CHAPTER 7

Chemistry of reactive dyes

John Shore

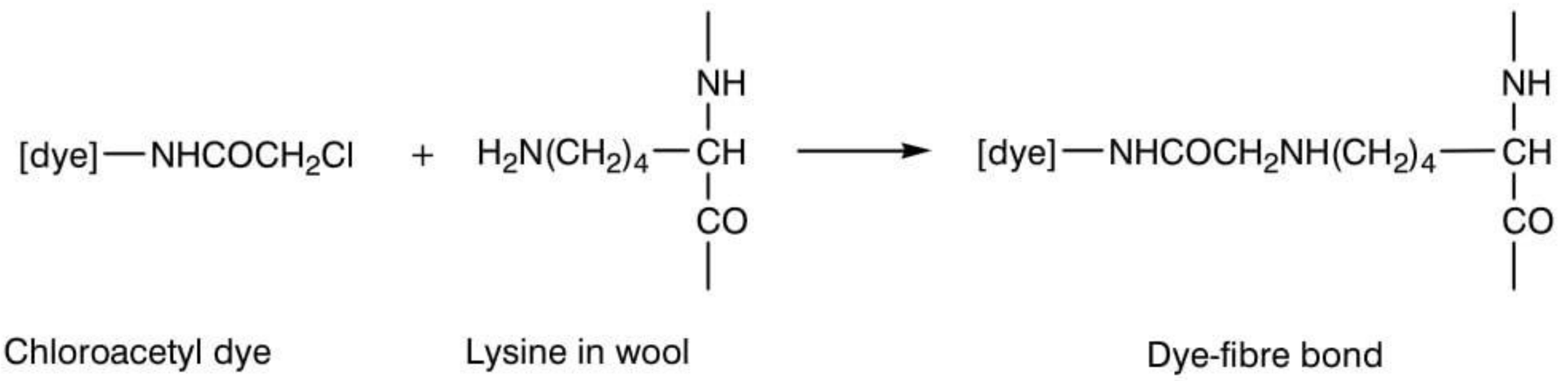
7.1 INTRODUCTION

The concept of attaching a coloured molecule to cellulose by means of a chemical bond is at least a century old, but until the 1950s a commercially viable technique for achieving dyeings of high wet fastness in this way remained elusive. The viscose process devised for the manufacture of regenerated cellulosic fibres involved the conversion of alkali-treated cotton to the soluble sodium cellulose xanthate by exposure to carbon disulphide vapour. While working on this process in the 1890s, Cross and Bevan described the synthesis of a coloured polymer by benzoylation of alkali-treated cellulose, nitration of the benzoate ester, reduction to the aminobenzoate and finally diazotisation and coupling [1].

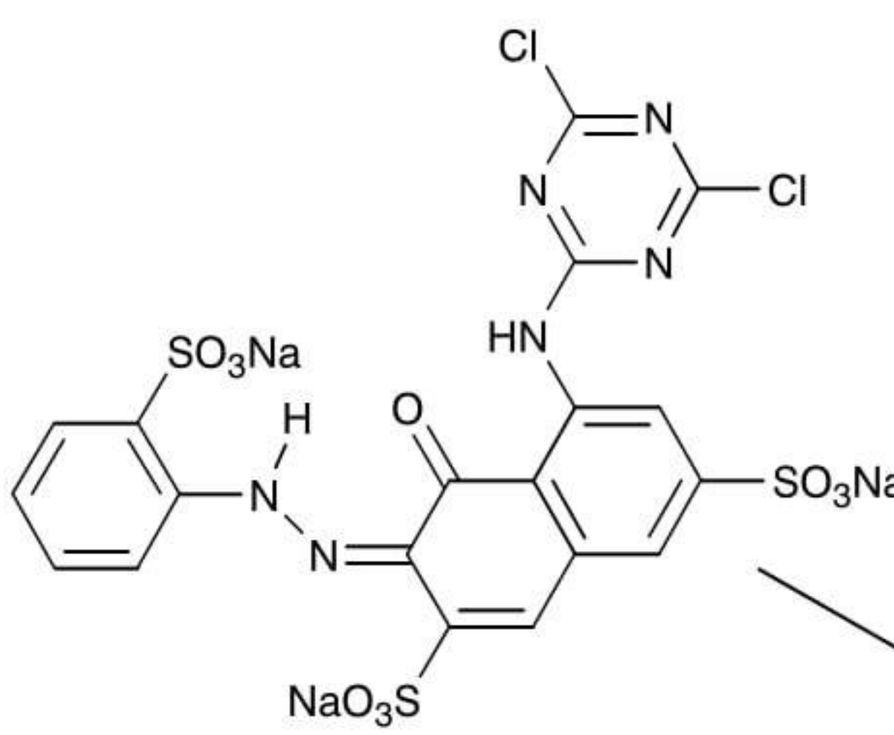
During the following half-century, much fundamental work on the structure of cellulosic fibres was undertaken and numerous esters and ethers of cellulose were prepared, occasionally involving the attachment of coloured sidechain substituents. Although such necessarily complex and esoteric reactions confirmed the formation of covalent bonds between typical chromogenic systems and the hydroxy groups in cellulose, they remained essentially of academic interest only [2,3]. Surprisingly, few attempts were made to adapt reaction conditions or to develop appropriate reagents that would allow such derivatives to be formed under typical dyehouse conditions. Drawbacks of the treatments applied in this period included their multi-stage complexity and the use of costly and hazardous solvent media. Degradative attack of the cellulosic fibres by the vigorous reagents or reaction conditions necessary, or sensitivity of the colorant–fibre linkage to hydrolytic attack during subsequent handling or storage of the coloured product, were further problems that prevented exploitation in practical dyeing systems.

The first commercially available dye capable of covalent reaction with a textile fibre is believed to be Supramine Orange R (CI Acid Orange 30). This was introduced by I G Farbenindustrie in the 1930s for the dyeing of wool. It contained a chloroacetylamino substituent from which the labile chlorine atom can be readily displaced under conventional weakly acidic dyeing conditions at the boil to form a dye–fibre bond (Scheme 7.1). It does not seem to have been realised at the time that the high fastness to washing shown by this acid dye was partly attributable to reaction with nucleophilic groups in wool.

In 1952 Hoechst marketed two Remalan vinylsulphone dyes that were capable of reacting with wool. These were applied under near-neutral conditions and functioned by nucleophilic addition across the activated double bond of the vinylsulphone group. The chemistry that had been elucidated in the development of these novel dyes provided a springboard for Hoechst to respond quickly with the first range of Remazol dyes when the possibility of dye–fibre reaction was finally achieved on cellulosic fibres.



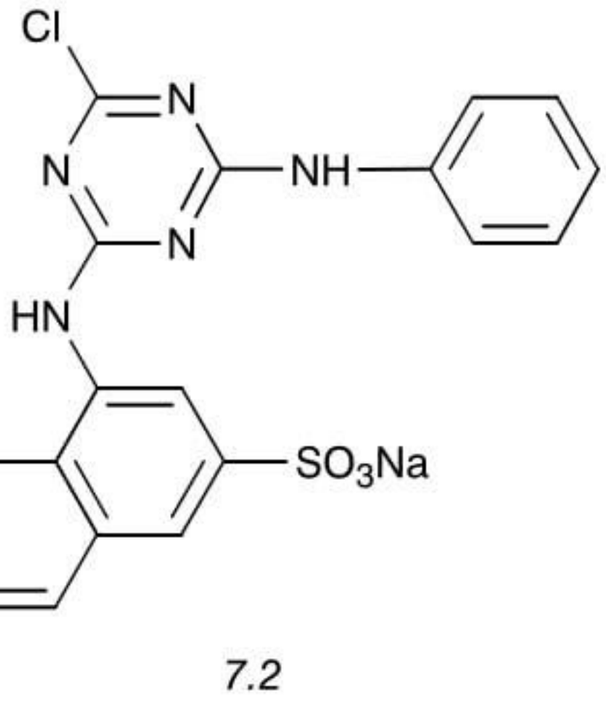
Scheme 7.1



7.1

CI Reactive Red 1

aniline



7.2

CI Reactive Red 3

Scheme 7.2

Stephen and Rattee at ICI were also evaluating speculative reactive dyes for wool in the early 1950s. These products included a series containing the dichloro-*s*-triazine reactive system [4]. Recognising that compounds with activated chloro substituents can be induced to react with cellulose under alkaline conditions, Rattee decided to investigate this by immersing alkali-treated cotton in solutions of these new dyes [5]. Various refinements of this process were necessary including the addition of salt to enhance substantivity and lowering of the pH to minimise hydrolysis of the highly reactive dichlorotriazine system, before a trichromatic set of three Procion (ICI) dyes could be marketed in 1956.

Exploitation of the dichlorotriazine dyes soon led to parallel development of the much less reactive aminochloro-*s*-triazine derivatives, which ultimately became the most successful of all reactive dye systems. Aminochlorotriazine dyes (such as 7.2) are readily prepared by a substitution reaction (Scheme 7.2) at 30–40 °C between an arylamine and the dichlorotriazine precursor (7.1 in this instance). Dyes of the aminochlorotriazine type [6] were launched simultaneously as Cibacron (Ciba) and Procion H (ICI) brands shortly after the dichlorotriazine dyes had been introduced. More stable pad liquors could be formulated

using these less reactive dyes. The range of reactivities offered by the two classes of dyes in combination with various alkalis greatly extended the scope of novel dyeing methods for them [7].

The growth of reactive dyes over the intervening years has been steady rather than spectacular [8]. It was originally thought that they would replace most of the other classes of dyes for cellulosic fibres, except for vat dyes in the most demanding sectors, and eventually dominate the field. This did not in fact occur and the traditional demands for the more economical direct and sulphur dyes on woven cotton goods remained largely unchanged. One reason for this was the need for complete removal of unfixed or hydrolysed dyes in order to achieve satisfactory wet fastness. As much as 50% of the total cost of a reactive dyeing process must be attributed to washing-off and treatment of the resulting effluent, a limitation that has prevented reactive dyes from attaining the level of success originally predicted for them [2].

7.2 REACTIVE SYSTEMS

The characteristic features of a typical reactive dye molecule include:

(1) the chromogen, contributing the colour and much of the substantivity for the fibre;
(2) the reactive system, enabling the dye to form a covalent bond with the fibre and often also contributing some substantivity;
(3) a bridging group that links the reactive system to the chromogen and often exerts important influences on reactivity, stability and substantivity;
(4) one or more solubilising groups, usually sulphonic acid substituents on the aryl rings of the chromogen;
(5) in some instances, as with the important aminochlorotriazine system, a colourless arylamino or other residue attached to the reactive grouping that also modifies solubility and substantivity.

All the important chemical classes of chromogen have been included in reactive dye structures. The sulphatoethylsulphone precursor of the vinylsulphone reactive group contributes significantly to the aqueous solubility of dyes of this type. The nature of the bridging group, especially in dyes of the haloheterocyclic type, greatly influences the reactivity and other dyeing characteristics of such dyes [9]. The structure of the reactive grouping and substituents attached to it is decisive with regard to the chemical stability of the dye–fibre bond that is formed.

Numerous factors have to be taken into account in designing reactive dyes of commercial interest [10]. Some of the most important are:

(1) Economy – any reactive system selected for a range of dyes must enable them to be produced at acceptable cost.
(2) Availability – the system selected must be free from patent restrictions, health hazards or other limitations to exploitation.
(3) Versatility – it must be possible to attach the reactive system to a variety of dye chromogenic groupings in manufacture.
(4) Storage stability – dyes containing the reactive system must be stable to storage under ambient conditions worldwide.

(5) Efficiency – the manufacturing yield must be economically viable and the dye fixation must be high under conventional conditions of application.
(6) Bond stability – the dye–fibre bonds must be reasonably stable to a range of relatively severe fastness tests.

Only a relatively few reactive systems (Table 7.1) have met these requirements sufficiently well to become commercially established in a significant segment of the market for reactive dyes. In addition to these important types, several others have been marketed [3,11] as alternative ranges that have failed to maintain a foothold in the marketplace, or as individual members of established ranges where they show reactivity characteristics similar to one of the more important systems. Many of these systems of relatively minor significance are listed in Table 7.2.

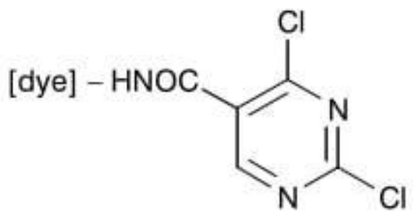
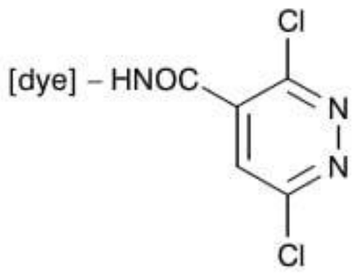
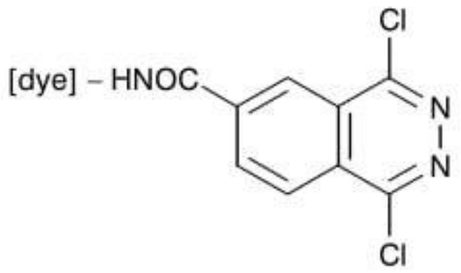
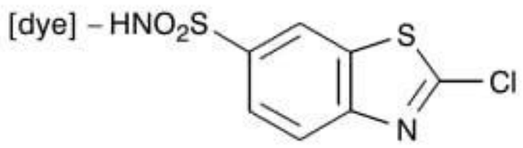
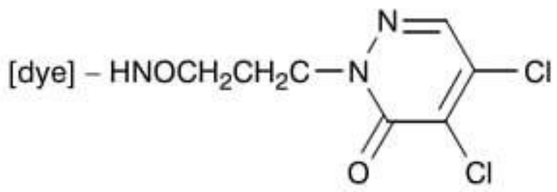
Interesting intermediates and reactions were involved in synthesis of some of the systems included in Table 7.2. A carbonamido bridging group was often used to attach the reactive system to the chromogen. This could be a weak point, in that it provided another site at which hydrolytic attack could rupture the dye–fibre bond. The carbonyl group in the highly reactive dichloropyrimidine-5-carbonamide system served to further activate the chloro substituents in the heterocyclic ring as well as providing the means of attachment to the chromogen. The route to this system started from urea and formylenemalonic ester, which were condensed to give 2,4-dihydroxypyrimidine-5-carboxylic acid. This was reacted with phosphorus oxychloride to yield 2,4-dichloropyrimidine-5-carbonyl chloride, which was then condensed with a suitable amino group in the dye chromogen.

Isomeric with the dichloropyrimidine was the 3,6-dichloropyridazine system, also linked to the chromogen through a carbonamido bridge. Analogous to the dichloropyridazine was the 1,4-dichlorophthalazine-6-carbonamide system. This was synthesised from trimellitic acid (benzene-1,2,4-tricarboxylic acid) by condensation with hydrazine and treatment of the resulting 1,4-dihydroxyphthalazine-6-carboxylic acid with phosphorus oxychloride and phosphorus pentachloride. Both sulphur and nitrogen were used as activating atoms in the 2-chlorobenzothiazole reactive system [12]. The intermediate 2-chlorobenzothiazole was chlorosulphonated in the 6-position and the derived 6-sulphonyl chloride was condensed with the amino group of the chromogen.

Table 7.1 Important reactive systems for cellulosic dyeing

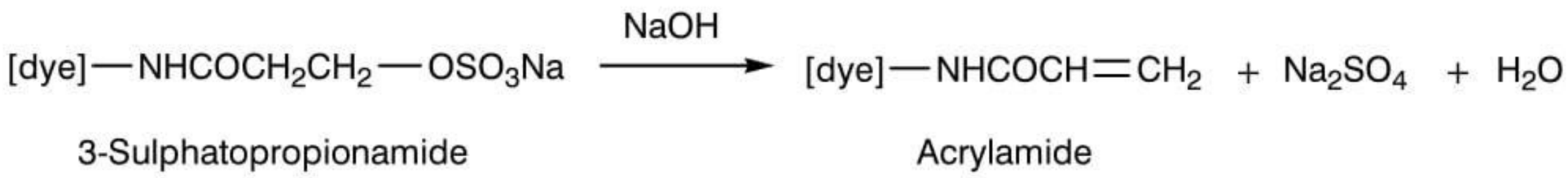
Monofunctional	Homobifunctional
Dichlorotriazine	Bis(aminochlorotriazine)
Aminochlorotriazine	Bis(aminofluorotriazine)
Aminofluorotriazine	Bis(aminonicotinotriazine)
Trichloropyrimidine	Bis(sulphatoethylsulphone)
Chlorodifluoropyrimidine	Heterobifunctional
Chlorofluoromethylpyrimidine	
Dichloroquinoxaline	Aminochlorotriazine-sulphatoethylsulphone
Sulphatoethylsulphone	Aminofluorortriazine-sulphatoethylsulphone
Sulphatoethylsulphonamide	Difluoropyrimidine-sulphatoethylsulphone

Table 7.2 Reactive systems of minor or historical significance only

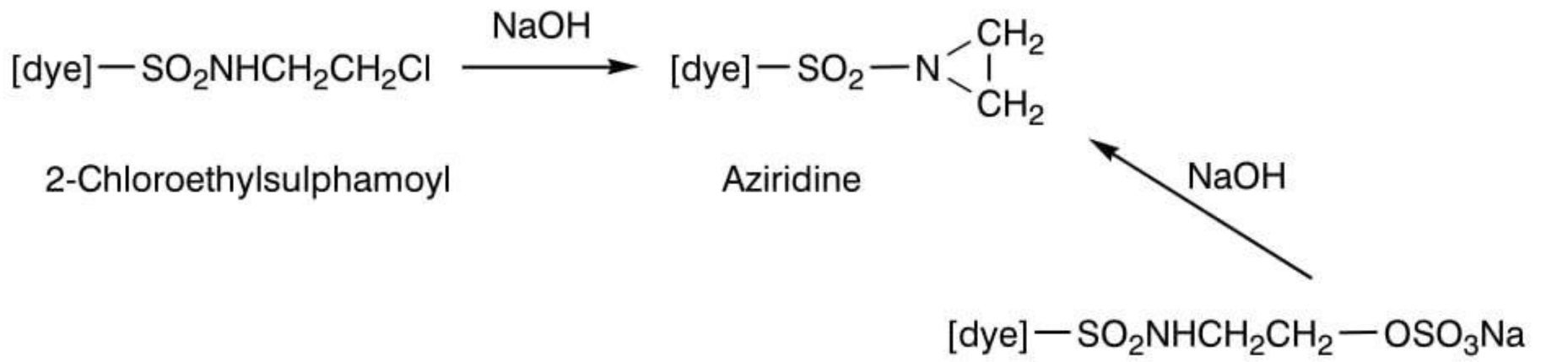
	2,4-Dichloropyrimidine-5-carbonamide
	3,6-Dichloropyridazine-4-carbonamide
	1,4-Dichlorophthalazine-6-carbonamide
	2-Chlorobenzothiazole-6-sulphonamide
	3′-(4,5-Dichloropyridaz-3-on-2-yl)propionamide
[dye]–NHCOCH=CH_2	Acrylamide
[dye]–$NHCOCH_2CH_2$–OSO_3Na	3-Sulphatopropionamide
[dye]–SO_2CH=CHCl	2-Chlorovinylsulphone
[dye]–$SO_2NHCH_2CH_2Cl$	2-Chloroethylsulphamoyl
[dye]–$SO_2NHCH_2CH_2$–OSO_3Na	2-Sulphatoethylsulphamoyl

A different type of activating arrangement was evident in the dichloropyridazone system. Here the reactive 4-chloro substituent is not activated directly by the two nitrogen atoms in this quinonoid heterocyclic ring but by the C=C–C=O grouping, which is a vinylogue of a carboxylic acid chloride [13]. The starting materials for this system were dichloromaleic acid, made by chlorination of 2-butyne-1,4-diol, and hydrazinopropionitrile from acrylonitrile and hydrazine. These were cyclised to give dichloropyridazonyl propionitrile, which was then hydrolysed and converted to the acid chloride using thionyl chloride.

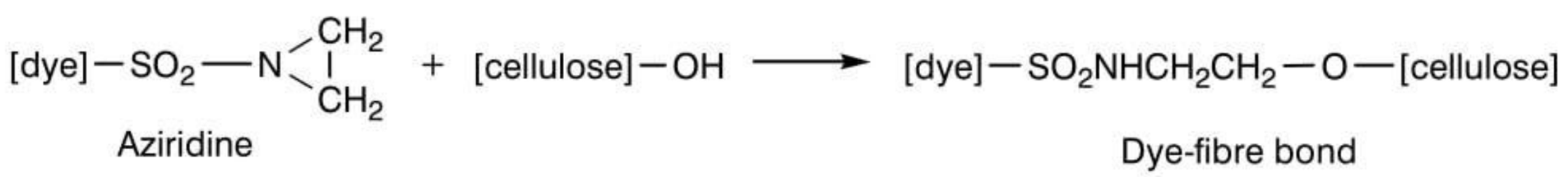
The acrylamide group and its precursor the 3-sulphatopropionamide system (Scheme 7.3) both show only feeble reactivity with cellulose under conventional alkaline dyeing conditions [14] and this has greatly limited their usefulness in spite of their economic attractiveness. Similar considerations apply to the 2-chloroethyl- and 2-sulphatoethyl-sulphamoyl systems, which are both precursors of the three-membered aziridine (cyclic ethyleneimine) ring system (Scheme 7.4). This unsaturated group undergoes a nucleophilic addition reaction [15] with alkali-treated cellulose (Scheme 7.5). The important vinylsulphone group and its various precursor systems are much more reactive and these provided the only really successful ranges of dyes that react by the nucleophilic addition mechanism.



Scheme 7.3



Scheme 7.4



Scheme 7.5

7.3 MONOFUNCTIONAL SYSTEMS

The monofunctional reactive systems of outstanding importance contain only one possible reactive centre, such as the halogeno substituent in the aminohalotriazine dyes, or the activated terminal carbon atom in the vinylsulphone system. In others there are two equivalent replaceable halogeno substituents, as in the dichloroquinoxaline or dichlorotriazine heterocyclic ring systems. When one of these halogen atoms is displaced by reaction or hydrolysis, the reactivity of the remaining halogeno substituent is greatly inhibited by the presence of the new hydroxy or cellulosyl substituent.

The influence of the reactive system itself on the substantivity of the dye containing it was recognised in the early years of the development of reactive dyes [16]. The dichlorotriazine grouping and even more so the aminohalotriazine or dichloroquinoxaline systems considerably enhance the overall substantivity of the dye molecule. The pyrimidine-based structures, with one less heterocyclic nitrogen atom than the corresponding triazine derivatives, contribute much less to the total substantivity of the dye. The non-aromatic, reactive systems, notably the 2-sulphatoethylsulphone group, modify the substantive effect of the chromogen only slightly or not at all. This can offer a significant practical advantage, since a low overall substantivity that remains unaffected by the reactive system greatly facilitates removal of the unfixed dye on washing-off, a property of especial value for printing or continuous dyeing.

The s-triazine ring is unique amongst the six-membered nitrogen heterocycles in possessing three electronegative atoms ideally placed to provide the necessary activation of the halogen atoms attached to the adjacent carbon atoms. Calculations of charge

distribution over these various heterocyclic rings [17] show that the largest possible charge attained in the series is found on the carbon atoms of the s-triazine ring (Figure 7.1). As a result, none of the dyes derived from the alternative chloro-substituted heterocyclic systems are capable of showing reactivity as high as that of the dichloro-s-triazine derivatives.

