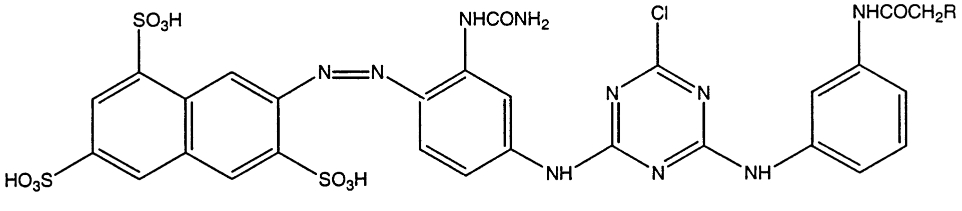
Dyebase **2** (see Section 2.3, 6.28 g, strength 46%, 0.005 mol), dissolved in water (50 ml), was added with stirring to a freshly prepared aqueous acetone suspension of cyanuric chloride (0.92 g, 0.005 mol) and the reaction mixture kept at pH 6–6.5 by using sodium carbonate (10% w/v) solution. After the condensation was complete, the temperature of the reaction mixture was raised to 35 °C and a small quantity of insoluble material was filtered off. Aqueous ammonia (0.08 g, 0.005 mol, specific gravity 0.880) was added, the pH was adjusted to 7–8 by the addition of dilute hydrochloric acid and the solution was stirred at 35–40 °C. After completion of the reaction, the reaction mixture was filtered and sodium chloride (9 g, 18% w/v) added very slowly to the stirred filtrate. The precipitated dye was collected by filtration and dried under vacuum at room temperature. Yield 3.0 g, 63%, strength 74%.

*2.6. Synthesis of dye **4** (see Structure 5)*

A commercial sample of C.I. Reactive Orange 86 (Structure 4, $R = NH_2$, $X = Cl$; 17.92 g, strength 52%) was dissolved in cold water (100 ml). A solution of *N*-(3-aminophenyl)chloroacetamide (2.39 g, 77%, 0.01 mol) in water (50 ml) at 35 °C and pH 6.5 was added with stirring. The pH of the reaction mixture was maintained at 6.5 by using sodium carbonate solution (10% w/v). The reaction was complete in 1 h, as judged by TLC, and the resultant solution (200 ml) was filtered to remove traces of insoluble impurities. The product was precipitated with ethanol, collected by filtration and dried under vacuum at room temperature. Yield 9.4 g, 48%, strength 43%, $(M+H)^+$ 841; Mv ($C_{28}H_{22}N_{10}O_{11}S_3Cl_2$) 840.

*2.7. Synthesis of dye **5** (see Structure 5)*

The synthesis of dye **5** was carried out using a similar procedure as adopted in the synthesis of dye **4**, but using meta aminoacetanilide (2.77 g, strength 54%, 0.01 mol) as the ‘second leg’ in place of *N*-(3-aminophenyl)chloroacetamide. Yield 6.4 g, 44%, strength 55%, ($M+H^+$) 807; Mv ($C_{28}H_{23}N_{10}O_{11}S_3Cl$) 806.



where

Dye 4, R = Cl

Dye 5, R = H

Structure 5.

2.8. Build-up properties of dyes by exhaust dyeing

Each dye was applied to bleached unmercerised woven cotton at five depths, viz. 1, 2, 4, 6 and 9% dye omf at 80 °C and liquor ratio 10:1, using the quantities of Glaubers salt (exhaustion for 30 min) and soda ash (fixation for 60 min) shown in Table 1. After dyeing, the fabric was rinsed well with cold and hot water before soaping at the boil for 10 min. Finally the fabric was rinsed with cold water and air dried at 50 °C.

3. Results

*3.1. Build-up properties of Procion Yellow H-E4R (C.I. Reactive Yellow 84), dyes **1** and **2***

3.1.1. Using conventional Na_2CO_3 quantities [see Table 1(a)]

The visual colour yields of the dyed fabrics were expressed as *K*/*S* values [11]. In order to facilitate the comparison of the build-up properties of the three dyes, *K*/*S* values versus dye concentrations in millimoles per 100 gram of fabric were plotted, as depicted in Fig. 1.