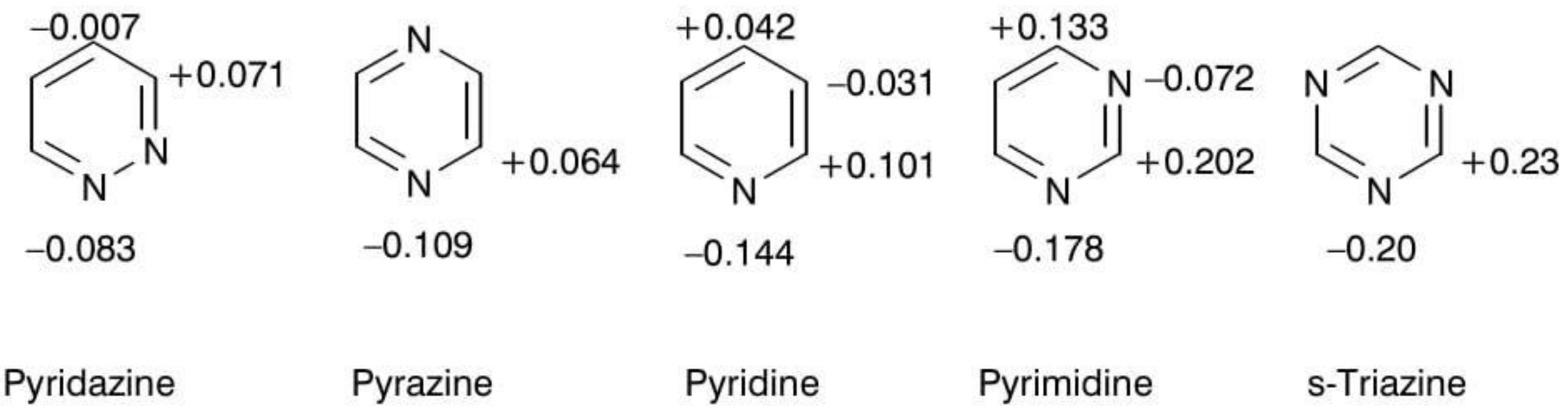


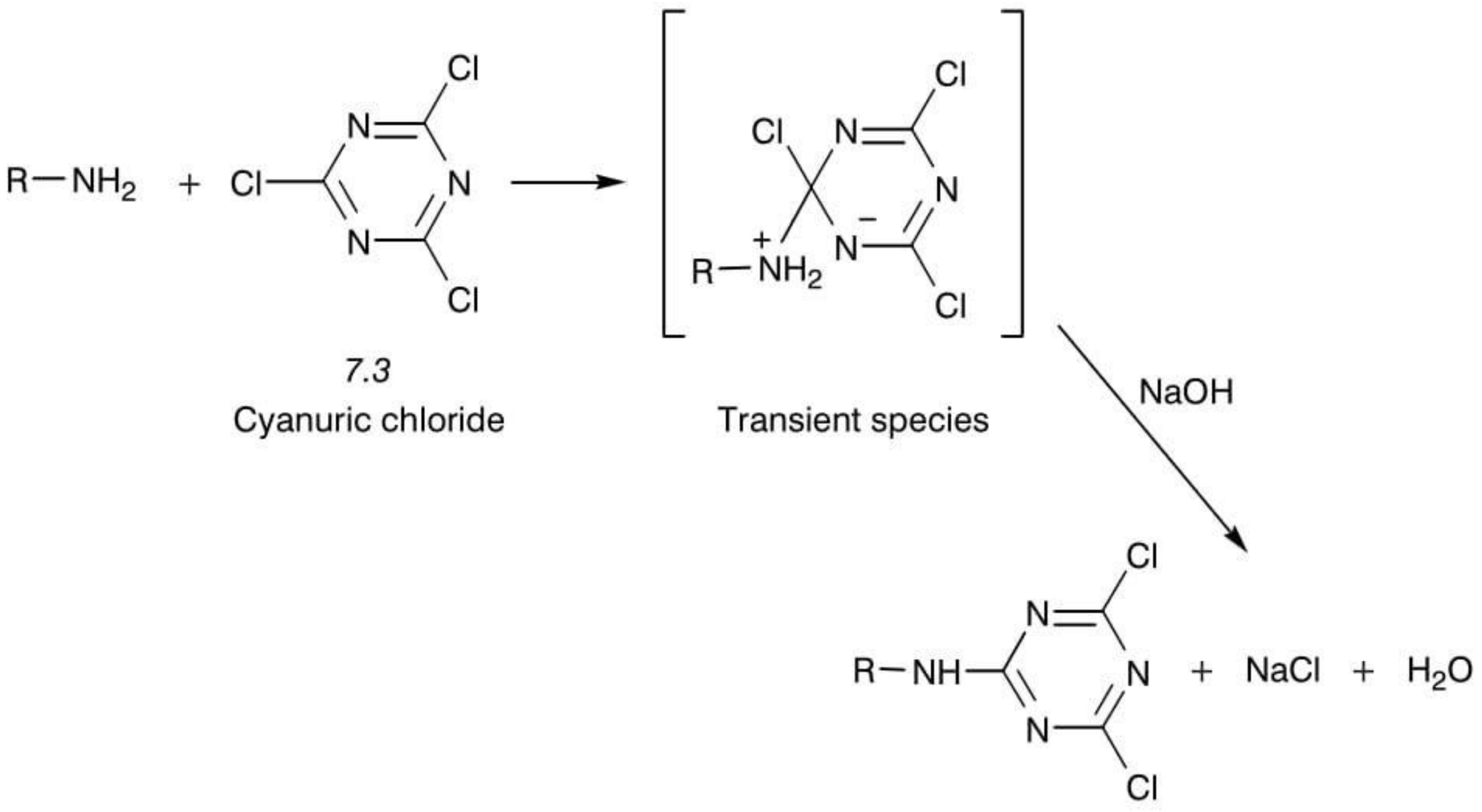
Figure 7.1 Levels of reactivity of various heterocyclic rings

Not all reactive systems are sufficiently versatile to be used successfully with a representative selection of chromogens covering the entire colour gamut. In some cases, attempts to achieve a complete range in this way based on the use of only one type of reactive group have resulted in lack of compatibility because of the dominant influences of different chromogens on reactivity and substantivity. An alternative approach designed to overcome such difficulties has been to decide beforehand on a target profile of moderate reactivity and high substantivity. The range is then built up accordingly, using various combinations of reactive system and chromogen that will yield the desired profile. When focusing in this way on gaps in a range of reactive dyes, this approach to research encourages the development of new chromogens as well as novel reactive systems [18].

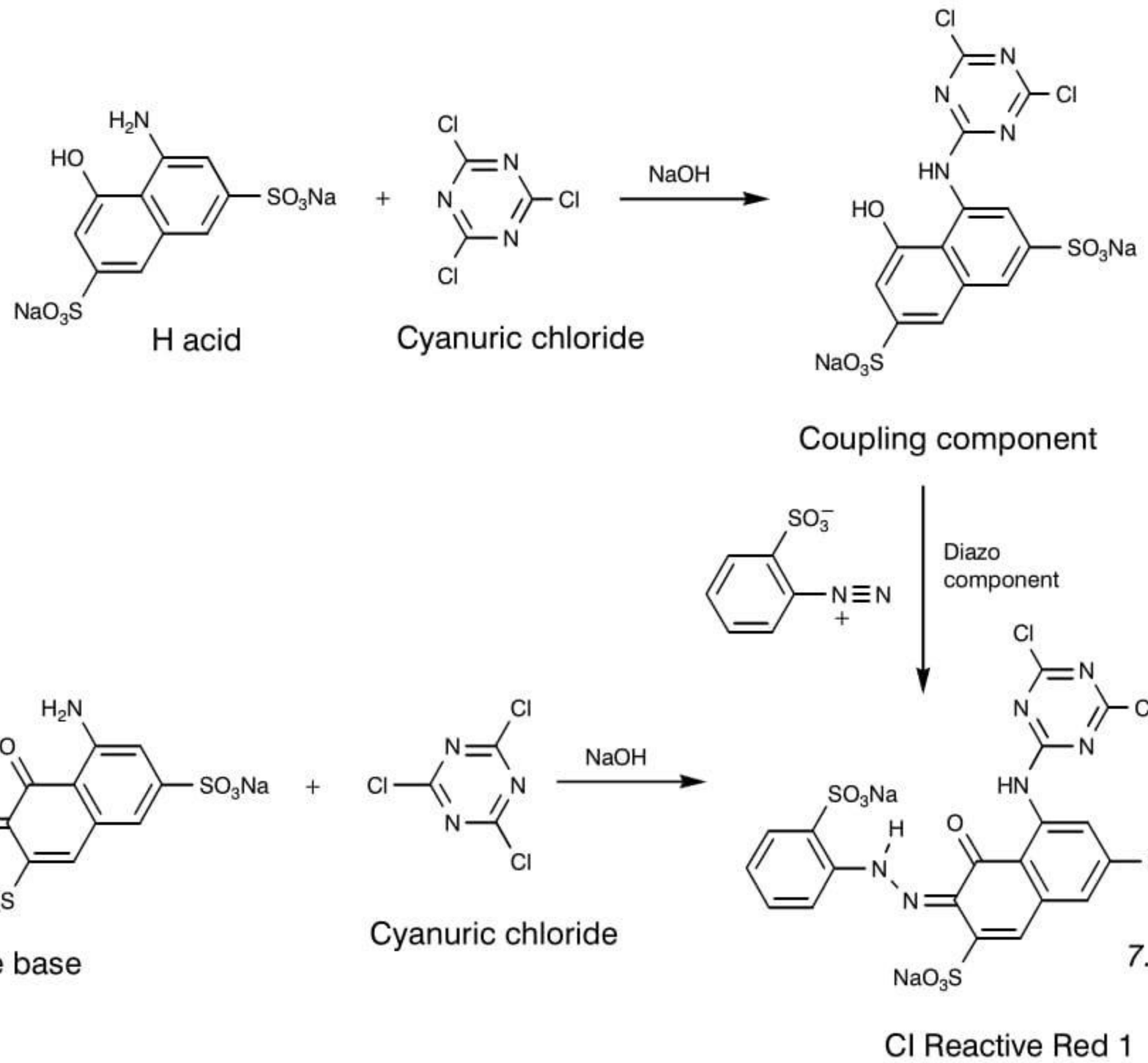
7.3.1 Dichloro-s-triazine dyes

The key intermediate for these dyes is cyanuric chloride (7.3), in which all three chloro substituents are attached to equivalent carbon atoms with fractional positive charges induced by the neighbouring negative nitrogen atoms. Polarisation of the carbon–chlorine bonds makes the chloro substituents labile and readily susceptible to stepwise nucleophilic substitution. If the attacking nucleophile is a water-soluble amine, the reaction can be conveniently carried out with the cyanuric chloride suspended in an agitated aqueous solution of the amine at a temperature close to 5 °C. Maintaining the pH close to neutrality by addition of alkali as required allows the first of the chlorine atoms to be smoothly displaced (Scheme 7.6), yielding the aminodichlorotriazine product (7.4). The optimum conditions for preparing various 6-alkyl-, 6-aryl- and 6-heteroaryl-substituted derivatives of 2,4-dichloro-s-triazine have been defined recently [19].

Selecting a sulphonated dye molecule containing an amino group as the nucleophile leads directly to a dichlorotriazine dye. In certain cases a suitable intermediate may be condensed with cyanuric chloride and then the chromogenic grouping is synthesised from this reaction product. Both of these routes are illustrated in a simple way for CI Reactive Red 1 (7.1) in Scheme 7.7. In these dyes the electronic effects responsible for the lability of the chloro substituents are muted by feedback of electrons from the electron-donating imino bridging



Scheme 7.6



Scheme 7.7

link, making the dye quite stable in neutral solution. This highly reactive system is susceptible to attack by hydroxide ions on the alkaline side and subject to autocatalytic hydrolysis on the acid side. To guard against decomposition in these ways a buffer is added to the dye solution to ensure stability during isolation and further buffer is incorporated into the isolated paste before drying.

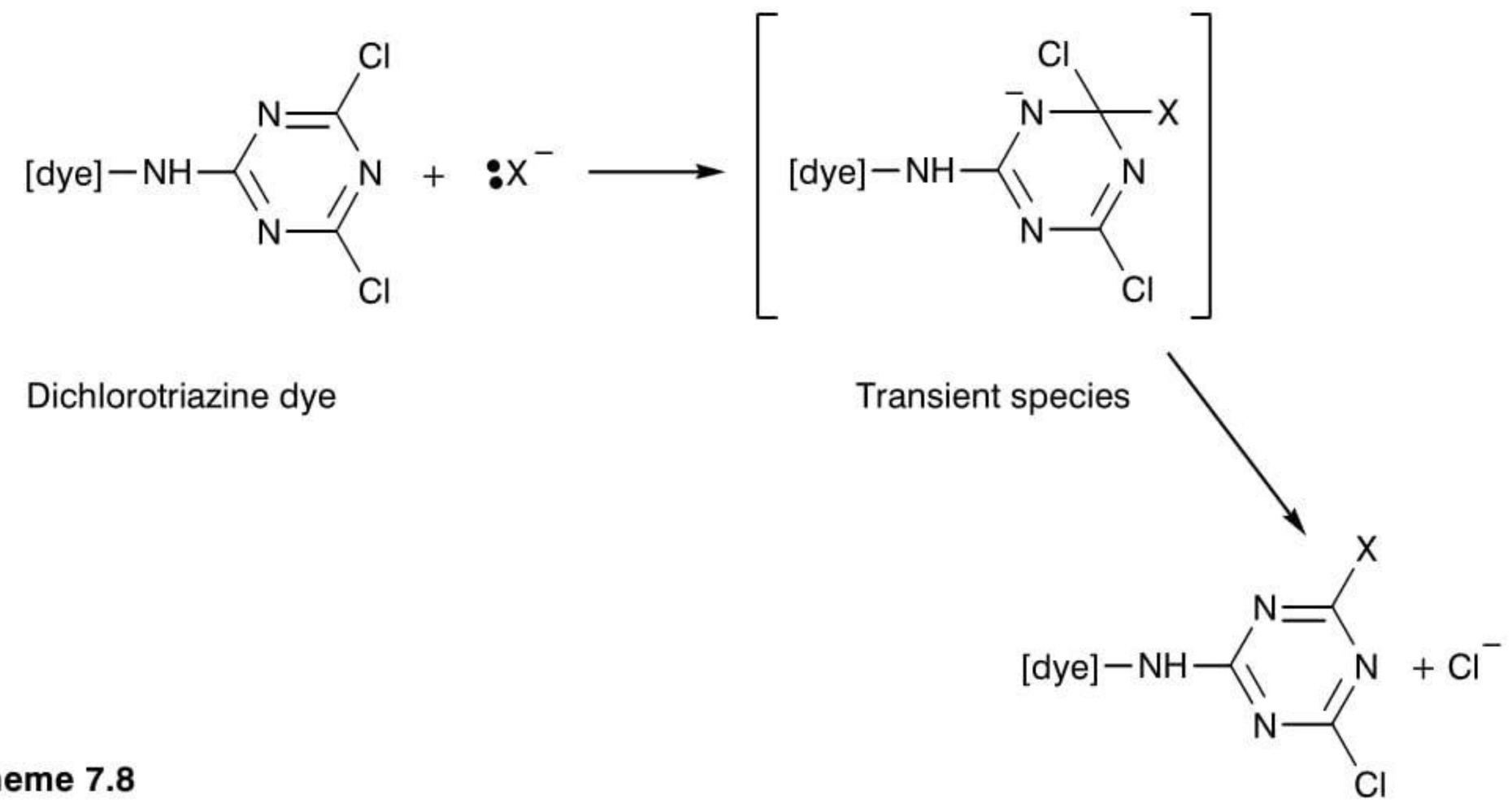
The dichlorotriazine dyes are so reactive that they can be readily fixed to cellulosic materials by pad-batch dyeing at ambient temperature or by exhaust methods at 30–40 °C. This means that relatively small chromogens are preferred to ensure adequate mobility of dye on the fibre during the exhaustion stage. This requirement makes these dyes eminently suitable for bright dyeings but less satisfactory for deep tertiary hues, since the larger-size chromogens used for this purpose often fail to give acceptable performance by low-temperature application. A weakness with certain dichlorotriazine dyes, particularly red monoazo derivatives of H acid such as CI Reactive Red 1 (7.1), is that under conditions of low pH the dye–fibre bond is susceptible to acid-catalysed hydrolysis leading to deficiencies in fastness to washing or acid perspiration.

Ionisation of the hydroxy groups in cellulose is essential for the nucleophilic substitution reaction to take place. At neutral pH virtually no nucleophilic ionised groups are present and dye–fibre reaction does not occur. When satisfactory exhaustion of the reactive dye has taken place, alkali is added to raise the pH to 10–11, causing adequate ionisation of the cellulose hydroxy groups. The attacking nucleophile ($:X^-$) can be either a cellulosate anion or a hydroxide ion (Scheme 7.8), the former resulting in fixation to the fibre and the latter in hydrolysis of the reactive dye. The fact that the cellulosic substrate competes effectively with water for the reactive dye can be attributed to three features of the reactive dye/cellulosic fibre system:

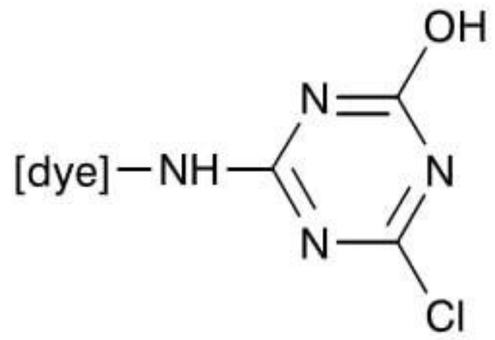
(1) the concentration of dye in the fibre phase is greater than that in the solution phase
(2) the greater nucleophilicity of the cellulosate anion compared with hydroxide
(3) the high selectivity of the electrophilic reactive group

Because the pK_a of the cellulosic substrate is lower than that of water, reaction with the fibre according to Scheme 7.8 is favoured [20].

When partial hydrolysis occurs as in Scheme 7.8 to form the 2-chloro-4-hydroxy species (7.5), the dye does not have a further chance to achieve fixation via the remaining chlorine atom. Under the alkaline conditions of fixation, ionisation of the acidic 4-hydroxy substituent leads to a massive feedback of electronegativity into the triazine ring, causing total deactivation of the remaining 2-chloro substituent. The remaining chlorine atom in



Scheme 7.8

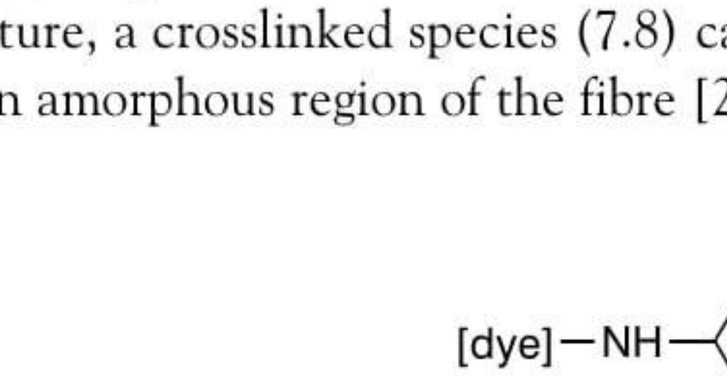


7.5

the still active but fixed species (7.6), on the other hand, may be subsequently hydrolysed (Scheme 7.9) to give an inactive fixed species (7.7). Under more extreme conditions of pH or temperature, a crosslinked species (7.8) can be formed linking two neighbouring cellulose chains in an amorphous region of the fibre [21,22].

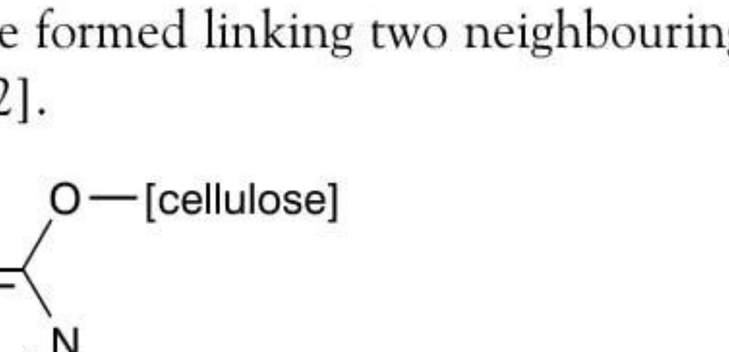
7.6

Active fixed dye



7.7

Hydrolysed fixed dye



7.8

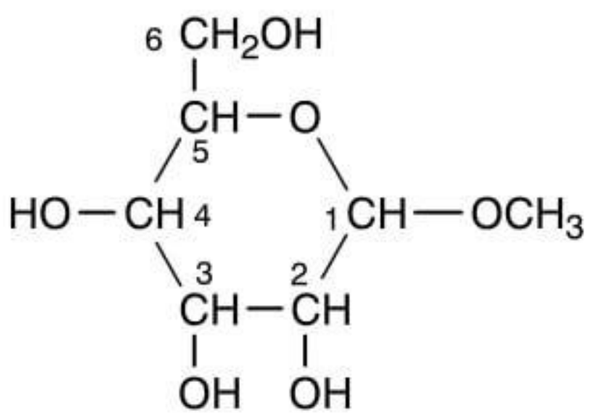
Crosslinked dye-fibre bond

Scheme 7.9

7.3.2 Monochloro-s-triazine dyes

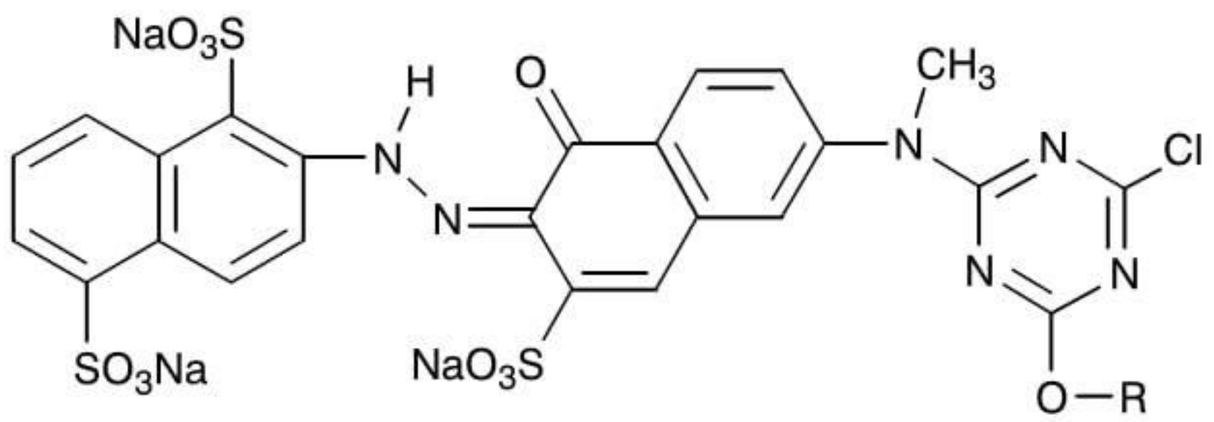
Controlled reaction of dichlorotriazine dyes with either amines or alcohols at 30–40 °C leads to two further classes of monofunctional dyes, the 2-amino-4-chloro- and 2-alkoxy-4-chloro-s-triazines respectively. The latter are more reactive than the former but less reactive than the parent dichlorotriazine types. They are now essentially of historical interest, the 2-isopropoxy-4-chloro system forming the basis of the Cibacron Pront (Ciba) range for printing. The bulky isopropoxy group was chosen in order to disrupt the planarity of the substituted triazine system and thus favour removal of unfixed dye at the washing-off stage. The mechanism of reaction of methyl-α-D-glucoside (7.9), as a soluble model for cellulose, with a model Cibacron Pront dye in homogeneous solution was examined recently. It was demonstrated that reaction occurs only with the hydroxy groups attached at the C_4 and C_6 positions, the ratio of reactivities being 12:1 in favour of the primary alcoholic site [23].

In another recent study, the relative rates of hydrolysis of a series of orange *N*-methyl J acid dyes of the 2-alkoxy-4-chloro-s-triazine type (7.10; R = methyl, ethyl or isopropyl)

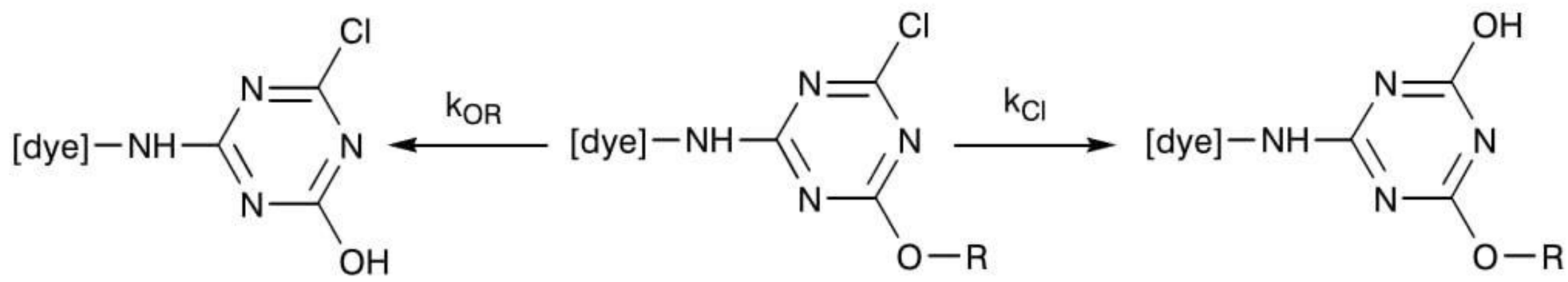


7.9

Methyl-α-D-glucoside



7.10



Scheme 7.10

were compared. Surprisingly, the hydroxide ion displaced the methoxy group about 1.5 times more rapidly than the chloro substituent (Scheme 7.10; $k_{OR} > k_{Cl}$). Increase in the size and electron-donating capacity of the alkoxy group resulted in a decreasing propensity for substitution, so that displacement of methoxide ion proceeded about twelve times quicker than that of isopropoxide ion [24].

More energetic conditions of fixation, typically 80 °C and pH 11 for exhaust application, are necessary to achieve efficient fixation of 2-amino-4-chloro-s-triazine dyes on cellulosic fibres. Early studies of the relationships between structure and substantivity of aminochlorotriazine dyes revealed that the NH bridging groups linking the chromogen and the uncoloured 2-arylamino substituent to the heterocyclic ring exert marked effects on the solubility and dyeing properties of these dyes [2]. Replacement of such an NH imino link by an *N*-methylimino group lowers the substantivity by inhibiting hydrogen bonding to cellulose hydroxy groups. The use of a sulphonated arylamine to form the uncoloured substituent in the 2-position of a monochlorotriazine system is helpful in enhancing dye solubility and migration behaviour. The relationship between the distortion angle caused by steric hindrance and the reactivity of aminochlorotriazine dyes has been demonstrated in a kinetic study of the hydrolysis of model compounds. Bulky substituents in the *ortho* position with respect to the imino bridge in 2-anilino derivatives cause sectional distortion of coplanarity between the phenyl and triazine rings, leading to an increase in reactivity owing to partial impediment of *p*-π conjugation [25].