3.1.2. Using reduced Na_2CO_3 quantities [see Table 1(b) and (c)]

The build up curves are shown in Fig. 2(a) and (b).

*3.2. Comparison of the build-up properties of Procion Yellow P-3R (C.I. Reactive Orange 12) versus dye **3** (using conventional quantities of Na_2CO_3)*

These are shown in Fig. 3.

Table 1
Quantities of salt and alkali applied

Depth of shade (% dye omf)	Glaubers salt (Na_2SO_4) (g l^{-1})	Soda ash (Na_2CO_3) (g l^{-1})		
		(a)	(b)	(c)
1	45	15	5	2.5
2	60	20	6.66	3.33
4	70	20	6.66	3.33
6	90	20	6.66	3.33
9	90	20	6.66	3.33

3.3. Comparison of the build-up properties of yellow dyes bearing meta aminoacetanilide and meta aminochloroacetanilide as 'second legs' (using conventional Na_2CO_3 quantities)

These are shown in Fig. 4.

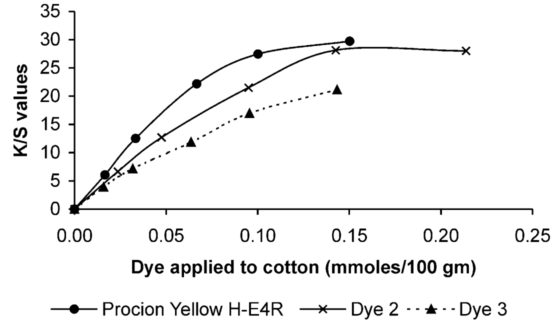


Fig. 1. Colour yield (*K*/*S*) versus dye applied [Procion Yellow H-E4R (C.I. Reactive Yellow 84), dyes **1** and **2**)] using conventional quantities of Na_2CO_3 (15–20 g/l) for fixation.

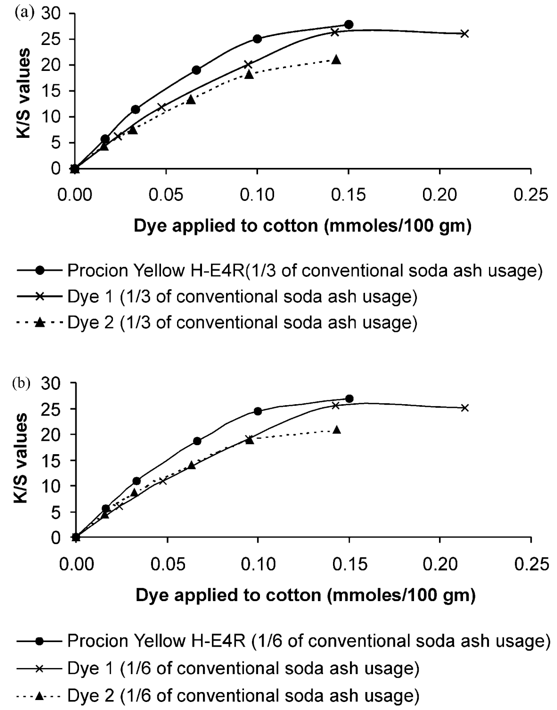


Fig. 2. (a) Colour yield (*K*/*S*) versus dye applied [Procion Yellow H-E4R (C.I. Reactive Yellow 84), dyes **1** and **2**] using reduced quantities of Na_2CO_3 for fixation. (b) Colour yield (*K*/*S*) versus dye applied (Procion Yellow H-E4R, dyes **1** and **2**) using reduced quantities of Na_2CO_3 for fixation.

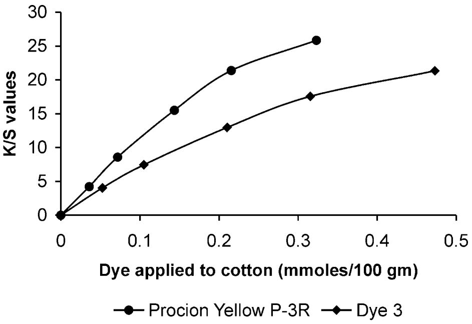


Fig. 3. Colour yield (*K*/*S*) versus dye applied [Procion Yellow P-3R (C.I. Reactive Orange 12) and dye 3] using conventional quantities of Na_2CO_3 for fixation.