7.3.3 Monofluoro-s-triazine dyes

Fluorine and chlorine are the only important choices for the labile substituents on a heterocyclic reactive system but numerous other leaving groups have been patented, mostly as substituent on an s-triazine ring. These include sulpho, cyano, thiocyanato, azido and trichloromethyl [26], as well as more elaborate groupings (Figure 7.2). Such derivatives are

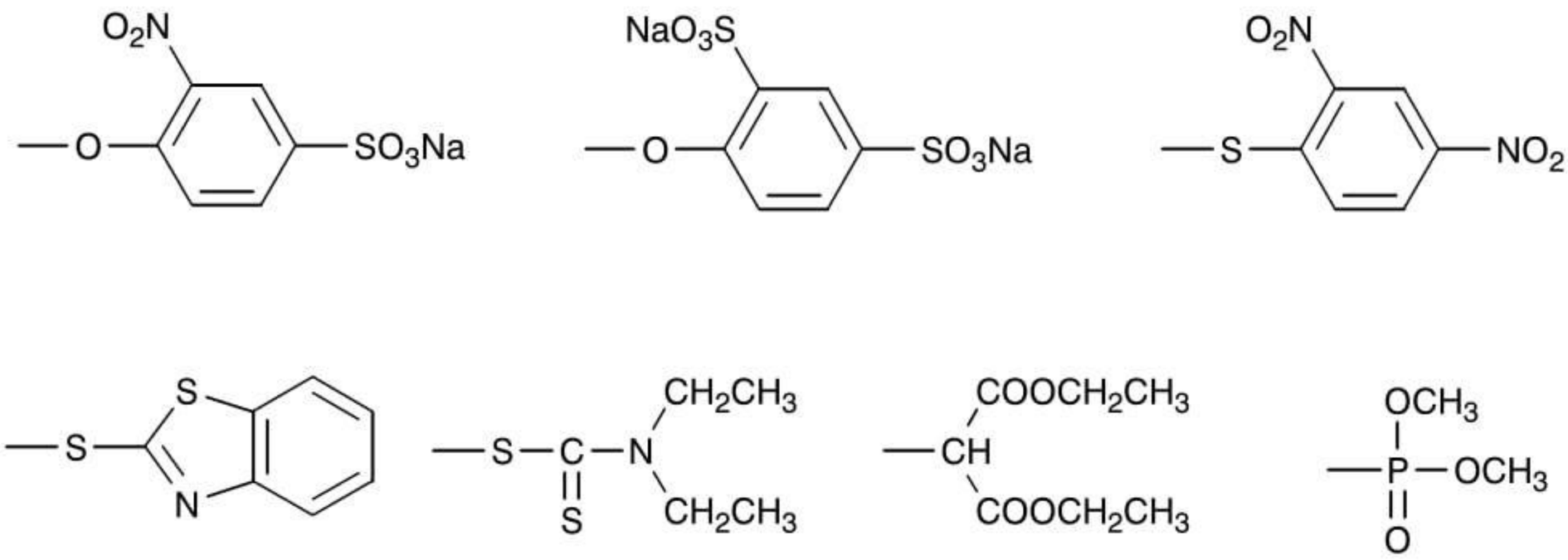
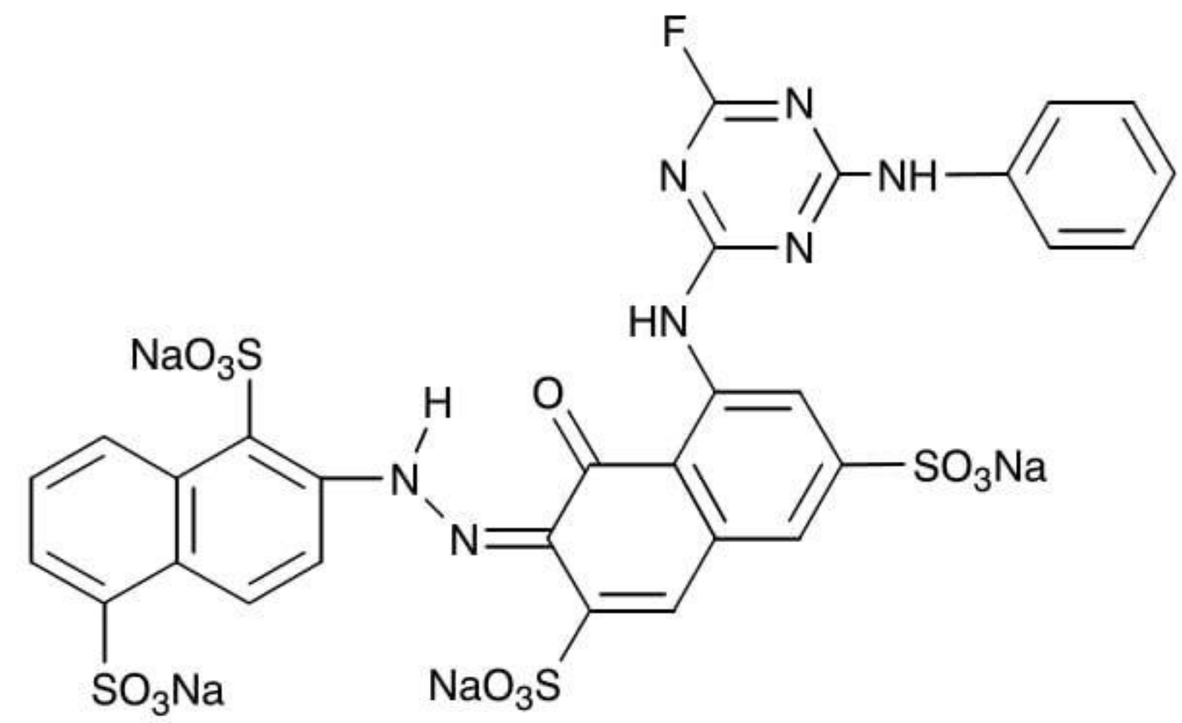
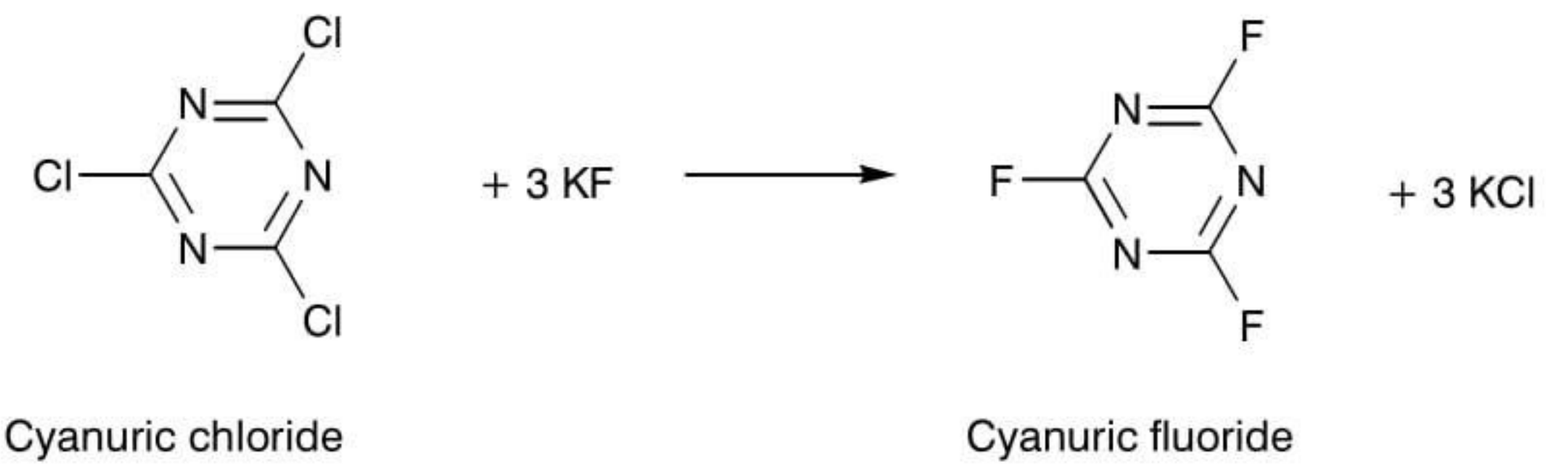


Figure 7.2 Alternative leaving groups for heterocyclic systems



7.11

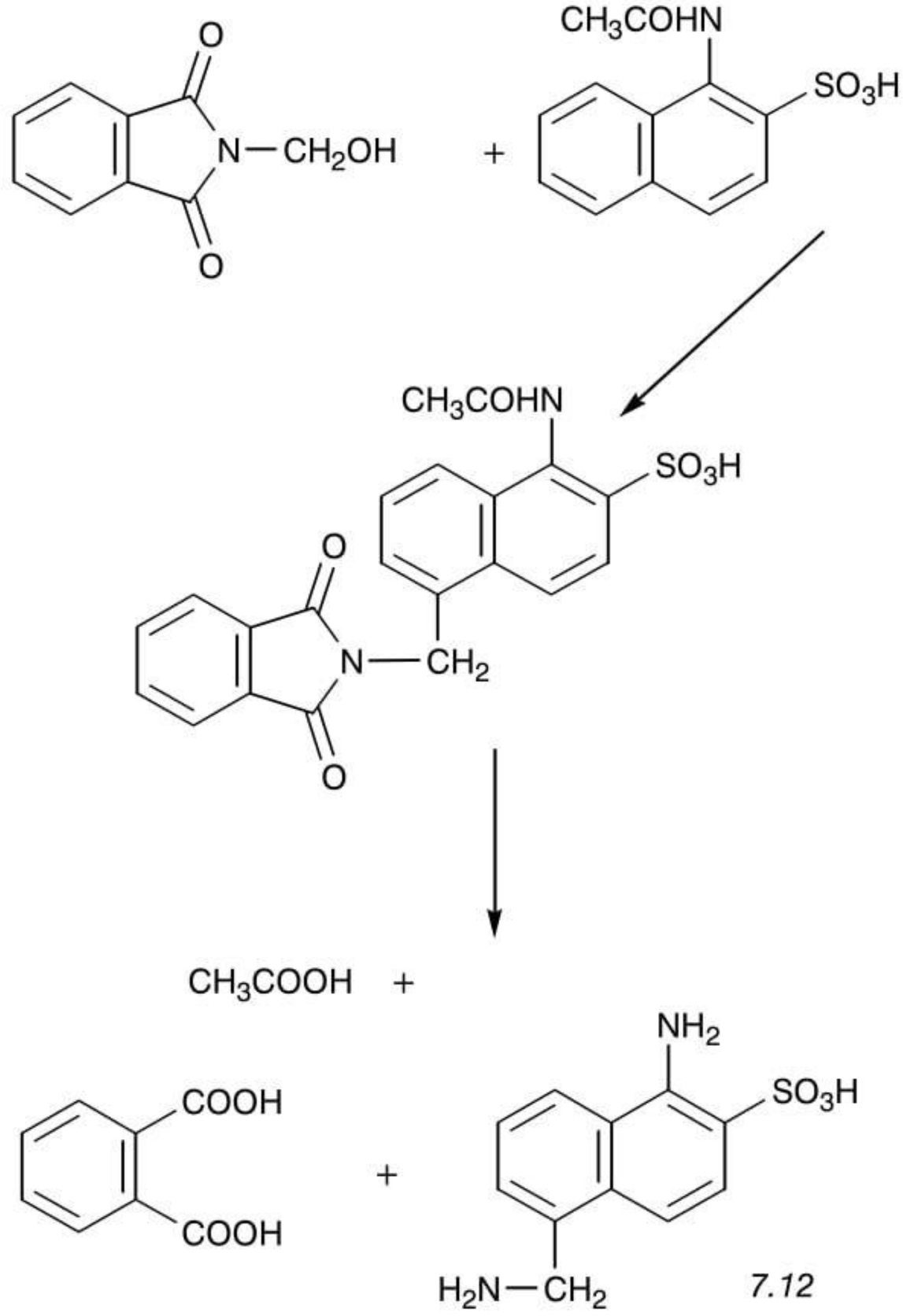


Scheme 7.11

almost always made by replacing a chlorine atom in a chloro-s-triazine dye by reaction with the sodium salt of the appropriate nucleophile. Thus they are invariably more costly than the parent chloro compound and offer no obvious benefits, so they have not been exploited commercially.

A fluorine atom is used as the leaving group in the Cibacron F (Ciba) range of 2-amino-4-fluoro-s-triazine dyes, as exemplified by the red monoazo H acid dye 7.11. The essential highly reactive intermediate cyanuric fluoride required for their manufacture is made from cyanuric chloride by an exchange reaction with potassium fluoride (Scheme 7.11). The greater electronegativity of fluorine compared with chlorine results in a markedly higher

level of reactivity for these dyes than for their 2-amino-4-chloro analogues. The compact character of the fluorine atom, resulting from the close binding of the nine-electron sphere around the atomic nucleus, favours reaction with dye bases carrying aliphatic amino groups. This need has prompted the synthesis and exploitation of novel dye intermediates bearing such substituents, such as 5-aminomethyl-l-naphthylamine-2-sulphonic acid (7.12). This is prepared (Scheme 7.12) by condensing 1-acetylaminonaphthalene-2-sulphonic acid with *N*-methylolphthalimide (Tscherniac–Einhorn reaction), followed by hydrolysis of the resulting 5-substituted derivative.

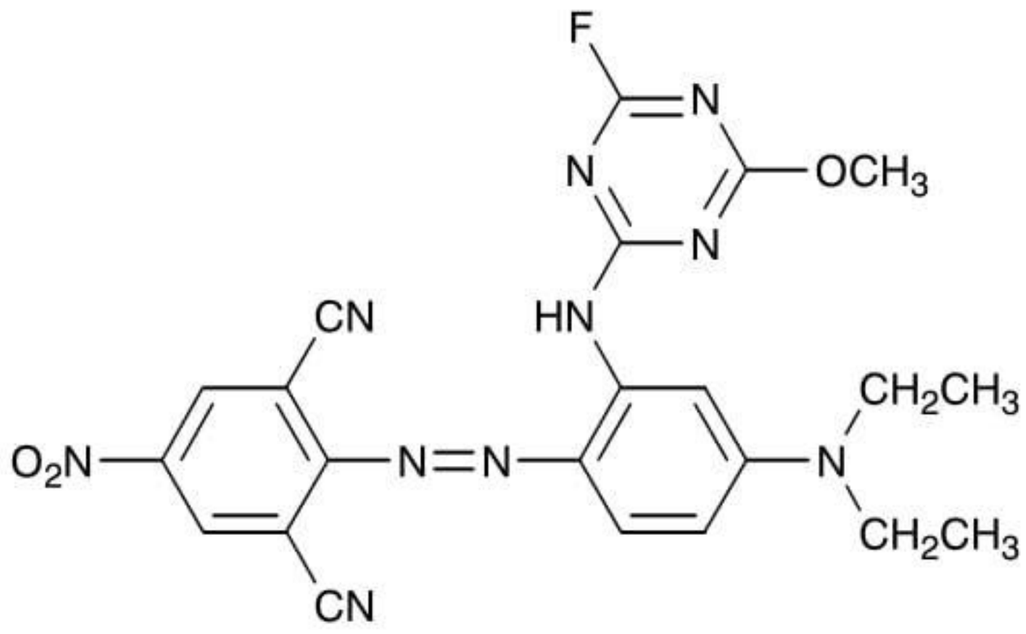


7.12

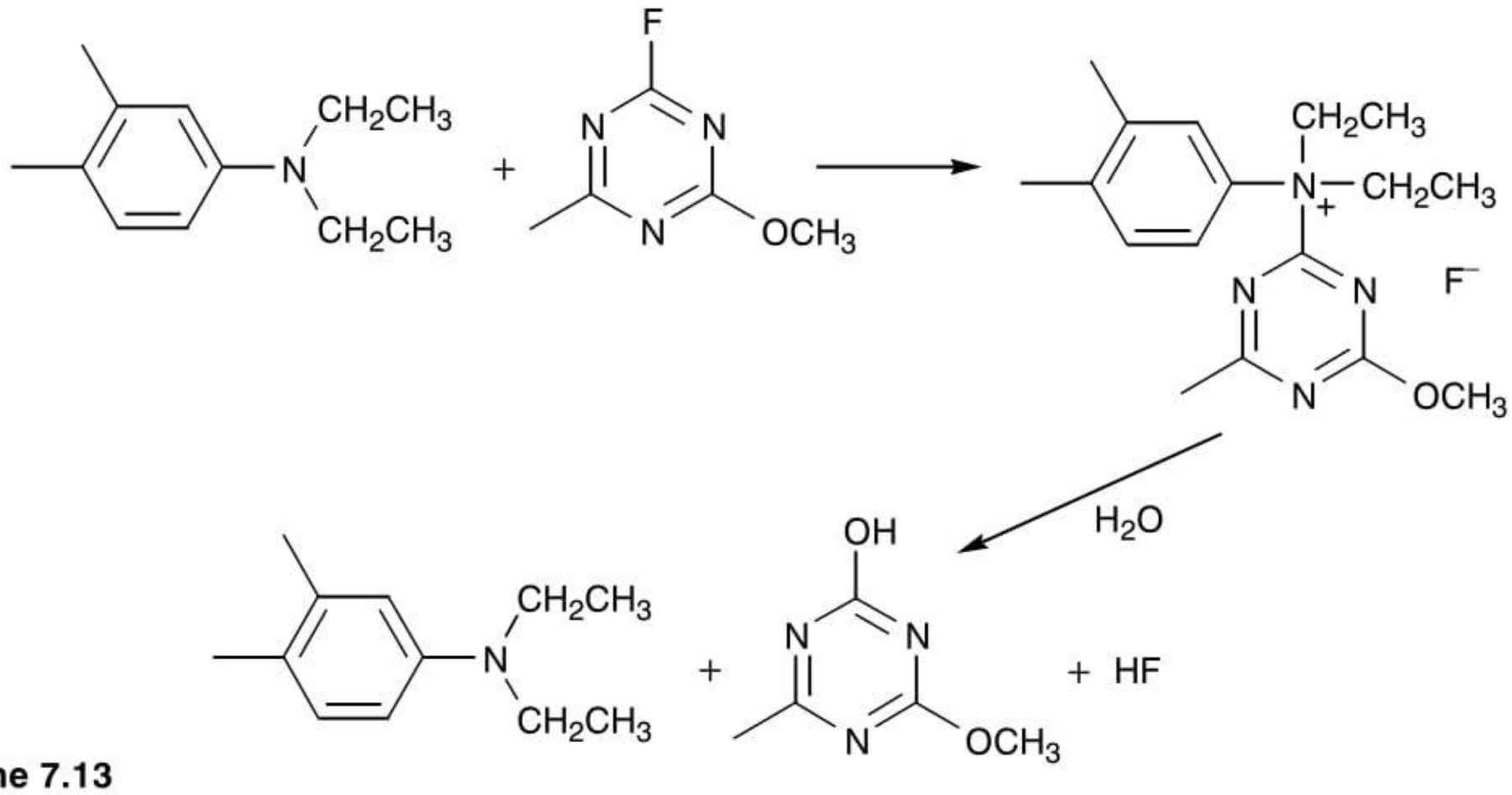
Scheme 7.12

Considerable work was carried out in the 1980s by Mitsubishi on the preparation and evaluation of disperse dyes containing the highly reactive 2-alkoxy-4-fluoro-s-triazine system, an example being the blue dicyanonitrophenylazo structure 7.13 [27]. These products were designed specifically for the dyeing of both component fibres in polyester/cellulosic blends. Although marketed commercially, these novel dyes have not gained widespread acceptance [8]. The absence of water-solubilising groups allowed these molecules to enter the polyester fibre but the high relative molecular mass (490 in the case of 7.13) implies slow diffusion and poor migration properties. The combination of high reactivity and lack of water solubility seems likely to favour fixation near the cellulosic fibre surface with poor penetration into the interior. In the case of structures like 7.13, there may be a possibility of some self-deactivation

of the reactive system by temporary quaternisation between the tertiary amino group in one molecule and the fluorotriazine centre in another (Scheme 7.13).



7.13

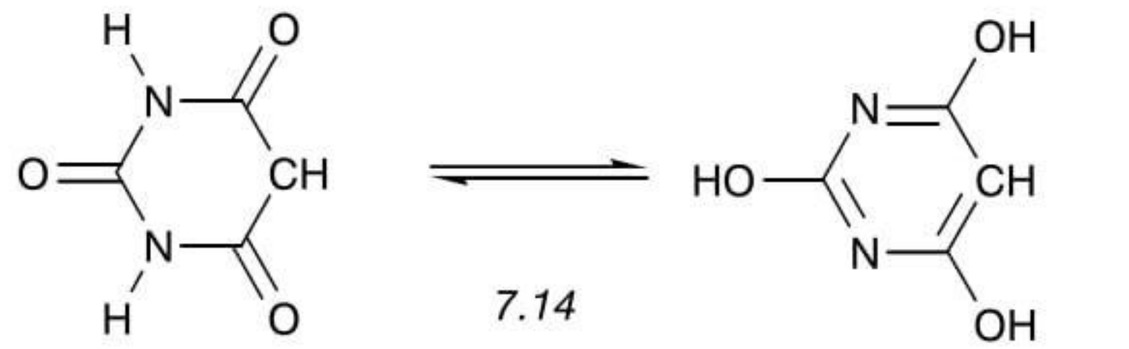


Scheme 7.13

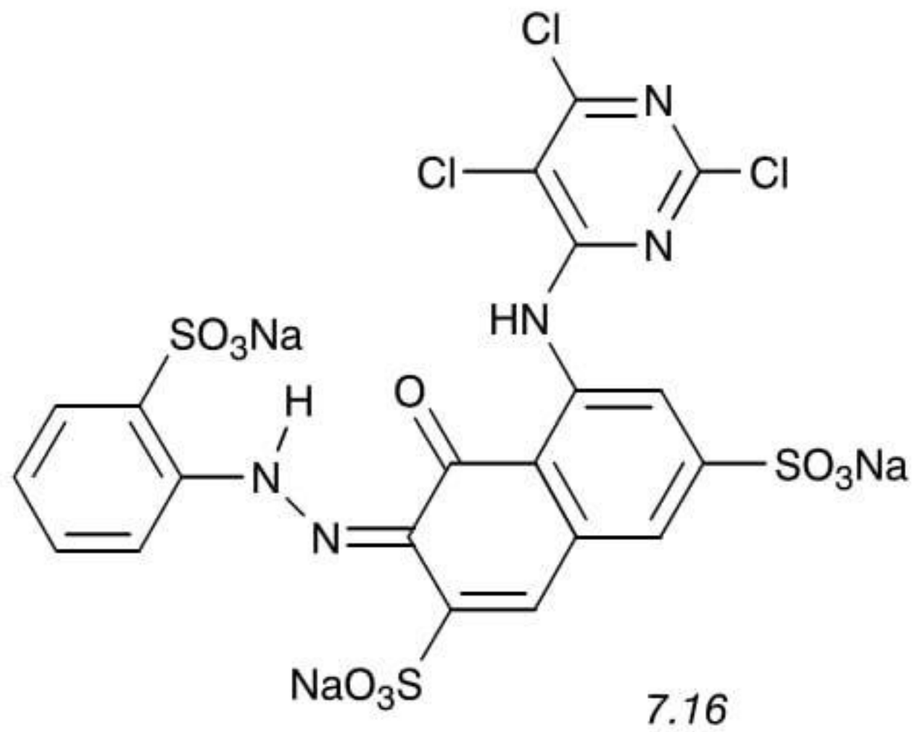
7.3.4 Trichloropyrimidine dyes

The 1,3-diazine arrangement in the pyrimidine ring provides less activation of chloro substituents than the s-triazine system (Figure 7.1). Fixation to a cellulosic fibre by exhaust dyeing methods requires treatment at the boil rather than the 80 °C found most suitable for aminochlorotriazine dyes, but the dye–fibre linkage through a diazine ring is more stable than that containing a triazine nucleus [16]. The intermediate required for these dyes, tetrachloropyrimidine (7.15), is prepared by chlorination of barbituric acid (7.14) and treatment of the resulting 5-chloro derivative with phosphorus oxychloride and dimethylaniline as catalyst (Scheme 7.14). Two isomeric aminotrichloropyrimidine structures are possible with the amino substituent in either the 2- or the 4-position. A study of the initial reaction between tetrachloropyrimidine and various arylamines demonstrated that nucleophilic substitution occurs mainly by displacement of the 4-chloro substituent [28], as illustrated for the red monoazo H acid dye CI Reactive Red 17 (7.16).

Preferential substitution at the 4-position is much less pronounced in the reaction of 2,4,6-trichloropyrimidine with arylamines, so that the dichloropyrimidine dyes formed in this

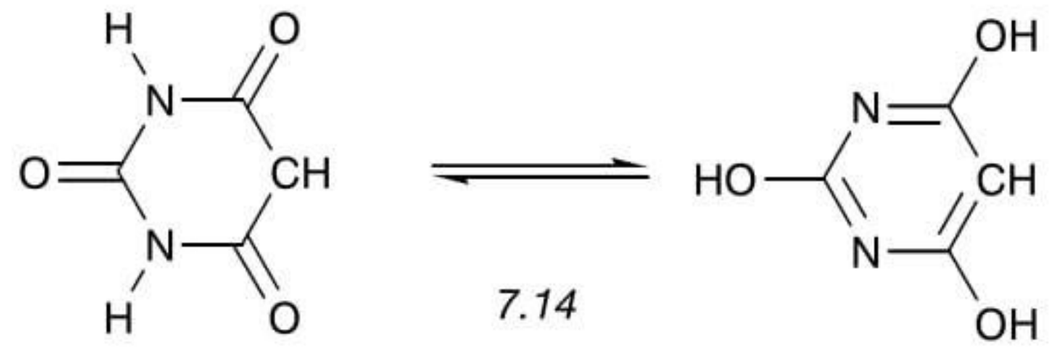


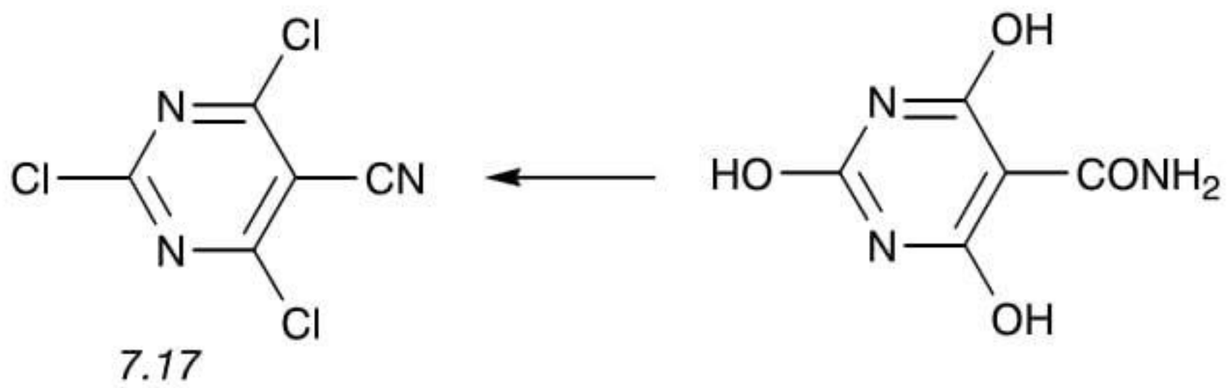
Scheme 7.14



way contain a mixture of 2,6- and 4,6-dichloro isomers. These dyes are even less reactive than the trichloropyrimidine dyes but are correspondingly more resistant to acidic or alkaline hydrolysis.

The 5-chloro substituent in the trichloropyrimidine reactive system is much less activated by the nitrogen atoms in the heterocyclic ring and is thus not normally capable of hydrolysis or reaction with the fibre. Dichloropyrimidine dyes containing a 5-methyl substituent are less reactive but more stable than their trichloropyrimidine analogues [16]. Dyes prepared with an electron-withdrawing group in the 5-position, such as 5-cyano or 5-nitro, show enhanced reactivity of the 2,6-dichloro substituents but somewhat lower stability of the dye–fibre bond. An example of a 5-cyano-2,4-dichloropyrimidine dye is CI Reactive Red 219, which is compatible in reactivity and dyeing behaviour with dichlorotriazine dyes. The intermediate required for dyes of this type is 5-cyano-2,4,6-trichloropyrimidine (7.17), prepared from barbituric acid (7.14). Reaction of this with sodium cyanate and hydrochloric acid yields the 5-carbonamido derivative and this is treated with phosphorus oxychloride and dimethylaniline as catalyst, resulting in simultaneous dehydration of the carbonamido group and replacement of the hydroxy groups to give the desired product (Scheme 7.15).

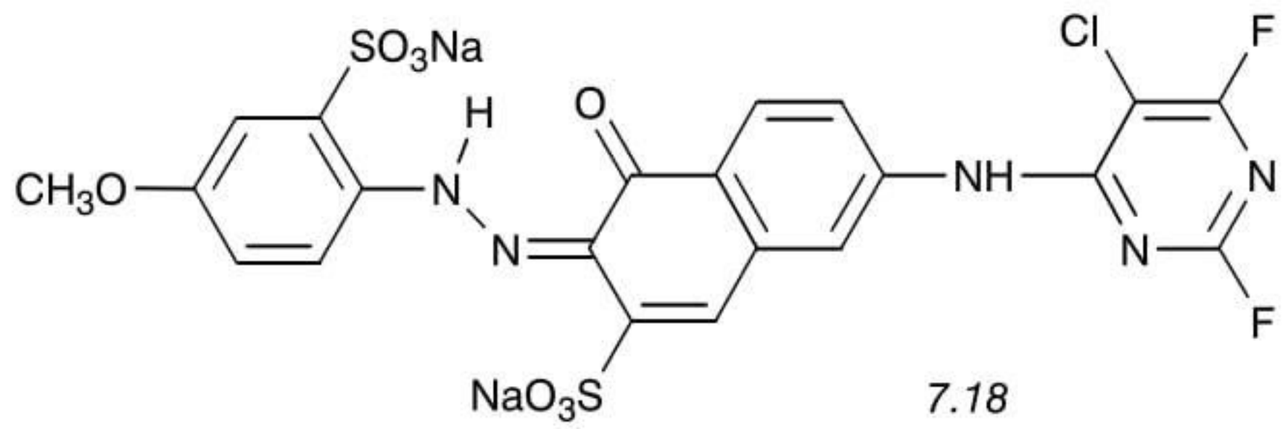


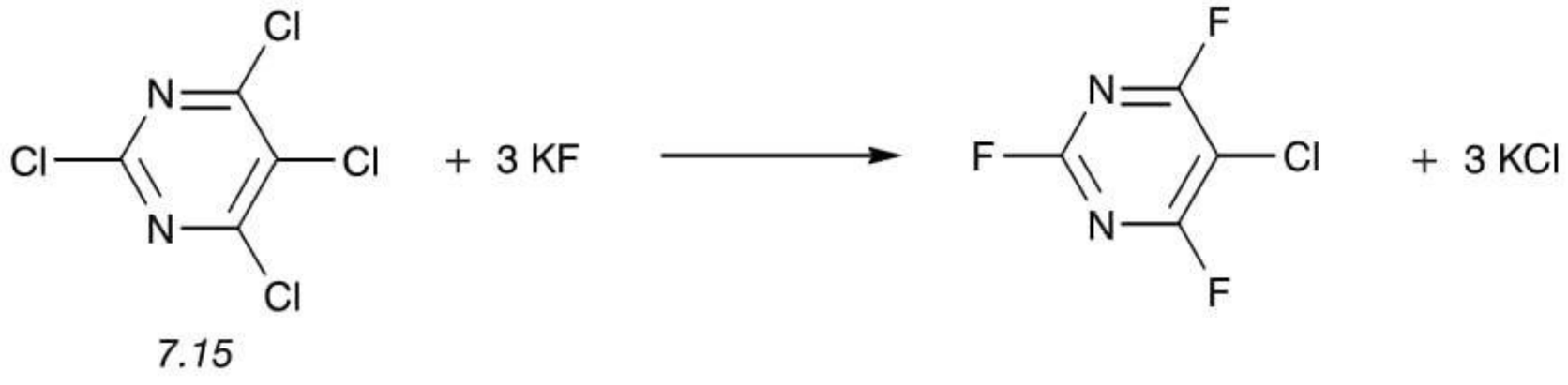


Scheme 7.15

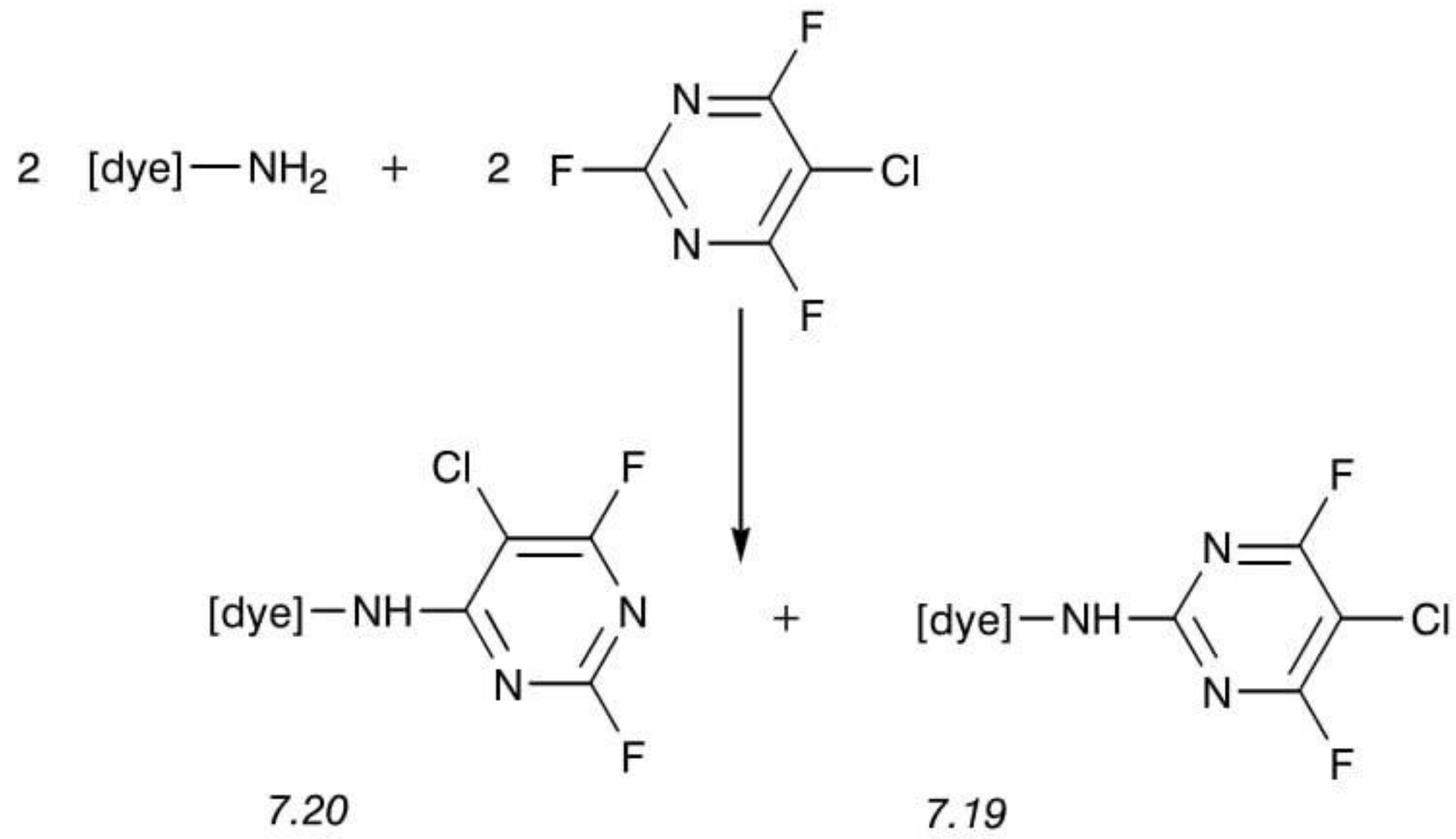
7.3.5 Chlorodifluoropyrimidine dyes

Another important route to more reactive halopyrimidine dyes is to use fluorine rather than chlorine in the reactive centres. As with the fluoro-s-triazine dyes, this results in a markedly higher level of reactivity compared with the corresponding chloro-substituted analogues. Exhaust dyeing temperature for optimal fixation of a 5-chloro-2,4-difluoropyrimidine derivative, such as the red monoazo J acid dye 7.18, is 40–50 °C. The dye–fibre bond formed with cellulose by fixation of these highly reactive products is more stable to acid conditions than that formed by the competing dichlorotriazine dyes but it does tend to undergo oxidative cleavage more readily under the influence of light exposure in the presence of peroxy compounds. The exchange reaction of tetrachloropyrimidine (7.15) with potassium fluoride yields 5-chloro-2,4,6-trifluoropyrimidine (Scheme 7.16). When this is reacted with the dye





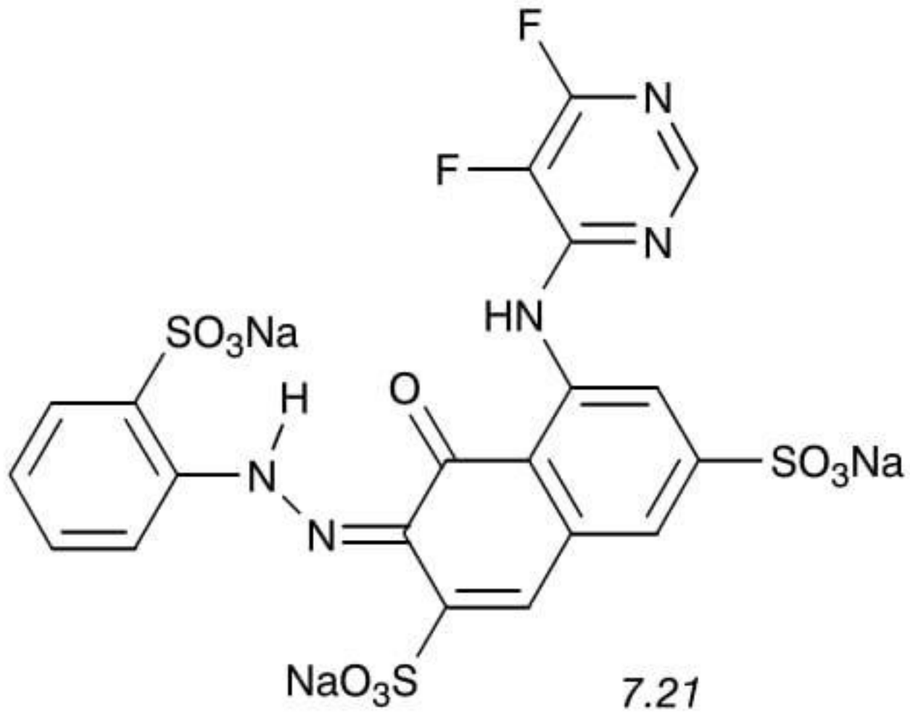
Scheme 7.16



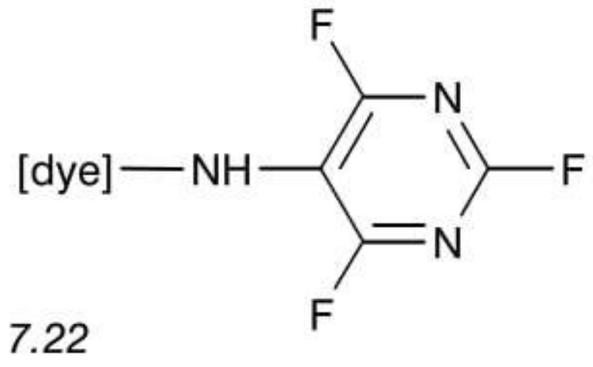
Scheme 7.17

base, however, a mixture of two isomers is formed (Scheme 7.17), the symmetrical 5-chloro-4,6-difluoro arrangement (7.19) and the asymmetrical 5-chloro-2,4-difluoro group (7.20).

Recent work at DyStar has led to the development of 4,5-difluoropyrimidine dyes such as the bluish red 7.21 for the dyeing of cellulosic and polyamide fibres [29]. This reactive system is reported to be superior to the conventional 5-chloro-2,4-difluoro arrangement in structure 7.18, for example. Another novel and interesting system is the 2,4,6-trifluoropyrimidine grouping (7.22) included by Clariant in dyes designed for cellulosic dyeing [20]. This is environmentally more attractive than the 5-chloro-2,4-difluoro system containing the relatively inert 5-chloro substituent that will contribute to AOX values. Dyes based on structure 7.22 should also be stable to perborate attack during laundering.



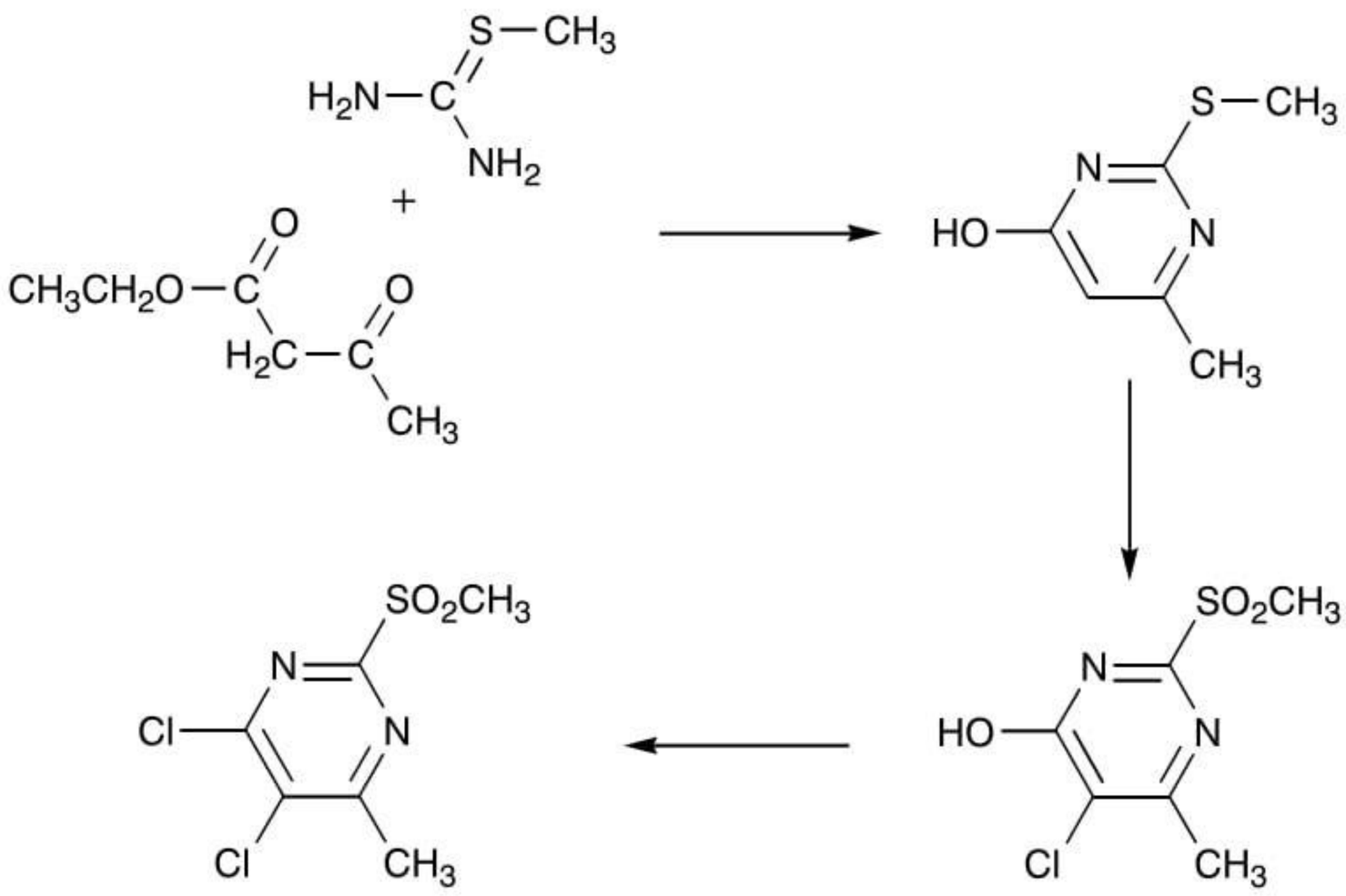
7.21



7.22

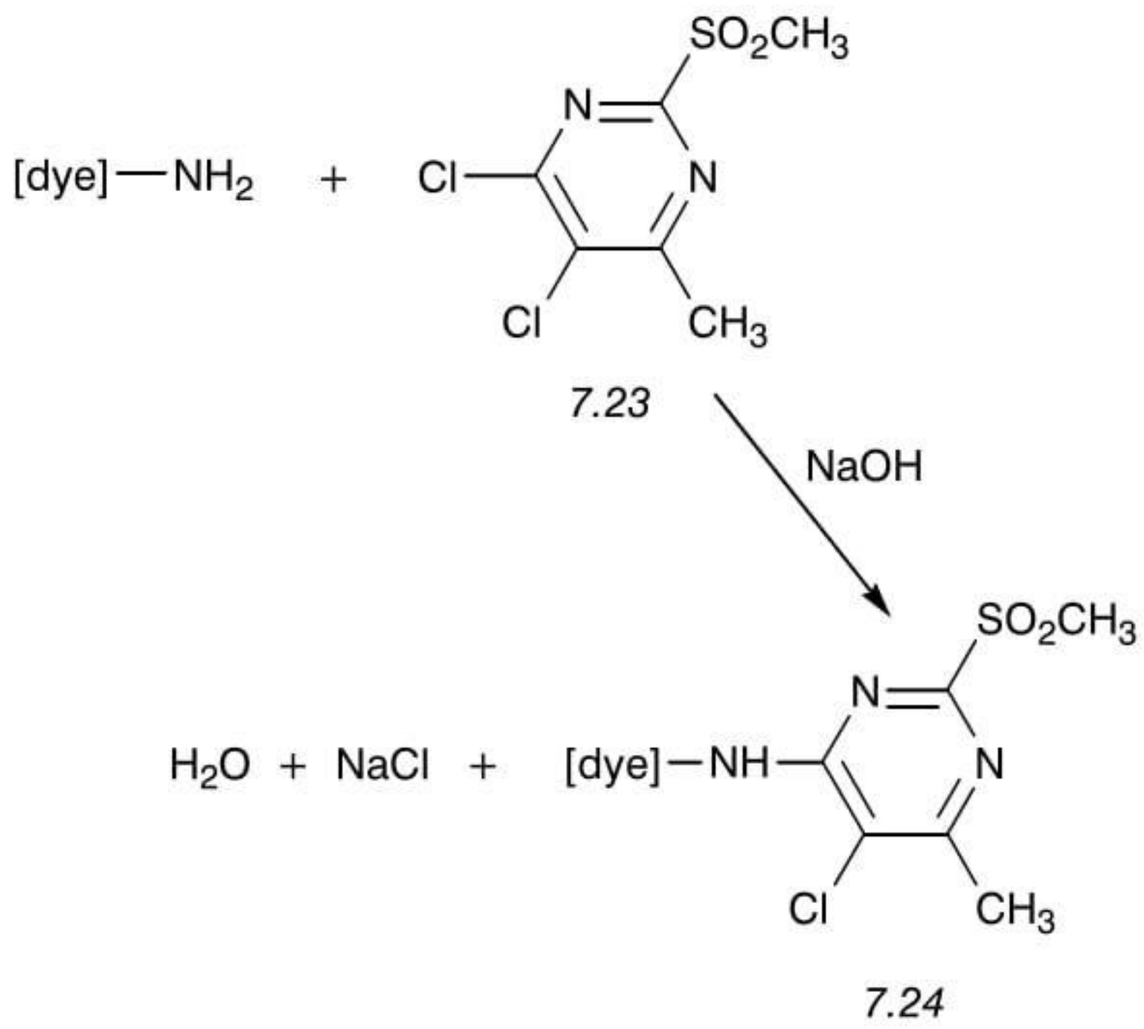
7.3.6 Chloromethylpyrimidine dyes

In the Levafix P (DyStar) range of rapid-fixing reactive dyes for printing, the leaving group was a methylsulphonyl substituent [30]. Preparation of the required reactive intermediate (7.23) involved condensation of S-methylthiourea with ethyl acetoacetate, chlorination of the product, oxidation of the methylthio group and conversion of the hydroxy group to chloro by the action of phosphorus oxychloride (Scheme 7.18). The 4-chloro substituent in structure 7.23 was preferentially eliminated by neutral condensation with the dye base



7.23

Scheme 7.18

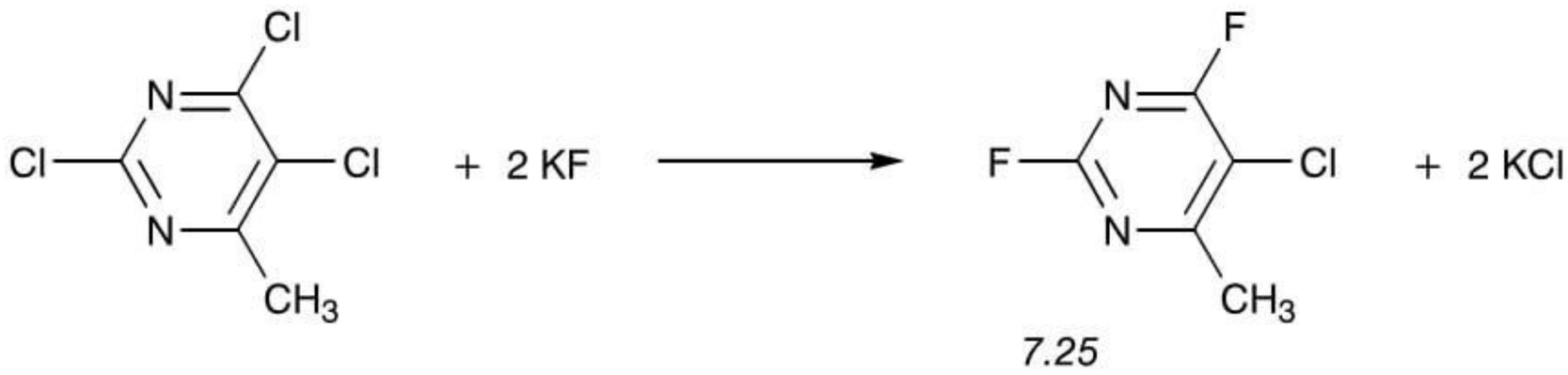


7.24

Scheme 7.19

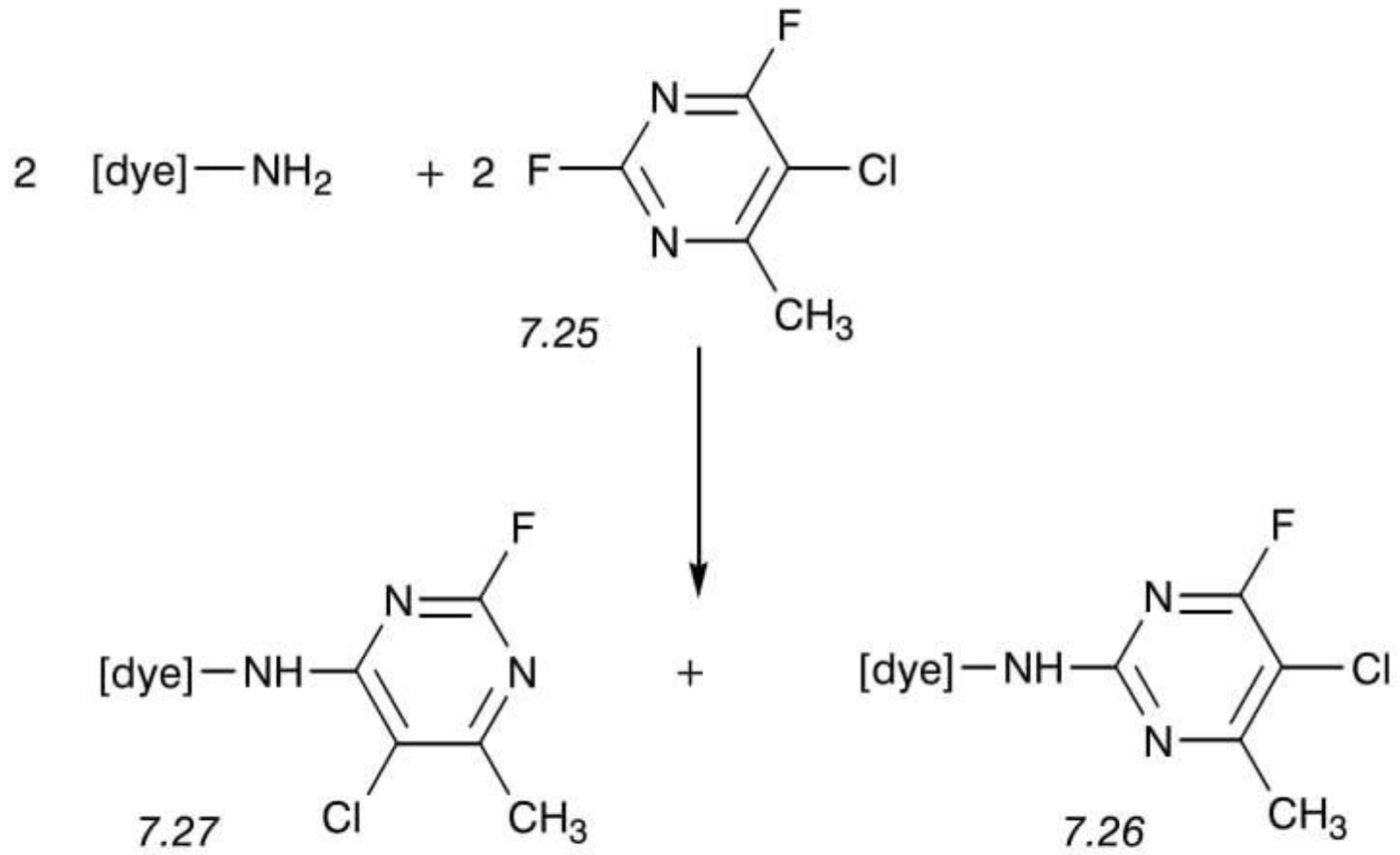
(Scheme 7.19), leading to dyes with a 5-chloro-4-methyl-2-methylsulphonylpyrimidine reactive system (7.24). During reaction with the cellulosic fibre under alkaline conditions, the methylsulphonyl moiety is a particularly effective leaving group and rapid fixation takes place when the reactive system approaches the cellulosate anion.

The Levafix P dyes have been replaced by the Levafix PN (DyStar) range, which is based on the 5-chloro-2-fluoro-4-methylpyrimidine system. These two systems are essentially similar, but the Levafix PN dyes have a fluorine atom as the labile entity rather than the methylsulphonyl grouping. The necessary intermediate 5-chloro-2,6-difluoro-4-methylpyrimidine (7.25) can be made from 4-methyl-2,5,6-trichloropyrimidine by an exchange reaction with potassium fluoride (Scheme 7.20). Condensation with the dye base (Scheme 7.21) will give a mixture of isomers, namely, the 5-chloro-6-fluoro-4-methyl (7.26) and 5-chloro-2-fluoro-4-methyl (7.27) derivatives.