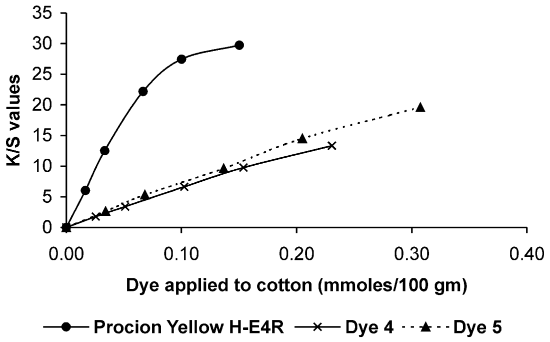


Fig. 4. Colour yield versus dye applied (Procion Yellow H-E4R, dyes **4** and **5**) using conventional quantities of Na_2CO_3 for fixation.

4. Discussion

The inherent build-up properties of both dyes **1** and **2** were inferior to those of the bis MCT commercial product, Procion Yellow H-E4R (C.I. ReactiveYellow 84, Fig. 1). In addition, dye **2** gave a series of dyeings which were redder and duller than those obtained from both Procion Yellow H-E4R and dye **1**. This bathochromic shade change, exhibited by dye **2**, is almost certainly due to de-chloroacetylation of the chromophore under the alkaline dyeing conditions. [When a small amount of dye **2** was subjected to treatment with 20 g l^{-1} Na_2CO_3 at 80 °C in the absence of cotton, a similar bathochromic shift in the visible absorption spectrum (402→412 nm) was noted.] The same effect was also observed when dye **3**, the chloroacetylamino analogue of the mono MCT dye, Procion Yellow P-3R (C.I. Reactive Orange 12), was dyed at 80 °C in the presence of Na_2CO_3. Fig. 3 also indicates that dye **3**, which nominally offers both an MCT and a chloroacetylamino reactive group for fixation with cotton, did not exhibit superior build-up properties to the mono MCT dye, Procion Yellow P-3R. Attempts to reduce/eliminate the de-chloroacetylation of dye **2**, by using lower alkali quantities for fixation (see Fig. 2), were not successful. It still exhibited the same bathochromic shade shift as when 20 g l^{-1} Na_2CO_3 was used, as well as the same inferior build-up properties compared with Procion Yellow H-E4R.

The contrasting stabilities of the acetylamino and chloroacetylamino groupings to the hot (alkaline) dyeing conditions is probably related to the electronegative nature of the chlorine atom, leaving the carbonyl group more susceptible to nucleophilic attack by hydroxide ion [12]. This situation will be exacerbated by the presence of the electron withdrawing azo group ortho to the chloroacetylamino grouping!

In order to produce a more stable chloroacetylamino residue, capable of reacting with cellulose under alkaline dyeing conditions, dye **4** was synthesised. This contained the chloroacetylamino group as a part of a ‘second leg’ arylamine in a potential hetero bi-functional, hot dyeing reactive dye.

Dye **4** gave the same shade as both dye **5** (the acetylamino analogue) and Procion Yellow H-E4R, suggesting that, if any hydrolysis of the chloroacetylamino group took place, its isolation from the chromophore did not have any significant influence on the shade of the dyestuff. Fig. 4 clearly shows that the inherent build-up properties of dye **4** was marginally inferior to dye **5** (acetylamino analogue) and much inferior to the (bis MCT) Procion Yellow H-E4R. This suggests that the chloroacetylamino group is not likely to be a commercially effective hot dyeing reactive grouping for alkaline fixation to cellulose.

5. Conclusions

1. The build-up performance of a small number of yellow reactive dyes containing both a monochlorotriazinyl and a chloroacetylamino reactive group, indicates that the use of the chloroacetylamino group will not be techno-commercially attractive in hetero bi-functional, hot dyeing reactive dyes.
2. To exploit the chloroacetylamino group as a potential hot dyeing reactive group for cellulose, it should be insulated from the chromophore. This will reduce the potential de-chloroacetylation under the alkaline fixation conditions, thereby minimising chances for irreproducible yields and shade changes on dyeing.

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