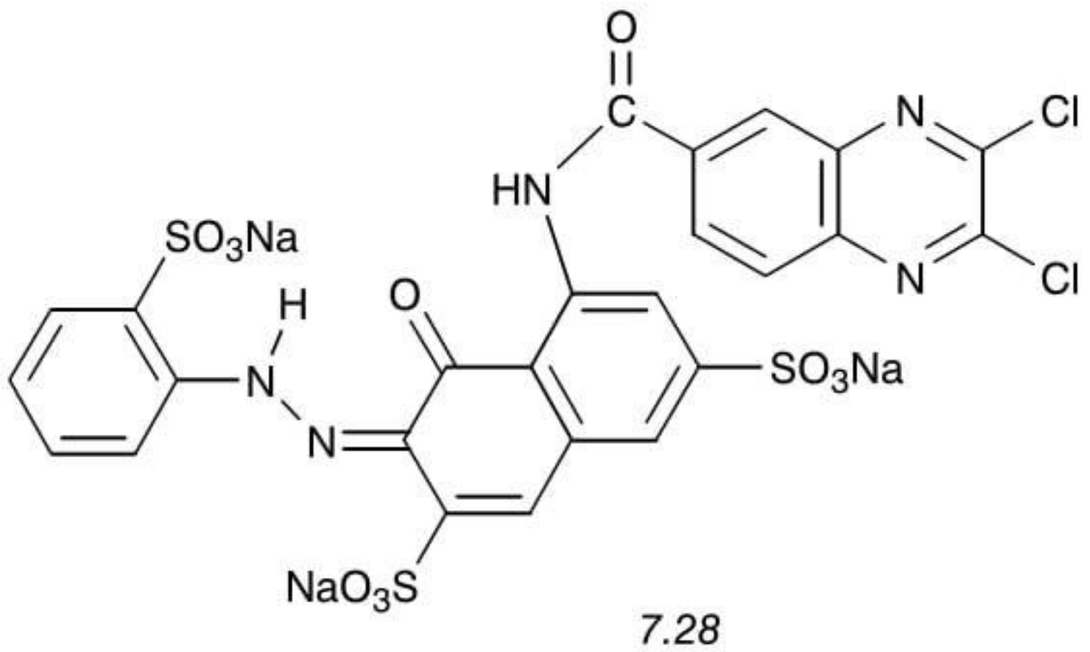
7.25

Scheme 7.20



7.27 *7.26*

Scheme 7.21

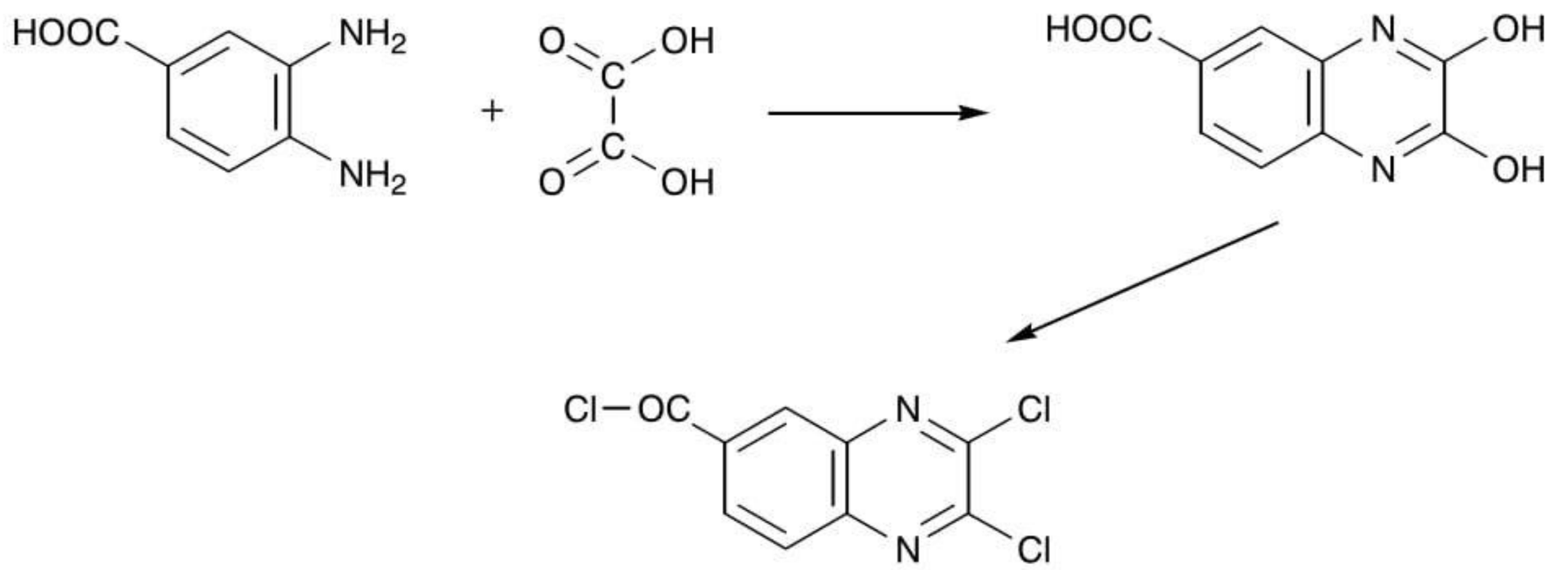


7.28

7.3.7 Dichloroquinoxaline dyes

The reactivity of this system is much higher than that of analogous dichloropyrimidine dyes and comparable with aminofluorotriazine or difluoropyrimidine dyes, optimal fixation being achieved by exhaust dyeing at about 50 °C. Thus these three reactive systems are mutually compatible with one another and all three have been used in members of the Levafix (DyStar) range for long-liquor dyeing. The structure of a typical red monoazo H acid dye containing the dichloroquinoxaline system is illustrated (7.28).

The key intermediate (7.29) required for reaction with the dye base is manufactured from 3,4-diaminobenzoic acid and oxalic acid [15]. These are condensed to yield 2,3-dihydroxyquinoxaline-6-carboxylic acid and the chloro substituents are introduced using phosphorus oxychloride and phosphorus pentachloride (Scheme 7.22). Unlike all other important haloheterocyclic reactive systems, the bridging link between the chromogen and the quinoxaline nucleus is amidic and thus expected to be readily hydrolysed under acidic conditions. The 1,4-diazine ring in the dye–fibre linkage formed by these dyes, like the 1,3-diazine ring present after fixation of the pyrimidine systems, tends to undergo oxidative cleavage when exposed to light or heat under peroxidic conditions. In spite of such potentially severe defects, the commercial success of these dyes over a long period indicates that they do not give rise to serious practical problems under normal circumstances [2].

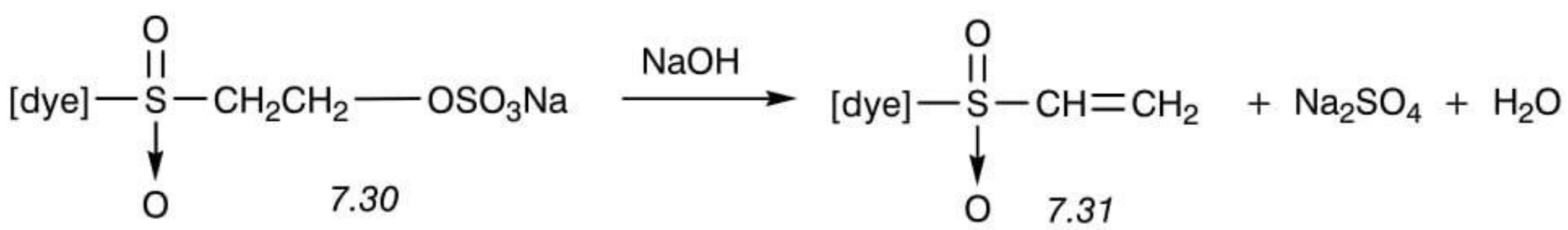


7.29

Scheme 7.22

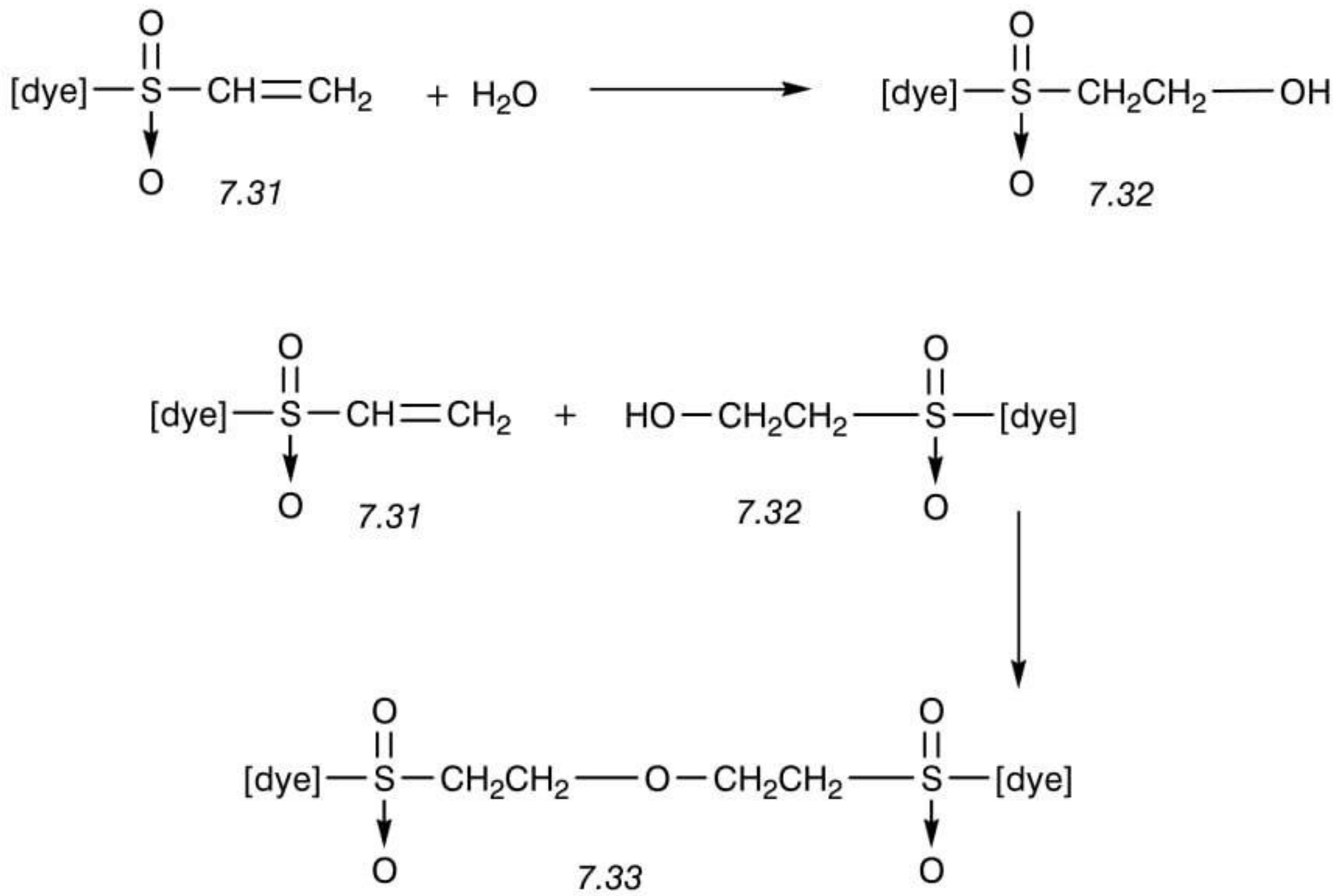
7.3.8 Sulphatoethylsulphone and -sulphonamide dyes

Reactive dyes of the vinylsulphone type (7.31) are normally marketed in the form of the 2-sulphatoethylsulphonyl precursor (7.30) in order to enhance the aqueous solubility and storage stability of the dye. In the presence of alkali the precursor group is converted into the active vinylsulphone form (Scheme 7.23), this being necessary for the reaction with the cellulosic fibre [31–33]. The aqueous solubility of commercial sulphatoethylsulphone dyes generally varies according to the number of sulphonate and sulphate ester groups present. Further reactions at 90–100 °C and pH values above 11.5 in the presence of hydroxide or carbonate anions (Scheme 7.24) result in generation of the 2-hydroxyethylsulphone (7.32) and eventually the diethyl ether form (7.33), which can amount to about 10% of the total dye present [34].



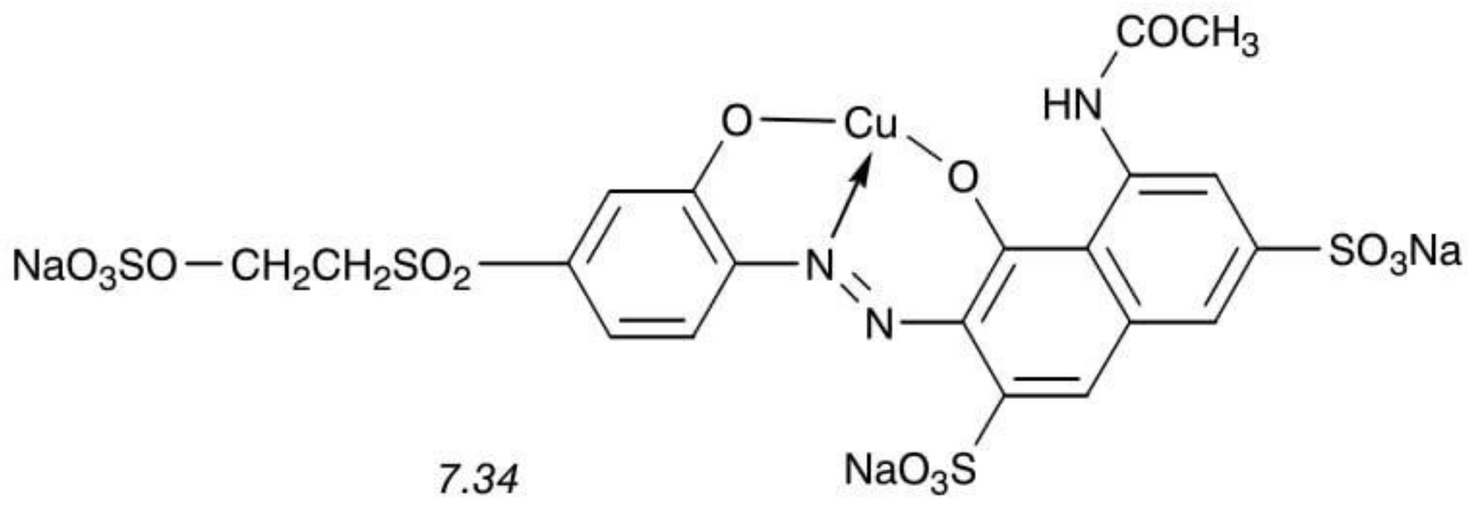
7.30 *7.31*

Scheme 7.23



Scheme 7.24

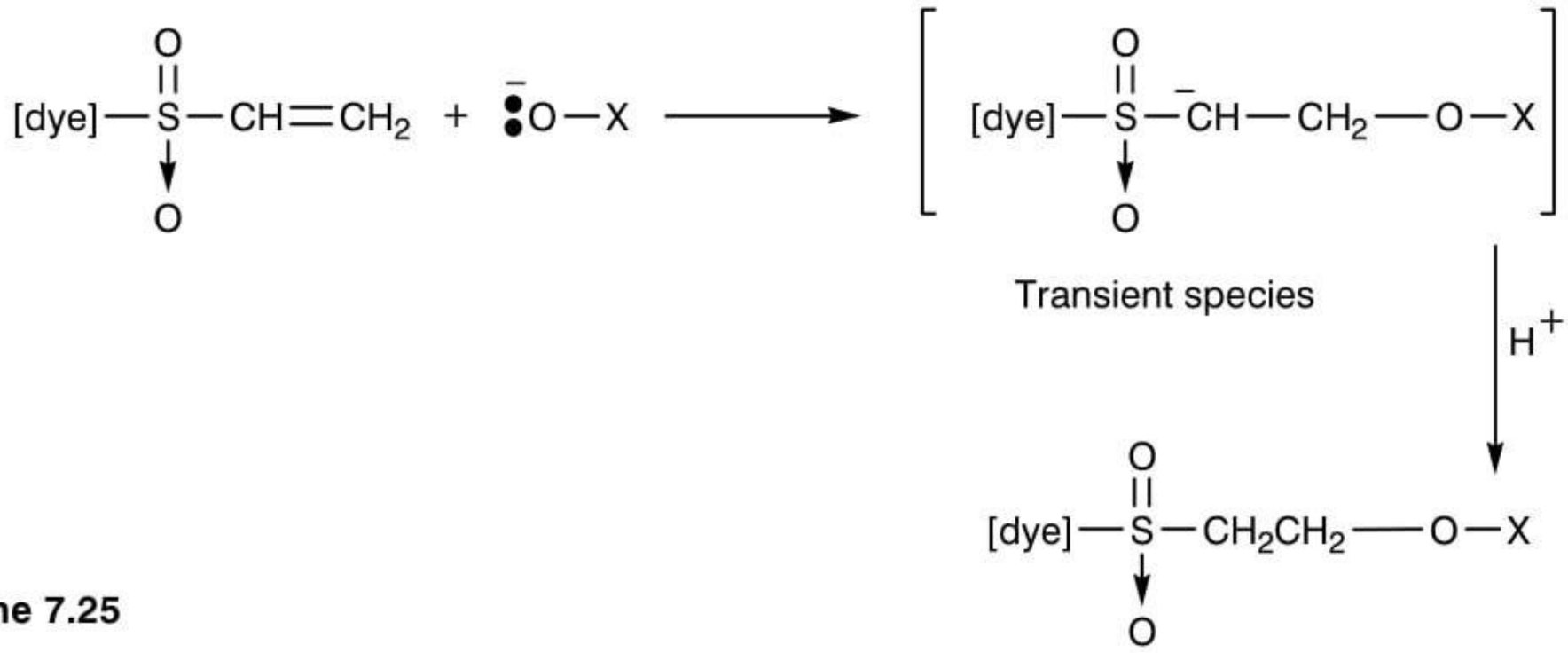
In a recent investigation of the effect of low-frequency ultrasonic waves on the stability of a 1:1 copper-complex phenylazo H acid dye (7.34), reaction rates were determined for the 1,2-elimination of the sulphato group to form the vinylsulphone (Scheme 7.23) and for the hydrolysis step that leads to the 2-hydroxyethylsulphone form [35]. Elimination of the sulphato moiety is strongly accelerated by the presence of the electron-attracting sulphone group situated in the β-position relative to the leaving group and is the rate-determining step [36]. This permits control of the kinetics of the fixation process and has important implications for dye application and level dyeing.



7.34

CI Reactive Violet 5

In contrast to the various haloheterocyclic reactive systems already discussed, the vinylsulphone group reacts by a nucleophilic addition mechanism rather than by substitution. The carbon–carbon double bond forming the vinyl moiety is polarised by the presence of the strongly electron-attracting sulphone group. This polarisation confers a partial positive charge on the terminal carbon atom, favouring nucleophilic addition (Scheme 7.25). The attacking nucleophile (:O–X) can be either a cellulosate anion or a hydroxide ion, the former resulting in fixation to the fibre and the latter in hydrolysis to the 2-hydroxyethylsulphone form.

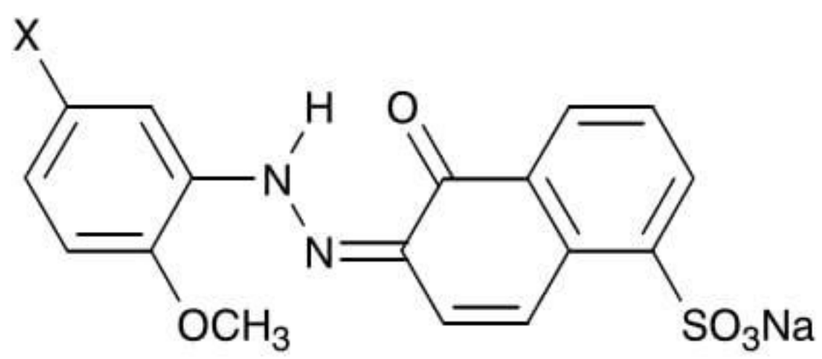


Scheme 7.25

The substantivity of the reactive vinylsulphone is much higher than that of the sulphatoethylsulphone precursor or the hydroxyethylsulphone hydrolysis product. Typical values for primary exhaustion of these three forms of CI Reactive Red 22 (7.35) on unmercerised cotton in the presence of 50 g/l sodium sulphate at neutral pH are given in Table 7.3. This dye system offers potentially high fixation through the highly substantive reactive form combined with excellent wash-off potential owing to the low substantivity of the hydroxyethylsulphone. The disadvantage of the system is the major difference in substantivity between the precursor form and the vinylsulphone because the rate of secondary exhaustion after alkali addition is more difficult to control [37].

Table 7.3 Relationship between substantivity and nature of the reactive group for monofunctional dyes [37]

Reactive group X	Primary exhaustion (%)
$-SO_2CH_2\ CH_2OSO_3Na$	20
$-SO_2CH=CH_2$	80
$-SO_2CH_2\ CH_2OH$	38



7.35

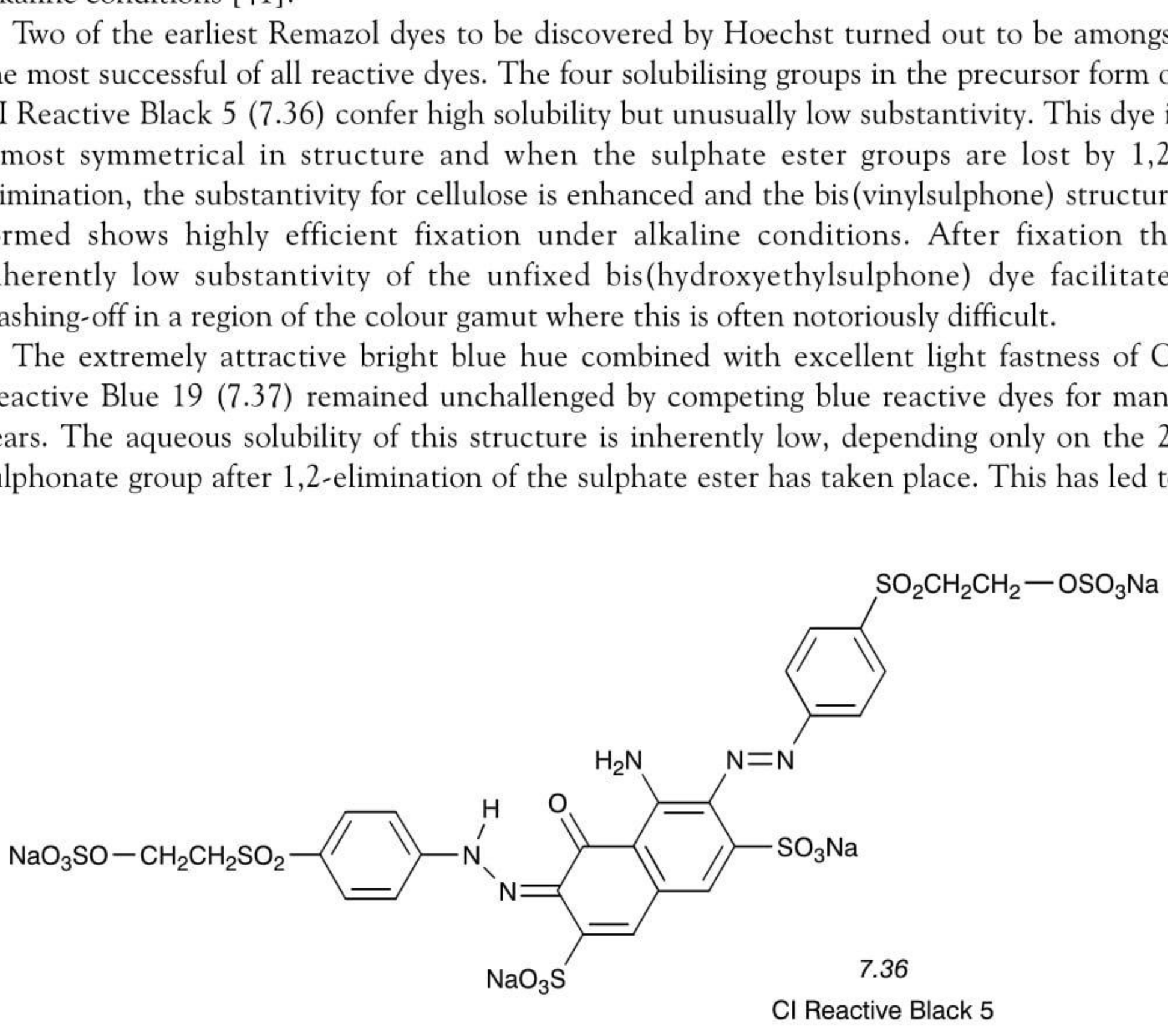
CI Reactive Red 22

The kinetics of homogeneous reaction of several reactive dyes of the vinylsulphone type with methyl-α-D-glucoside (7.9), selected as a soluble model for cellulose, were studied in aqueous dioxan solution. The relative reactivities of the various hydroxy groups in the model compound were compared by n.m.r. spectroscopy and the reaction products were separated by a t.l.c. double-scanning method [38]. The only sites of reaction with the vinylsulphone system were the hydroxy groups located at the C_4 and C_6 positions [39,40].

Sulphatoethylsulphone dyes are intermediate in reactivity between the high-reactivity heterocyclic systems, such as dichlorotriazine or difluoropyrimidine, and the low-reactivity ranges, such as aminochlorotriazine or trichloropyrimidine. Exhaust dyeing temperatures between 40 and 60 °C may be chosen, depending on pH, since caustic soda is often selected to bring about alkaline hydrolysis of the precursor sulphate ester. The substantivity of many of these dyes is markedly lower than that of typical haloheterocyclic dyes. Not only has the vinylsulphone group, unlike the heterocyclic ring systems, little if any inherent affinity for cellulose, but the terminal sulphato group enhances the aqueous solubility of the precursor form before 1,2-elimination to the vinylsulphone. In contrast to the haloheterocyclic systems, the dye–fibre bonds formed by the vinylsulphone dyes are at their weakest under alkaline conditions [41].

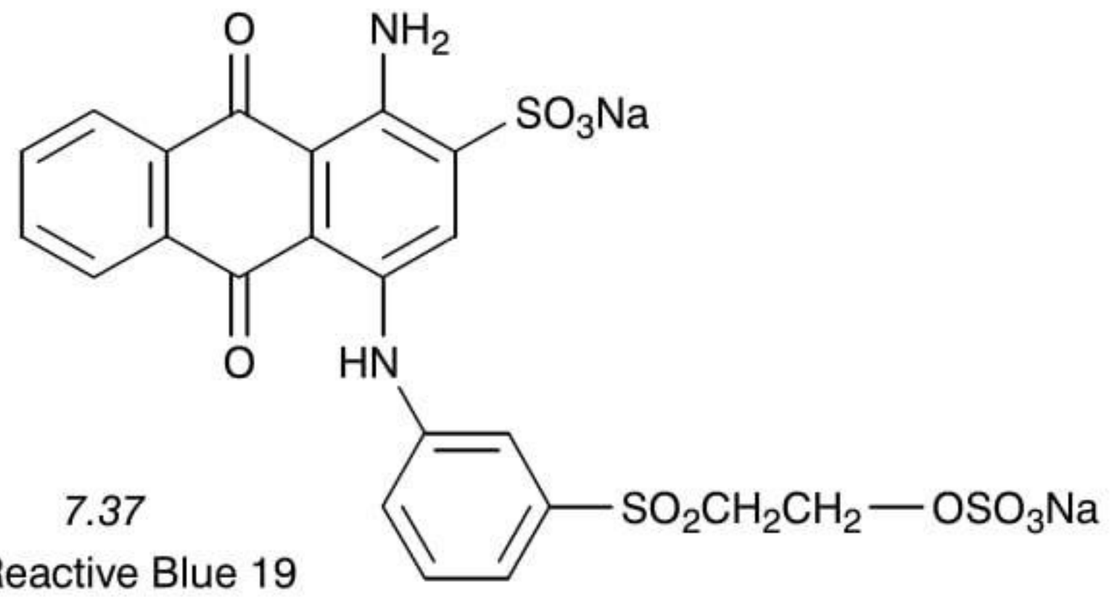
Two of the earliest Remazol dyes to be discovered by Hoechst turned out to be amongst the most successful of all reactive dyes. The four solubilising groups in the precursor form of CI Reactive Black 5 (7.36) confer high solubility but unusually low substantivity. This dye is almost symmetrical in structure and when the sulphate ester groups are lost by 1,2-elimination, the substantivity for cellulose is enhanced and the bis(vinylsulphone) structure formed shows highly efficient fixation under alkaline conditions. After fixation the inherently low substantivity of the unfixed bis(hydroxyethylsulphone) dye facilitates washing-off in a region of the colour gamut where this is often notoriously difficult.

The extremely attractive bright blue hue combined with excellent light fastness of CI Reactive Blue 19 (7.37) remained unchallenged by competing blue reactive dyes for many years. The aqueous solubility of this structure is inherently low, depending only on the 2-sulphonate group after 1,2-elimination of the sulphate ester has taken place. This has led to



7.36

CI Reactive Black 5



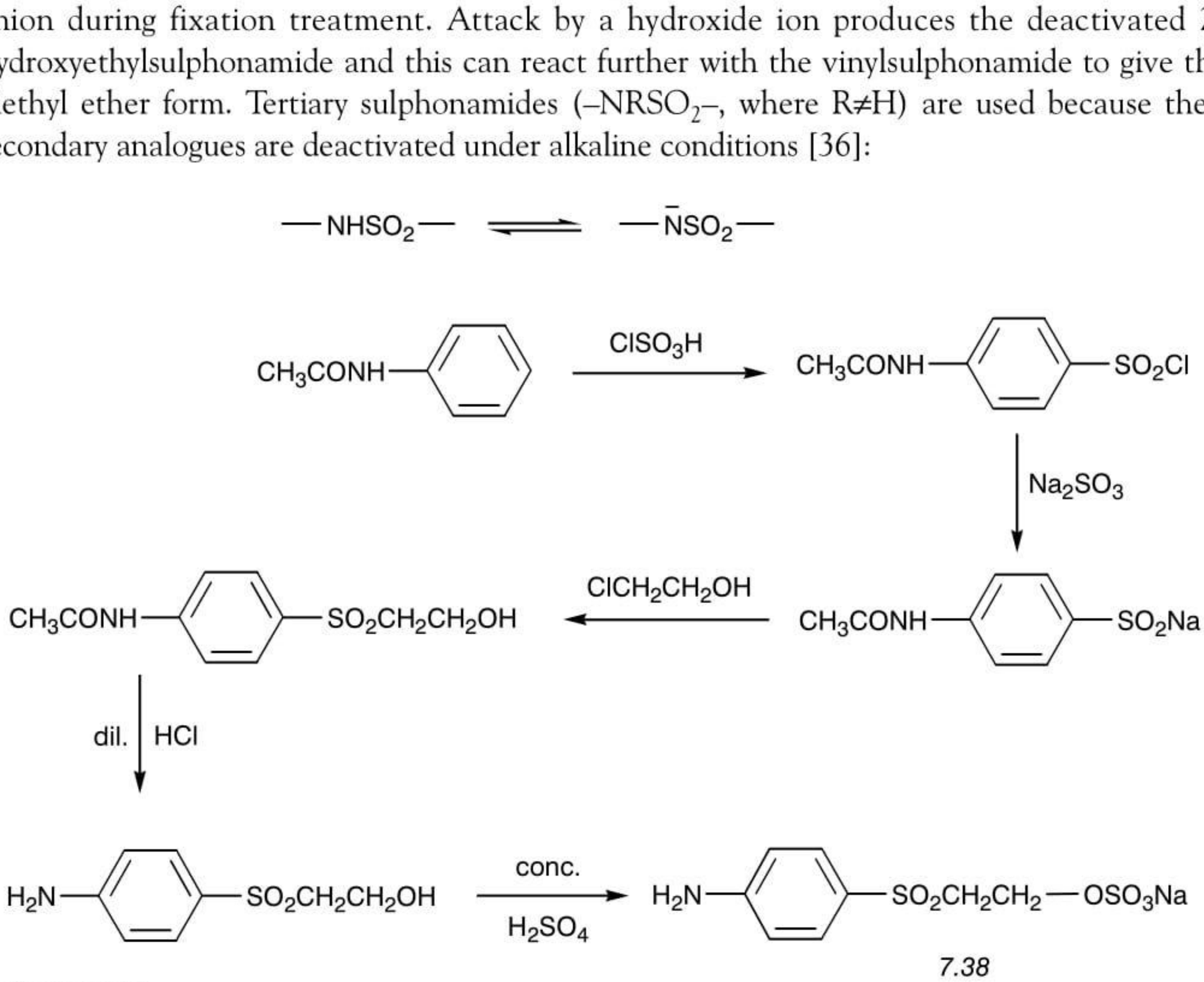
7.37

CI Reactive Blue 19

poor reproducibility and levelling problems, but nevertheless this dye has remained second only to Black 5 in terms of market share amongst reactive dyes.

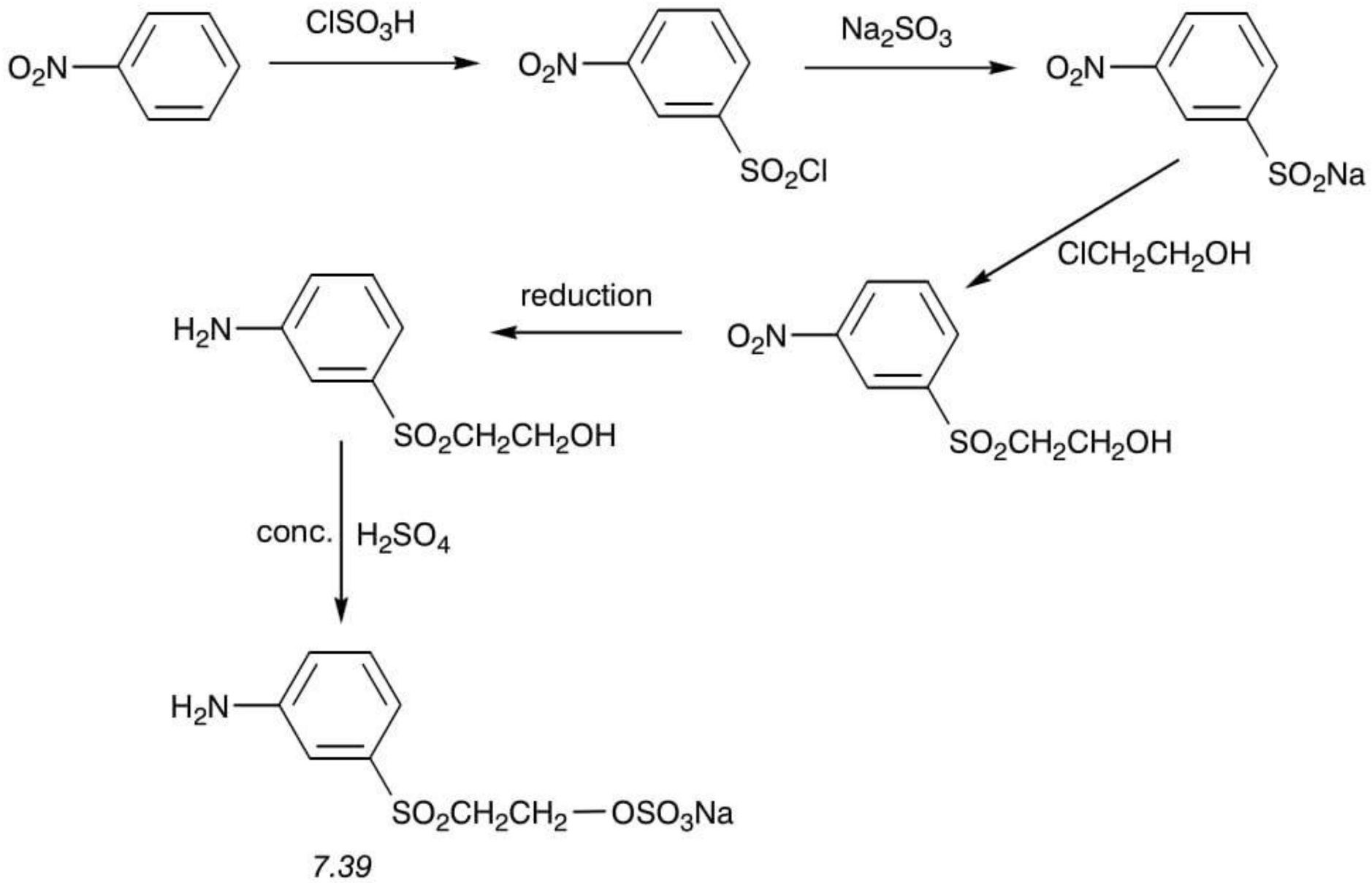
In the various ranges of haloheterocyclic reactive dyes, the reactive system is usually attached to the chromogen via a simple NH imino or methylimino linkage. Preparation of dyes in the vinylsulphone series, however, often requires the synthesis of special arylamine intermediates that contain the reactive system. These are mostly anilines or naphthylamines containing a β-sulphatoethylsulphonyl substituent. The intermediate 4-(β-sulphatoethylsulphonyl)aniline (7.38), used as the diazo component for Black 5 (7.36), is synthesised by the chlorosulphonation of acetanilide, reduction with sodium sulphite and condensation of the sulphinate with 2-chloroethanol to give the 2-hydroxyethyisulphone. Hydrolysis of the acetylamino group and esterification of the hydroxy group with concentrated sulphuric acid yields the desired product (Scheme 7.26). Synthesis of the isomeric 3-(β-sulphatoethylsulphonyl)aniline (7.39), the key intermediate for Blue 19 (7.37), proceeds by chlorosulphonation of nitrobenzene, reduction to the sulphinate, condensation with 2-chloroethanol, reduction of the nitro group and finally formation of the sulphate ester (Scheme 7.27).

A level of reactivity similar to the vinylsulphone dyes is offered by the vinylsulphonamide system. The essential intermediate in this instance is carbyl sulphate (7.40), the cyclic anhydride of ethionic acid, which is readily available from ethylene and sulphur trioxide. Reaction with the amino group of an intermediate or the dye base yields the 2-sulphatoethylsulphonamide (7.41) precursor system directly (Scheme 7.28). As with the sulphatoethylsulphone analogues (Schemes 7.23–7.25), in the presence of alkali these dyes generate the active vinylsulphonamide form and this undergoes nucleophilic addition with a cellulosate anion during fixation treatment. Attack by a hydroxide ion produces the deactivated 2-hydroxyethylsulphonamide and this can react further with the vinylsulphonamide to give the diethyl ether form. Tertiary sulphonamides ($-NRSO_2-$, where $R \neq H$) are used because their secondary analogues are deactivated under alkaline conditions [36]:



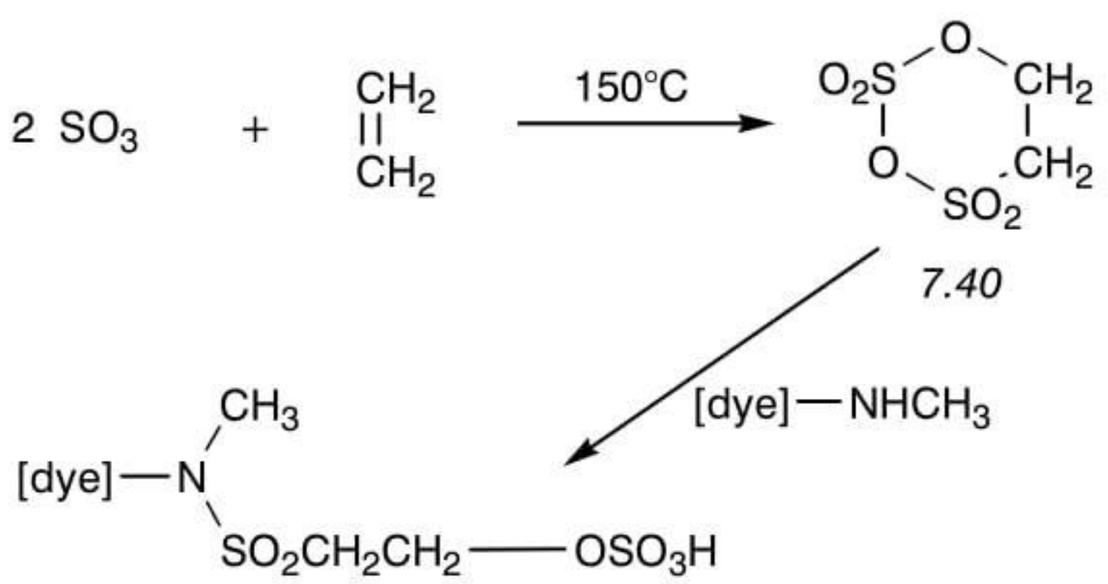
7.38

Scheme 7.26



7.39

Scheme 7.27



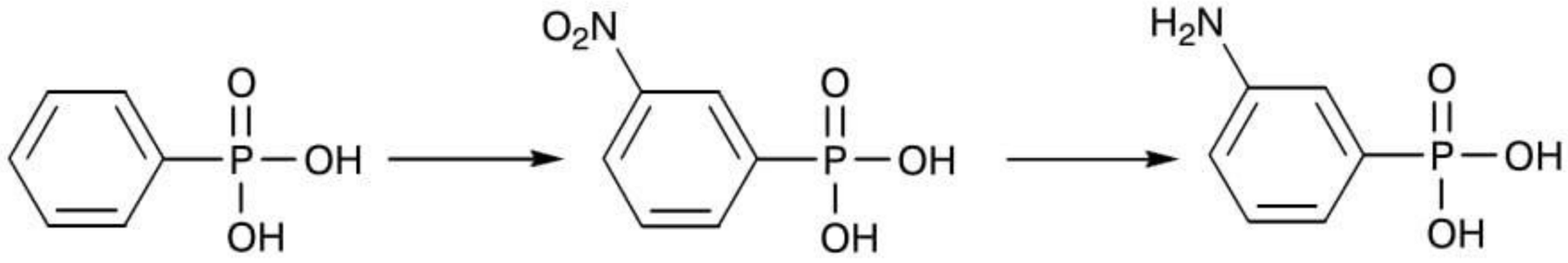
7.41

Scheme 7.28

7.3.9 Acid-fixing reactive dyes

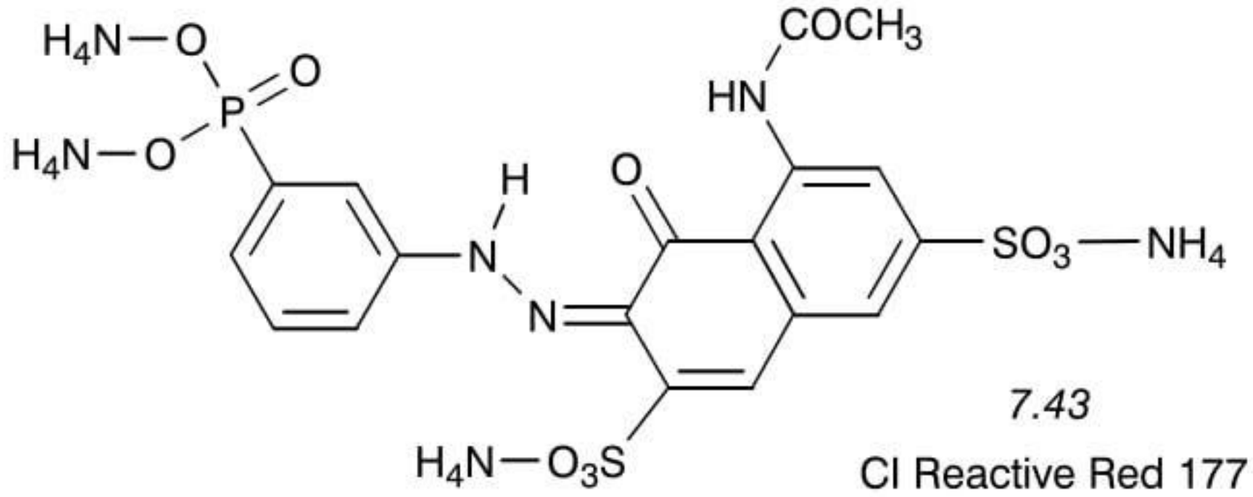
The realisation that the reaction of phosphonic acid derivatives with alcohols to give phosphonate monoesters could be exploited in a reactive dyeing system originated at the Stanford Research Institute in 1973. Four years later the Procion T (ICI) range of dyes containing such groups was launched commercially. They were intended for the continuous dyeing and printing of cellulosic fabrics, especially polyester/cellulosic blends. The unusual conditions of application under mildly acidic conditions (pH 5–6) followed by thermofixation at 200–220 °C were quite different from those of conventional reactive dyes, making them much more compatible with the thermofixation of disperse dyes on the polyester component of the blend.

The entire range of Procion T dyes was based on one versatile intermediate, 3-aminophenylphosphonic acid (7.42), readily manufactured by nitration of phenylphosphonic acid followed by reduction (Scheme 7.29) In most instances this intermediate became the



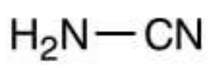
7.42

Scheme 7.29



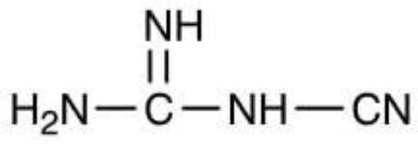
7.43

CI Reactive Red 177



7.44

Cyanamide



7.45

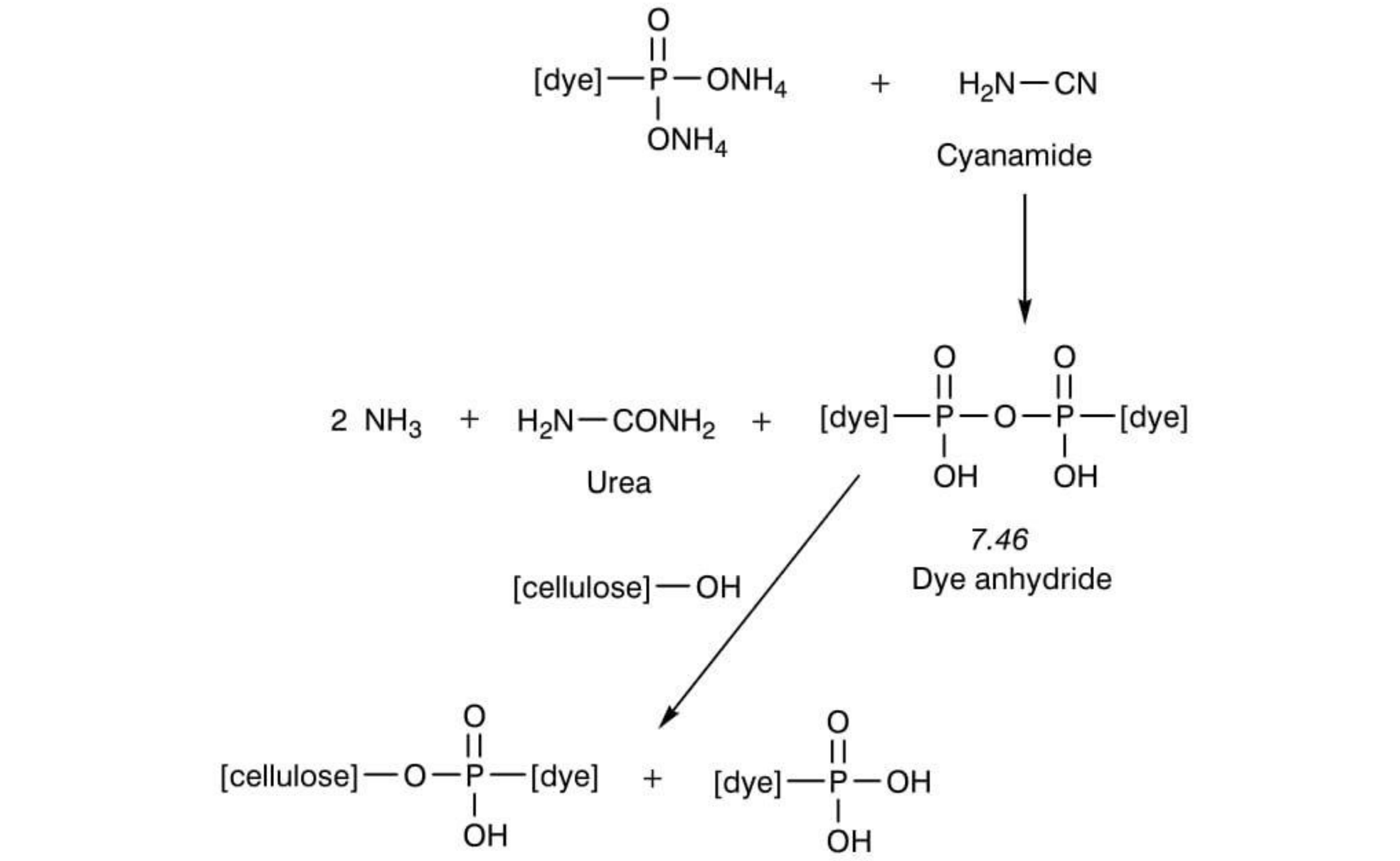
Dicyandiamide

diazo component as in structure 7.43, but it could also be attached to a naphthylamine coupler or to a non-azo chromogen through the imino link [8]. These dyes were marketed as aqueous solutions of their ammonium salts, which generated the free phosphonic acid form under thermofixation conditions.

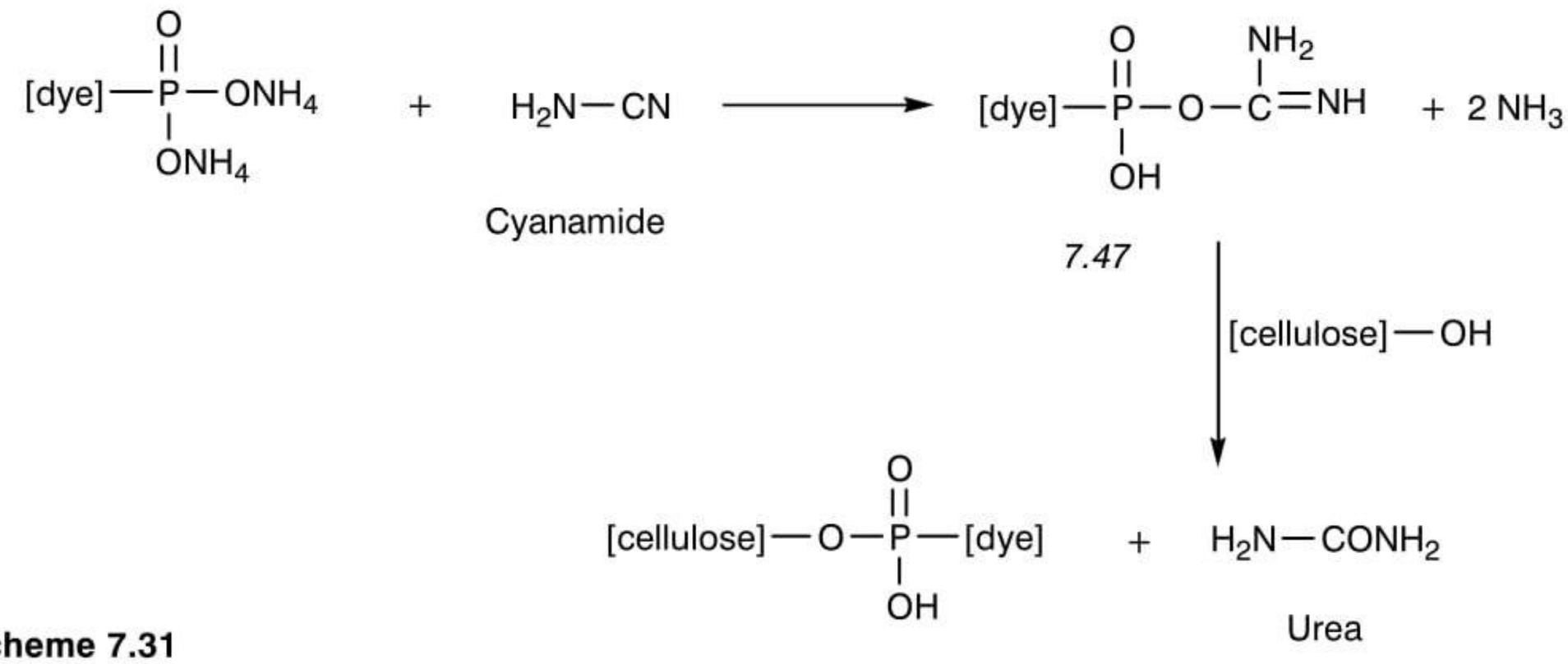
An activating agent of the carbodiimide type, such as cyanamide (7.44) or dicyandiamide (7.45), is necessary to bring about fixation to cellulose and this plays a decisive part in the reactions involved. At least two possible mechanisms of fixation have been proposed and it seems likely that either or both may be operative [8]. In the early work with dyes containing the phosphonic acid group [42], formation of the phosphonic anhydride (7.46) was believed to precede the esterification step, with one dye phosphonate moiety being released for further reaction with another molecule of the carbodiimide activator (Scheme 7.30). It had already been shown [43], that monoesters of arylphosphonic acids could be prepared in high yield by reaction with alcohols in the presence of dicyclohexyl carbodiimide, the esterification proceeding via the arylphosphonic anhydride.

An alternative mechanism [8] entails reaction of cyanamide (or dicyandiamide) with the dye phosphonate to give an O-acylisourea derivative (7.47). This is able to react directly with cellulose to form dye-fibre bonds, urea being released as the anticipated by-product (Scheme 7.31). In support of this mechanism, it is known that O-acylisourea derivatives of arylcarboxylic acids react readily with alcohols and this constitutes an efficient route for the preparation of carboxylic esters [44].

More recently, the fixation efficiency on cotton of CI Reactive Red 177 (7.43) and its 4-carboxyphenylazo analogue in the presence of various carbodiimides (including 7.44 and 7.45) was investigated, as well as homogeneous reactions of selected carboxylic acids with alcohols (including acetylcellulose in acetone). The carboxylated dye reacted more effectively with cotton cellulose in the presence of cyanamide rather than dicyandiamide,



Scheme 7.30



Scheme 7.31

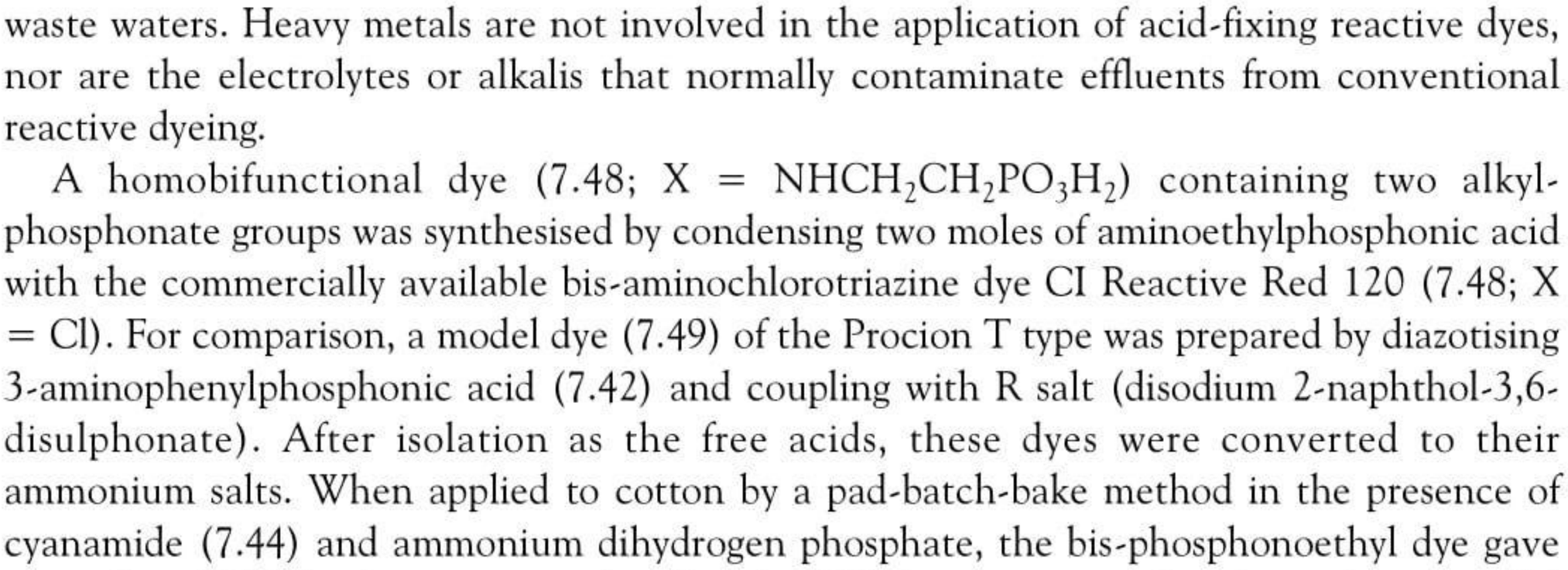
whereas either type of carbodiimide was fully effective with the dye phosphonate. Loss of carbodiimide by hydrolysis to urea, followed by thermal decomposition to ammonia and carbon dioxide is the most important factor limiting the optimum level of dye fixation [45].

Further work with the same dye (7.43) and carbodiimides (7.44 and 7.45) concentrated on this problem of limited efficiency. Cotton fabric padded with the dye phosphonate solution was aftertreated with the carbodiimide dissolved in various alcoholic solutions to avoid hydrolytic decomposition. Under these conditions cyanamide was much more effective than dicyandiamide. With conventional reactive dyes the efficiency of the dye–fibre reaction is limited by competing hydrolysis of the active dye. Although phosphonated or carboxylated reactive dyes do not hydrolyse, their level of fixation is limited by competing hydrolysis of the carbodiimide activator [46].

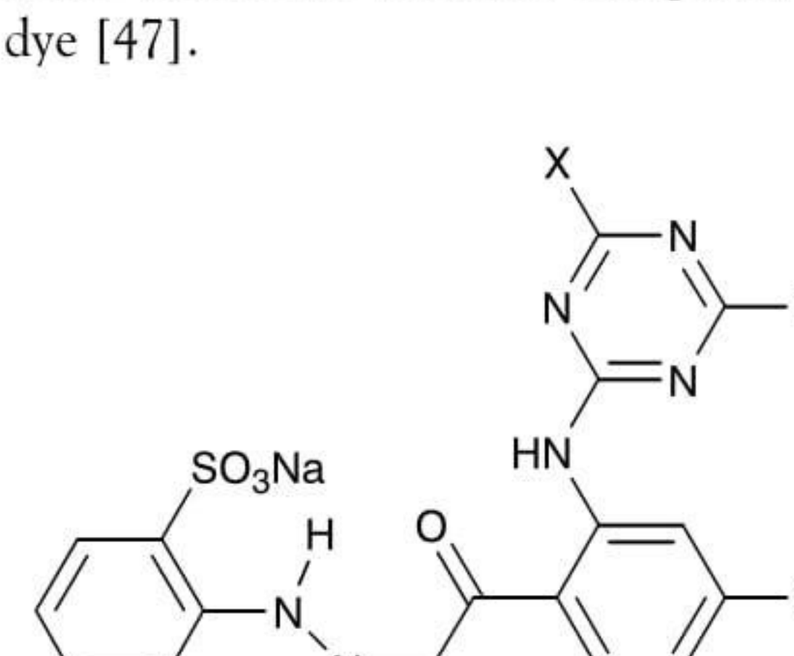
Although offering significant benefits, the Procion T (ICI) dyes suffered from certain technical drawbacks. These included dye migration during drying, especially on heavy fabrics such as corduroy, and strength losses of cellulosic fabrics during thermofixation under the acidic conditions required. The main reasons for their withdrawal in 1987, however, were economic rather than technical [8].

Interest in acid-fixing reactive dyes has remained active because of their environmentally attractive features (section 1.7). The freedom from competing hydrolytic reactions potentially offers exceptionally high fixation, extreme stability of the dye–fibre bonds and complete suitability of the unfixed dyes for recycling. In contrast to conventional reactive dyes, sensitisation problems arising from reaction with skin proteins are not anticipated. Unlike the haloheterocyclic reactive dyes, there is no risk of release of AOX compounds to waste waters. Heavy metals are not involved in the application of acid-fixing reactive dyes, nor are the electrolytes or alkalis that normally contaminate effluents from conventional reactive dyeing.

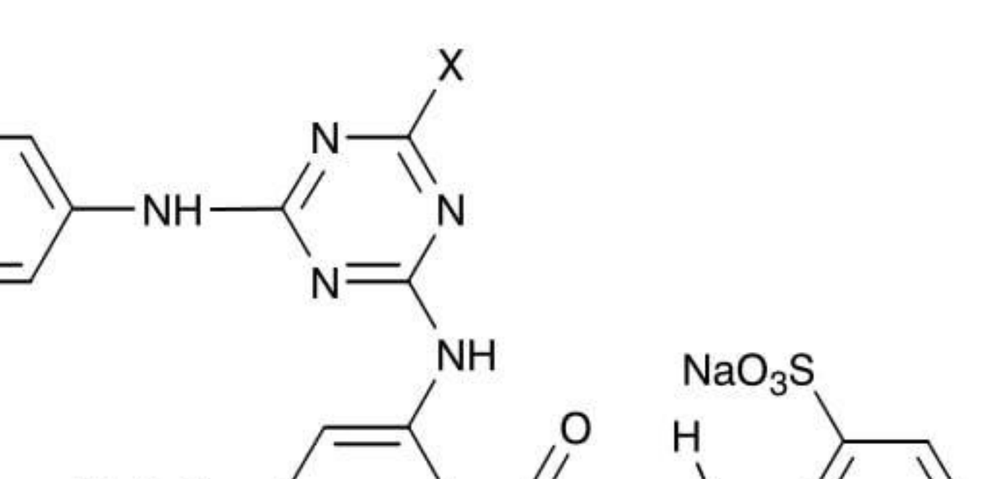
A homobifunctional dye (7.48; X = $NHCH_2CH_2PO_3H_2$) containing two alkylphosphonate groups was synthesised by condensing two moles of aminoethylphosphonic acid with the commercially available bis-aminochlorotriazine dye CI Reactive Red 120 (7.48; X = Cl). For comparison, a model dye (7.49) of the Procion T type was prepared by diazotising 3-aminophenylphosphonic acid (7.42) and coupling with R salt (disodium 2-naphthol-3,6-disulphonate). After isolation as the free acids, these dyes were converted to their ammonium salts. When applied to cotton by a pad-batch-bake method in the presence of cyanamide (7.44) and ammonium dihydrogen phosphate, the bis-phosphonoethyl dye gave more than 90% fixation, compared with only 54% for the mono-phosphonophenyl model dye [47].



7.48

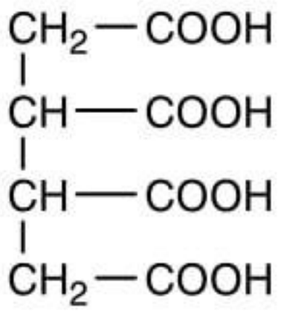


7.49



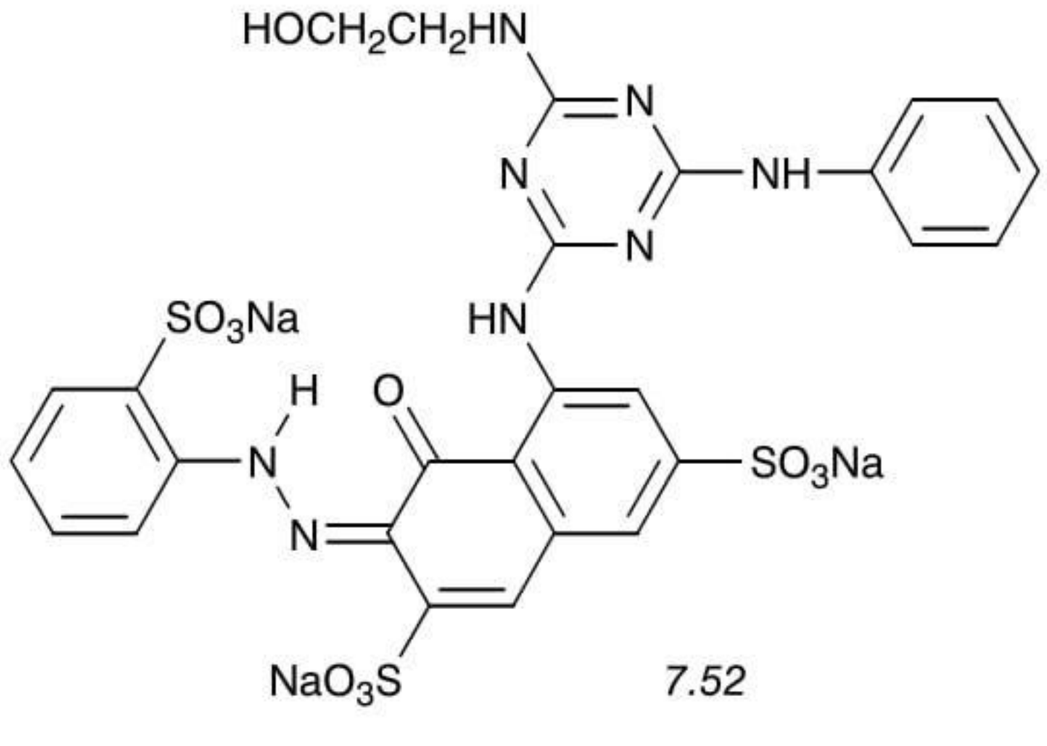
7.50

EDTMP



7.51

BTCA

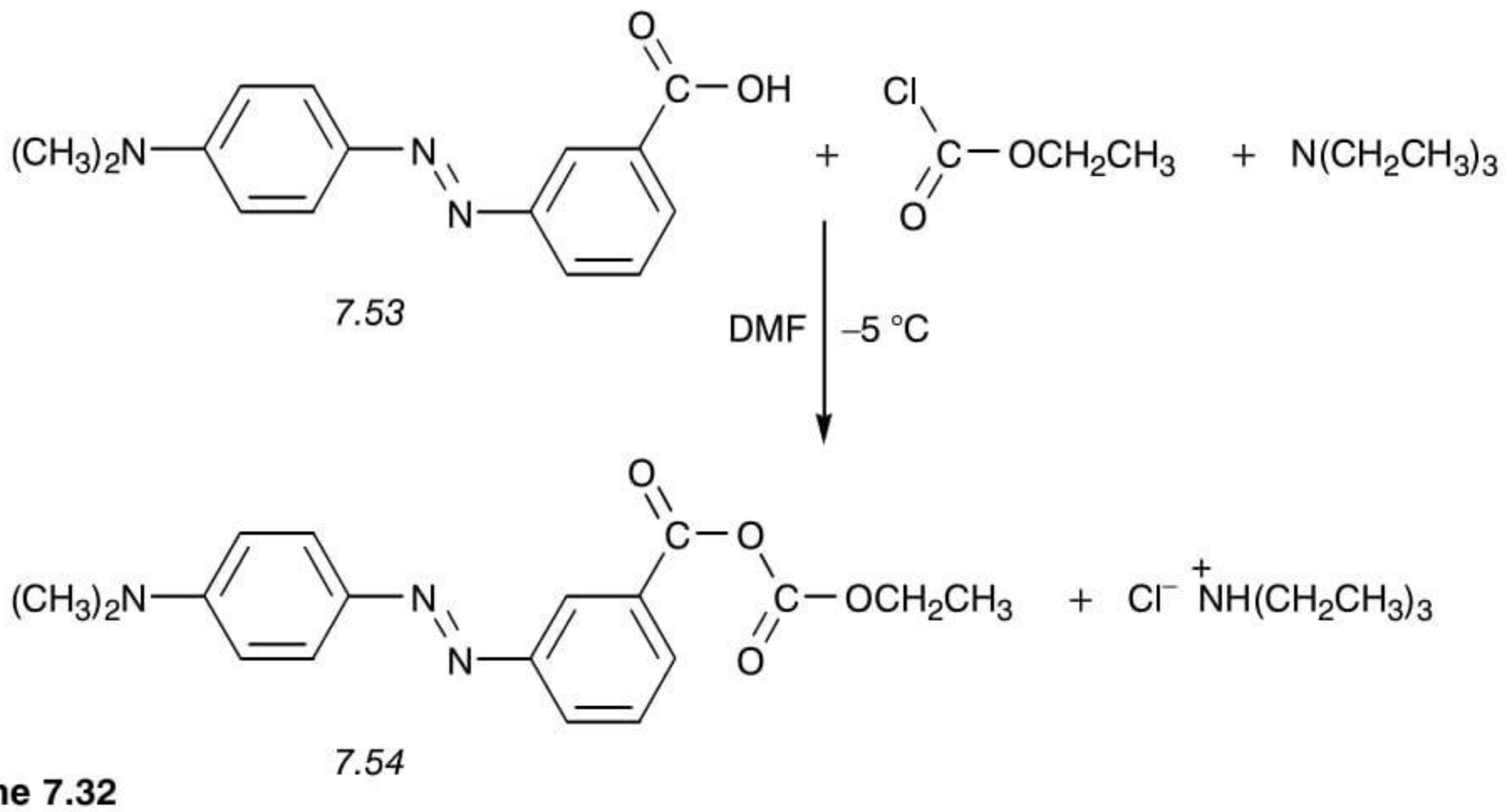


7.52

An interesting variation on this type of pad-bake fixation system is to use the commercial sequestering agent ethylenediaminetetramethylphosphonic acid (7.50) as a crosslinking agent to react with cotton cellulose and with a dye containing nucleophilic hydroxyethyl groups. A suitable bis-hydroxyethyl dye structure (7.48; X = $NHCH_2CH_2OH$) of this kind was derived by condensing two moles of ethanolamine with CI Reactive Red 120 (7.48; X = Cl). Dye fixation values exceeding 80% were achieved in this way in the presence of cyanamide as dehydrating catalyst [47].

A similar concept evaluated recently depends on pad-bake application of the commercial crosslinking agent butane-1,2,3,4-tetracarboxylic acid (7.51) capable of esterification reactions with a hydroxyethyl group in the dye molecule and with cellulose OH groups. The hydroxyethyl derivative (7.52) was made by condensing ethanolamine with the chlorotriazine group in the commercial dye CI Reactive Red 3 (7.2). Thermofixation treatment at 170 °C in the presence of sodium hypophosphite (NaH_2PO_2) as catalyst gave dyeings of high fastness to washing but no fixation values were reported [48].

A tetracarboxylated derivative was prepared recently by reaction of a commercial reactive dye with two molar equivalents of aspartic acid. This novel derivative was evaluated by pad–dry–bake and pad-batch–bake methods under slightly acidic conditions in the presence of cyanamide as activator [49]. An interesting disperse dye containing a novel reactive anhydride system (7.54) was prepared from the parent dye carboxylate (7.53) by reaction with ethyl chloroformate in the presence of a tertiary base (Scheme 7.32). Such dyes will



7.53 *7.54*

Scheme 7.32

react with wool at the boil and pH 6–7, liberating ethanol as a by-product of the reaction. Unlike conventional reactive dyes for wool, no aftertreatment with ammonia is necessary to attain optimum fastness [50].

7.4 BIFUNCTIONAL SYSTEMS

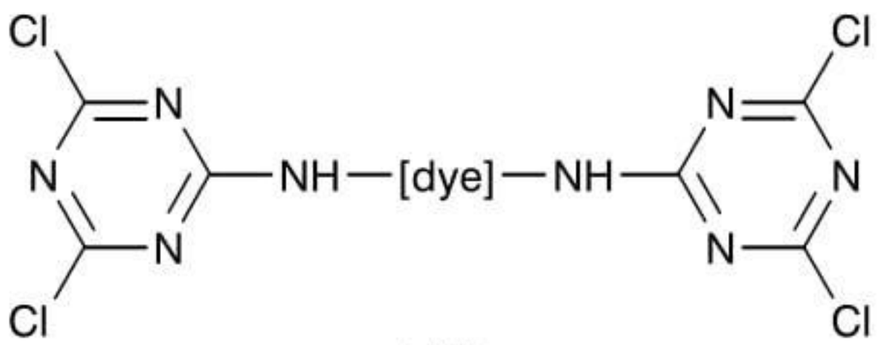
Evidence soon emerged in the 1960s that monofunctional reactive dyes containing two reactive centres, such as the dichlorotriazines, were capable of forming crosslinks between adjacent cellulose chains (7.8). This resulted in cellulosic fibres that had been dyed in this way showing anomalous behaviour in cuprammonium solubility tests [51]. Individual members of the early ranges of reactive dyes, including CI Reactive Black 5 (7.36), contained more than one reactive system but it was not until around 1970 that ICI introduced the Procion Supra (printing) and Procion H-E (dyeing) ranges of high-fixation dyes containing two aminochlorotriazine groups per molecule.

If other factors are equal, the use of a reactive dye containing two reactive groups rather than its analogue with only one reactive group per molecule increases the fixation from a typical 60% to approximately 80% on average in exhaust dyeing. In pad–batch processes the corresponding fixation efficiency levels are about 75% and 95% respectively [52]. Bifunctional systems containing two different kinds of reactive group are popular in exhaust dyeing and gaining ground, especially on account of their relative insensitivity of fixation to fluctuations in dyeing temperature [53].

A detailed study of representative bis(aminochlorotriazine) dyes, as well as other potentially crosslinking reactive systems (dichlorotriazine, chloromethoxytriazine, trichloropyrimidine, chlorodifluoropyrimidine and dichloroquinoxaline) provided convincing evidence of the extent of crosslinking that could take place. Crosslinking was non-existent or relatively insignificant for typical pad–batch dyeings at ambient temperature, but thermal fixation by the pad–dry–steam method resulted in much more prevalent crosslinking by dye molecules [54].

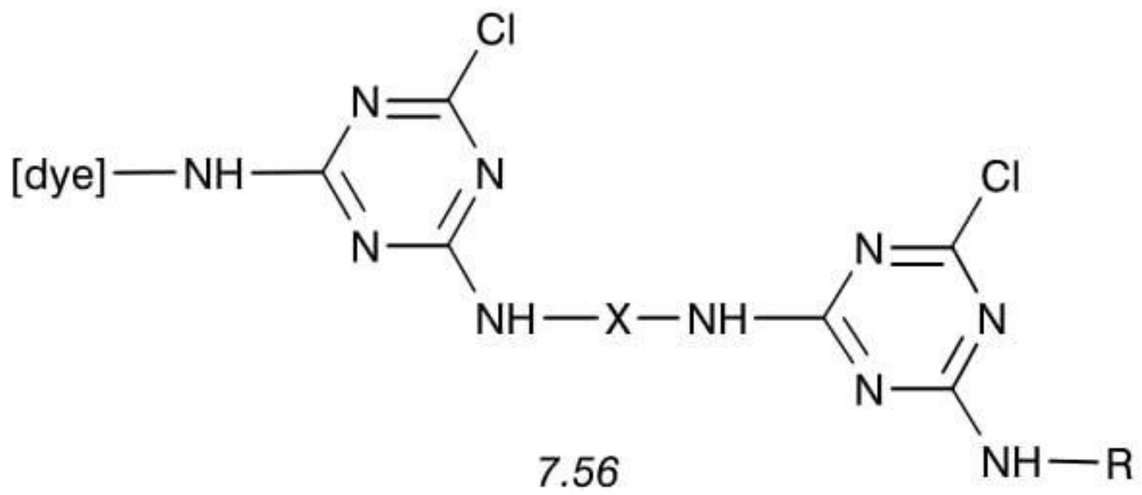
7.4.1 Bis(aminochlorotriazine) dyes

Several different approaches have been employed in order to build the bifunctionality concept into known dye chromogens. In the case of bis(dichlorotriazine) dyes, which were not exploited commercially, only the arrangement 7.55 is feasible. The difficulty of introducing sufficient extra sulphonic acid groups into the chromogen to compensate for the presence of these two reactive systems and provide adequate solubility and mobility at the low dyeing temperature necessary for such highly reactive molecules proved insuperable.

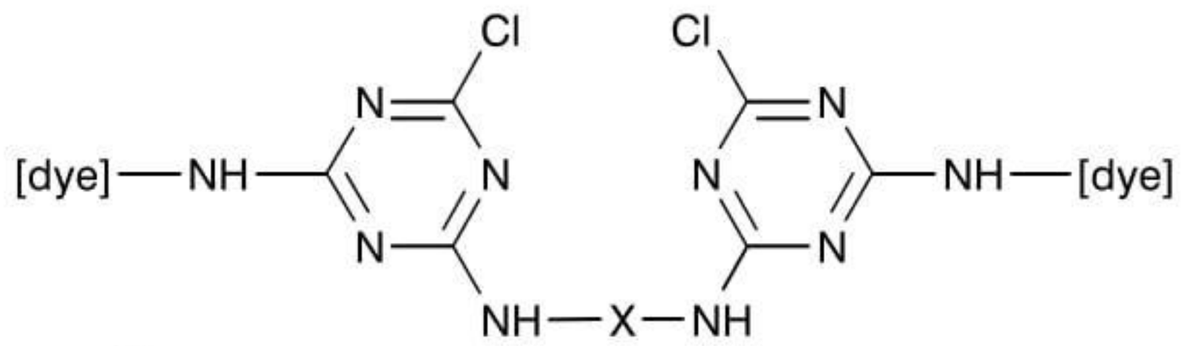


7.55

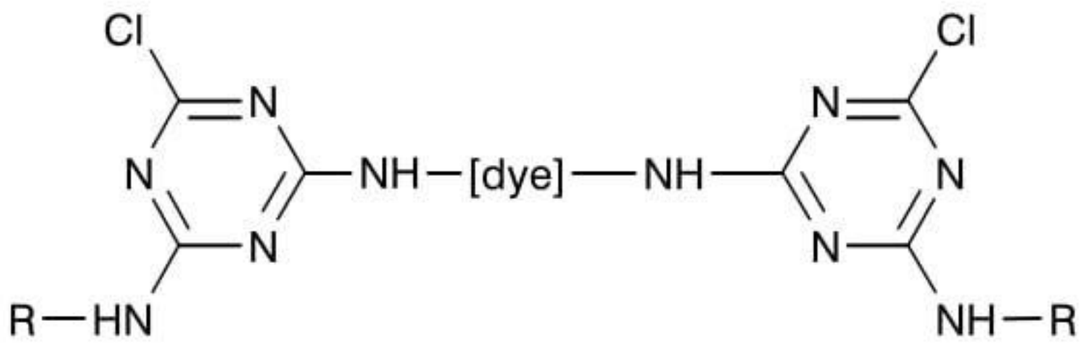
The versatility of the bis(aminochlorotriazine) concept is much greater, with three different arrangements being possible (7.56–7.58; RNH_2 = arylamine, –NH–X–NH– = linking diamine). In the Procion Supra (ICI) dyes marketed for textile printing, the relatively more costly 7.56 pattern was preferred for technical reasons. Arrangements 7.57 and 7.58 have been used to design low-reactivity dyes of high substantivity intended primarily for exhaust dyeing. Structures of the 7.57 type are symmetrical about the central linking diamine and most of them contain a simple yellow, orange or red monoazo chromogen at each end of the molecule, CI Reactive Red 120 (7.48; X = Cl) being a typical example. Blue and green bis(aminochlorotriazine) dyes, including those derived from non-azo chromogens as well as the twice-coupled H acid disazo blues (7.59), usually fit the general structure 7.58.



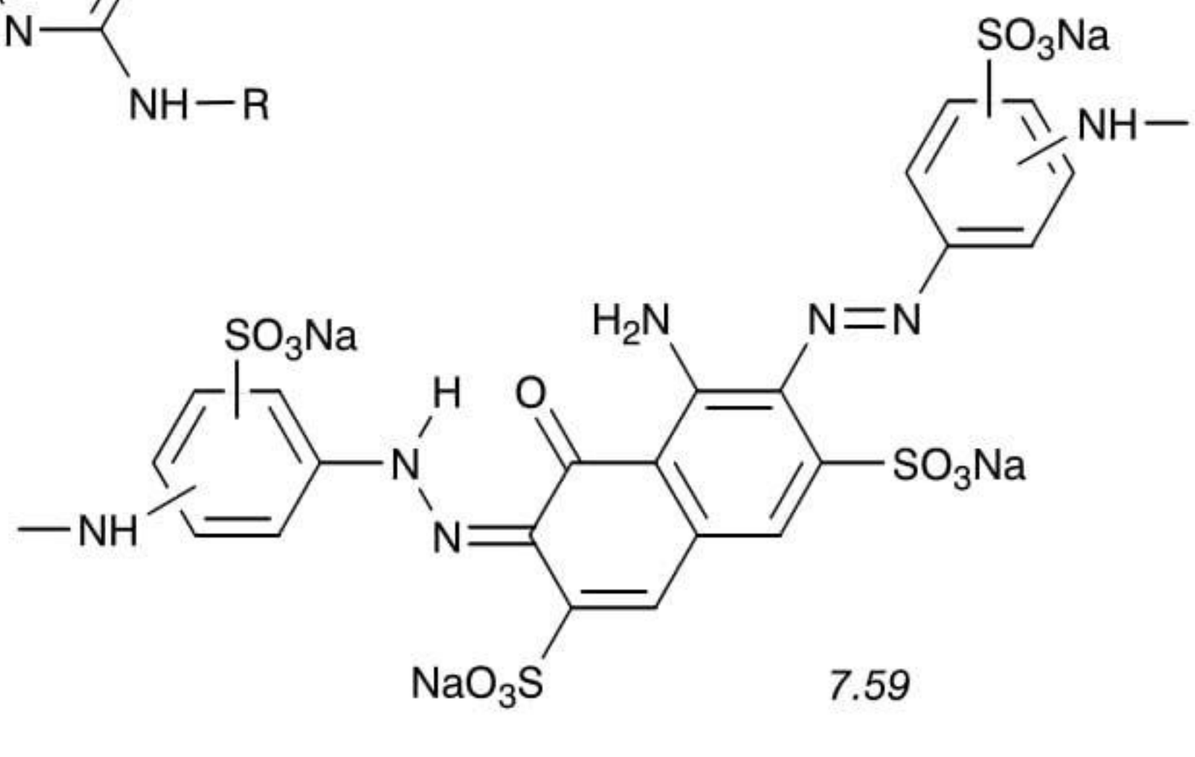
7.56



7.57



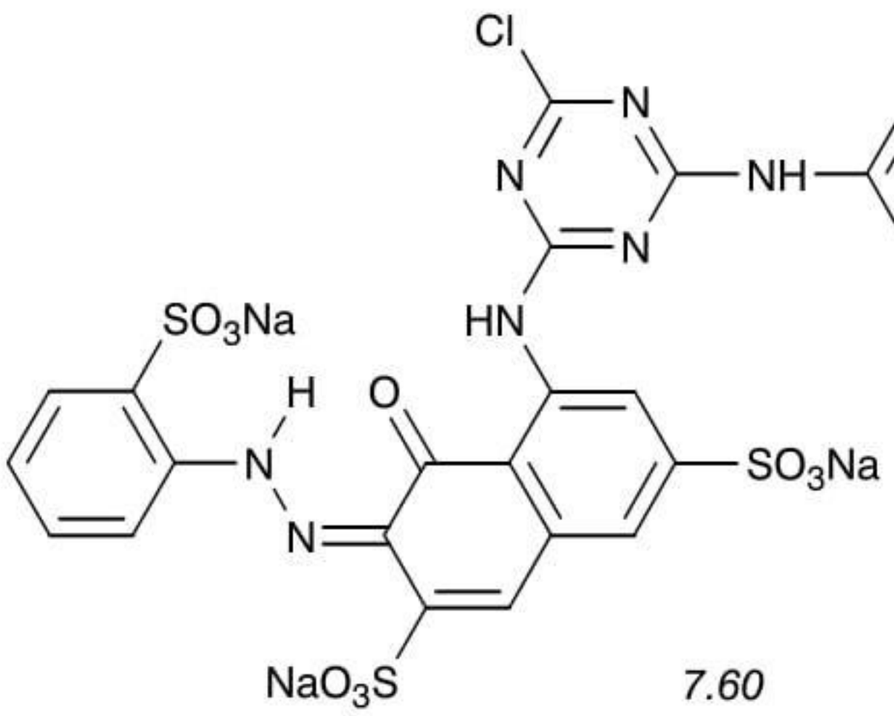
7.58



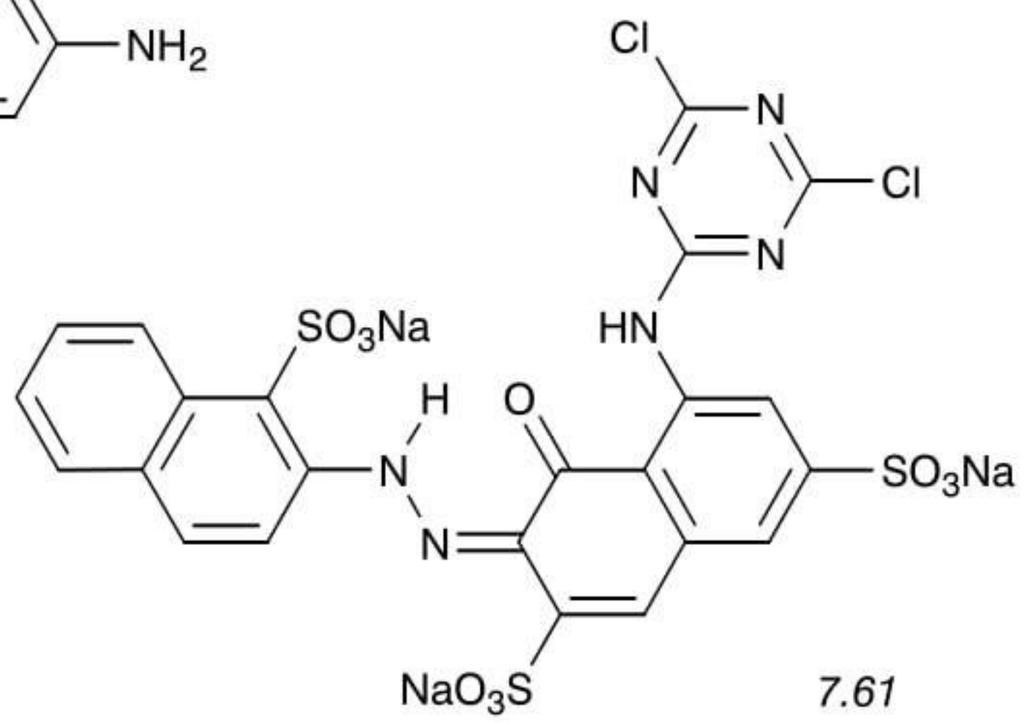
7.59

Unsymmetrical analogues of type 7.57 can be readily prepared using phenylene-1,3-diamine-4-sulphonic acid as the central linking unit, because the bulky sulpho grouping protects the 3-amino group by steric hindrance whilst monoacylation takes place at the 1-amino position. This approach, however, introduces a generally undesirable extra sulphonic acid group into the structure. Recent research has demonstrated, however, that it is possible to monoacylate phenylene-1,3-diamine itself using one dichlorotriazine dye and to react the

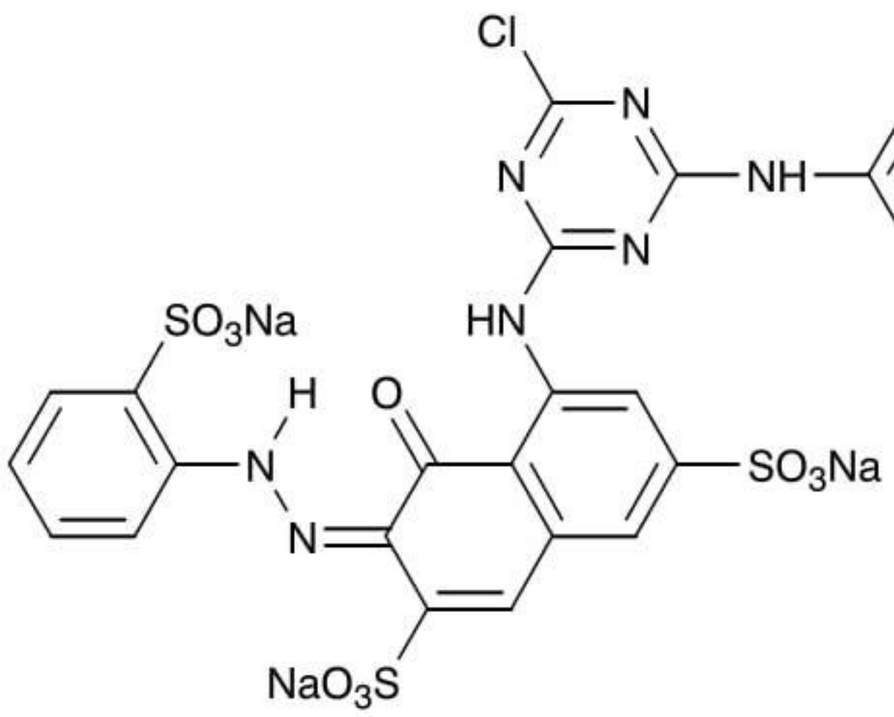
product with a different dichlorotriazine dye to yield novel unsymmetrical structures [55]. Thus CI Reactive Red 1 (7.1) was condensed with one mole of the diamine to give the intermediate 7.60. In the second acylation step the analogous dye CI Reactive Red 11 (7.61) was used, resulting in the formation of the unsymmetrical bis(aminochlorotriazine) dye 7.62.



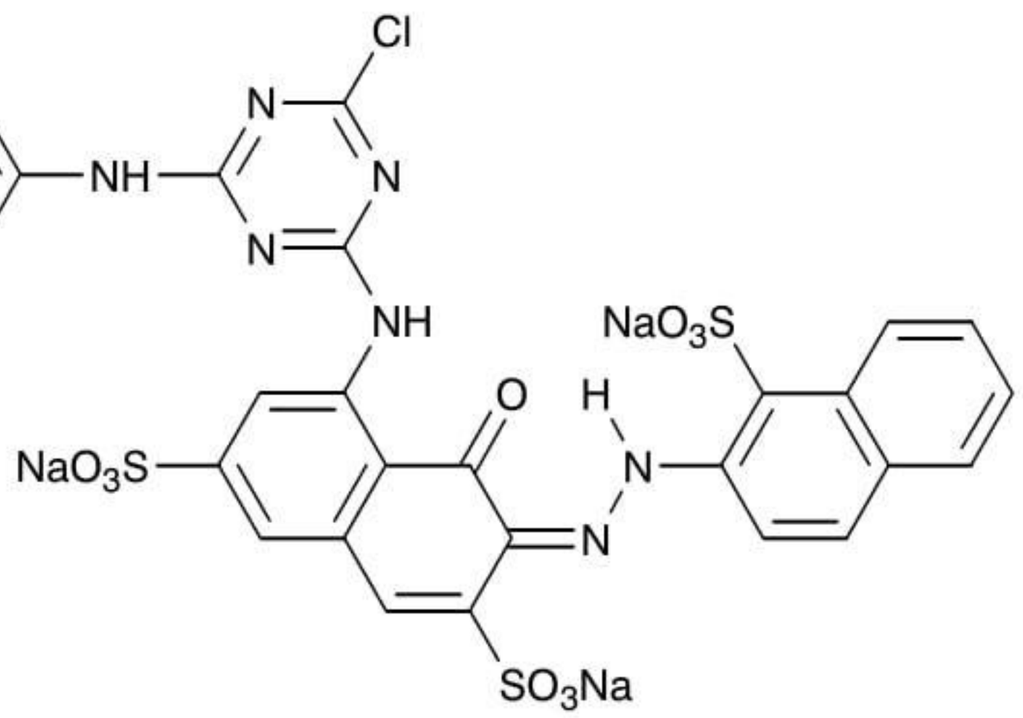
7.60



7.61

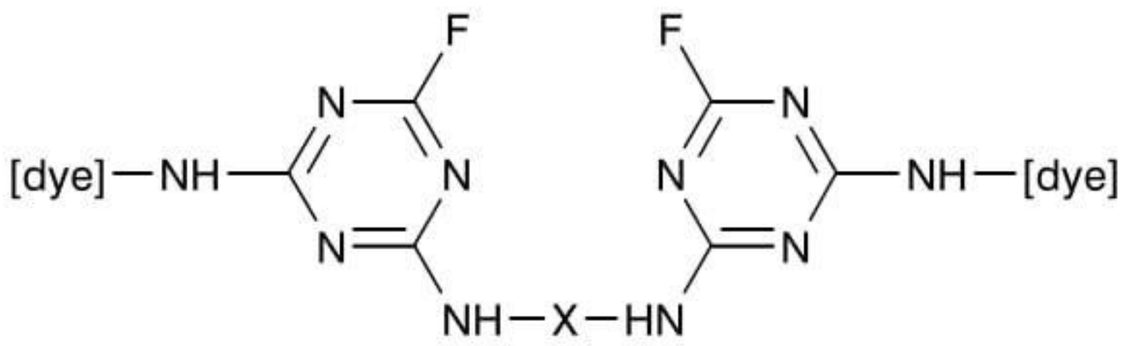


7.62



These bifunctional dye molecules are approximately twice the size of analogous monofunctional structures (compare 7.2 with 7.48). Their high substantivity ensures excellent exhaustion at the preferred dyeing temperature of 80 °C, leading to fixation values of about 70–80%, although in full depths typical members of the range may require salt concentrations as high as 100 g/l for optimal yield. High-temperature application conditions ensure good levelling and the high fixation leads to better utilisation of the dyes applied with less hydrolysis and less coloration of the effluent. Unfortunately, the rate of removal of unfixed dyes at the washing stage is slow owing to the high intrinsic substantivity of these dyes.

A range of bis(aminofluorotriazine) dyes has been marketed by Ciba for long-liquor dyeing under the brand name Cibacron LS, which require only a low salt (LS) concentration in the dyebath. The patent literature indicates that the most likely structures (7.63) to meet this requirement contain two high-substantivity chromogens linked through the central unit carrying the fluorotriazine reactive groups [56]. This system offers an environmental



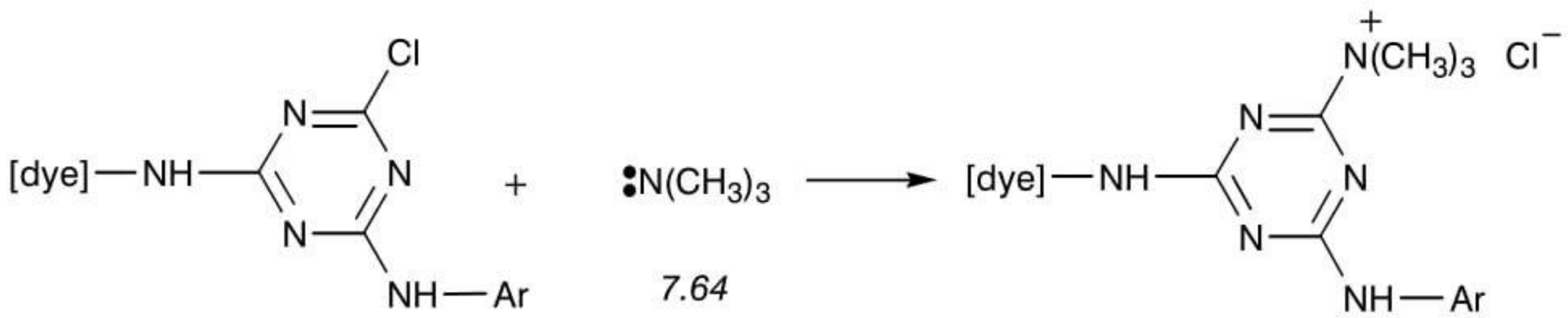
7.63

advantage over the chlorotriazine analogues; organofluorine compounds do not fall into the AOX classification because the fluoride ion liberated as soluble silver fluoride according to the test protocol is not detected [57].

Conferring high substantivity to the dye molecule in these various ways can lead to problems when dyeing in full depths, especially when it comes to the soaping-off stage. It would therefore be interesting to develop labile central linking units between the chromogenic groupings that could be cleaved during fixation or soaping. Such dyes would provide intrinsically high substantivity in the primary exhaustion stage to reduce the salt requirement but in the later alkaline fixation stage their molecular size would be halved and the unfixed single chromogens of much lower substantivity would show good soaping-off behaviour [56].

7.4.2 Bis(aminonicotinotriazine) dyes

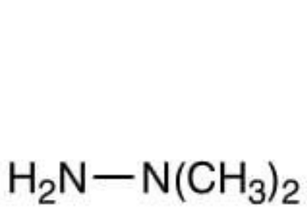
An aminochlorotriazine dye will react with a tertiary amine possessing a sterically accessible nitrogen atom to form a quaternary ammonium derivative (Scheme 7.33). The positive charge carried by the quaternary nitrogen atom increases the polarisation of the C–N bond that links it to the triazine ring, so making such a compound much more reactive than the parent dye. Within a few years of the introduction of reactive dyes, the utility of tertiary amines as catalysts to assist the fixation of aminochlorotriazine dyes to cellulose was evaluated [58]. Suitable tertiary amines include trimethylamine (7.64), *N,N*-dimethylhydrazine (7.65), 1,4-diazabicyclo[2,2,2]octane (DABCO, 7.66), pyridine (7.67; R = H) and substituted pyridines such as nicotinamide (7.67; R = $CONH_2$) or nicotinic acid (7.67; R = COOH).



7.64

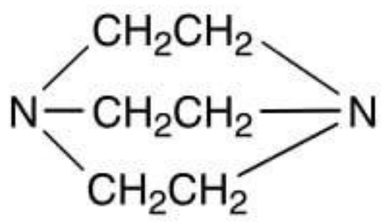
Trimethylamine

Scheme 7.33



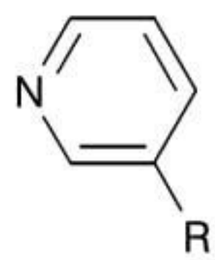
7.65

Dimethylhydrazine



7.66

DABCO



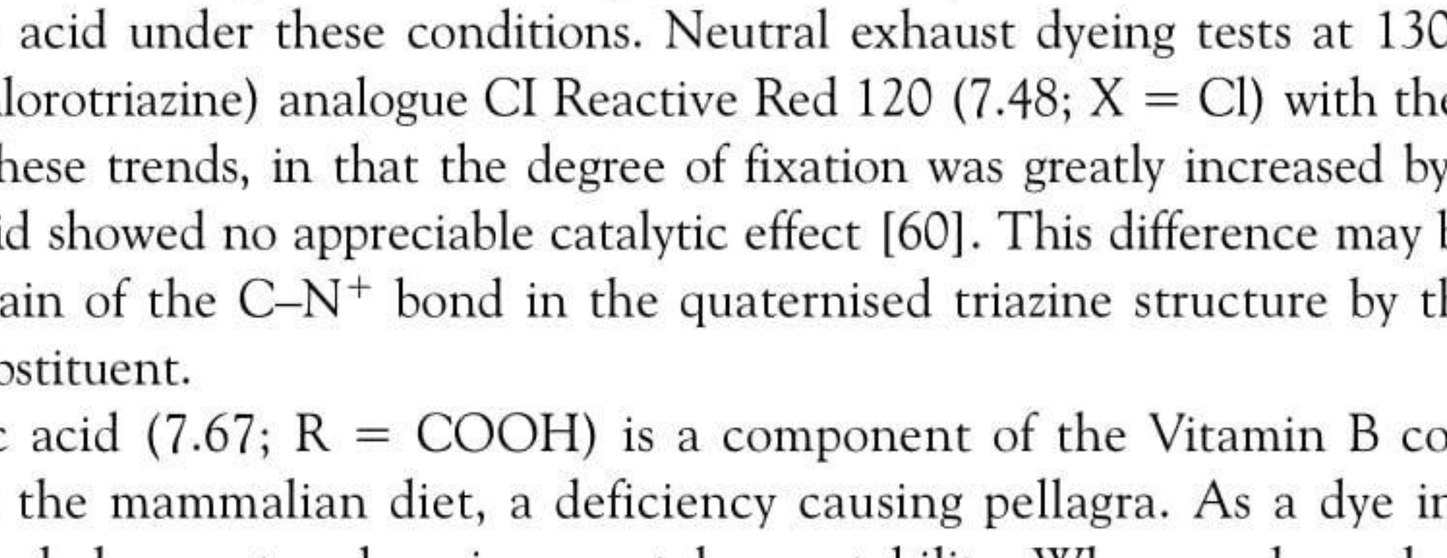
7.67

In the case of quaternary derivatives made from the non-planar aliphatic amines 7.64, 7.65 and 7.66, steric strains further destabilise the C–N^+ bond so that reaction with cellulose occurs under alkaline conditions at 30 °C, whereas temperatures of about 40–50 °C are required for the pyridinium derivatives 7.67. The quaternisation approach appeared to offer the opportunity to prepare dyes yielding reactivity levels intermediate between those of aminochloro- and dichlorotriazine dyes without loss of the desirable stability of the dye–fibre bond to acidic conditions that is characteristic of aminohalotriazine dyes. Unfortunately, this ideal was not attainable because of the objectionable odours of the tertiary amines liberated by the fixation reaction and the sensitivity of the reactivity behaviour of the quaternised derivatives to the nature of the chromogen attached to the triazine ring, making it difficult to select compatible combinations of dyes.

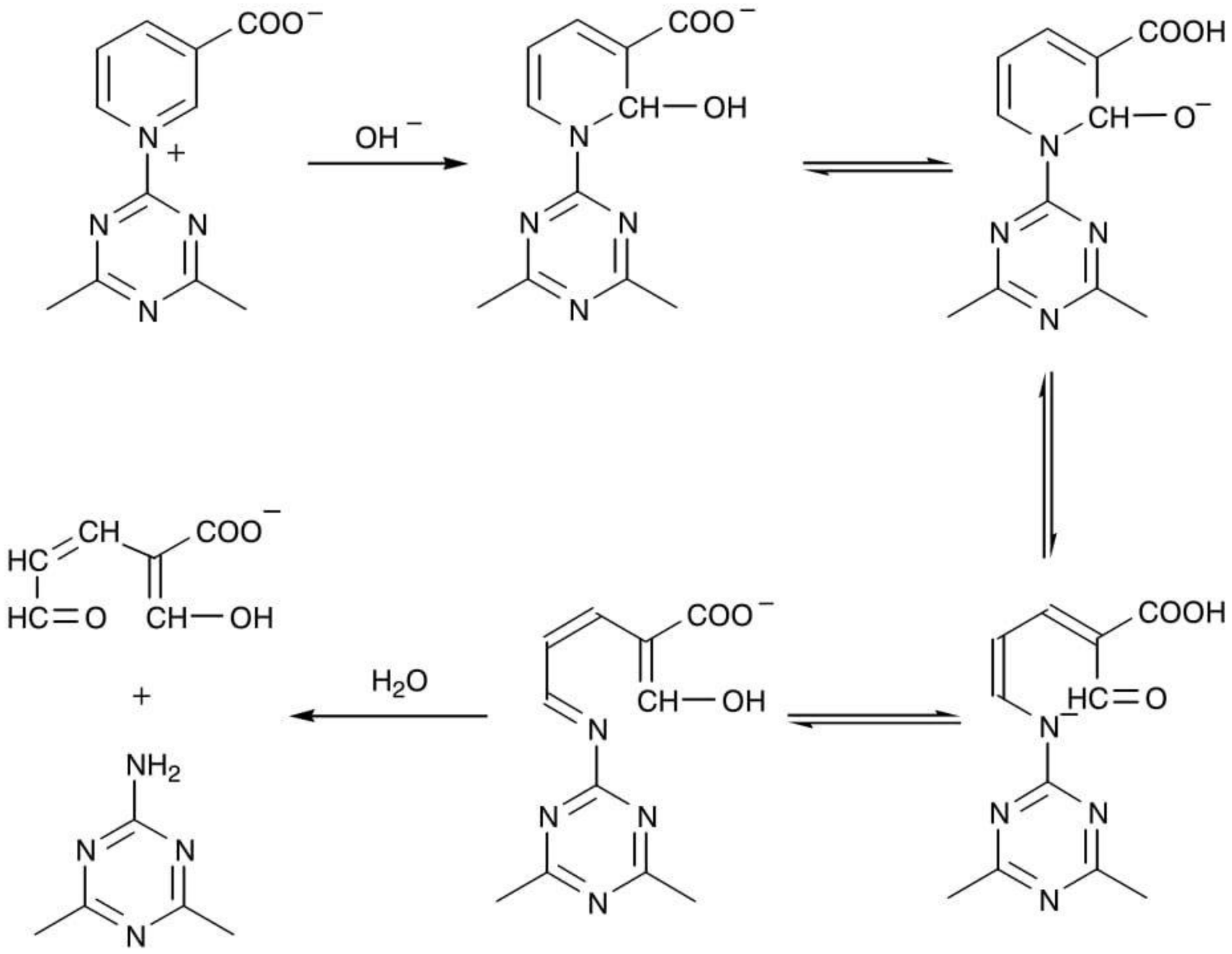
A further difference in behaviour between certain substituted pyridinium dyes and other analogues was revealed when the relative rates of hydrolysis of a series of quaternary derivatives of a monoazo *N*-methyl J acid dye (7.68) were compared. It was found that where the leaving group X was nicotinamide (7.67; R = $CONH_2$) or nicotinic acid (7.67; R = COOH) the dye was rapidly and unexpectedly converted to the aminotriazine, whereas with pyridine (7.67; R = H), isonicotinic acid (4-carboxypyridine) or other leaving groups the expected hydroxytriazine was produced, although much more slowly [59]. The mechanism of aminotriazine formation apparently involves attack by hydroxide ion at the 2-position, deprotonation by the 3-carboxylate ion, ring-opening by cleavage of the 1,2-bond and finally hydrolysis of the 1,6- bond (Scheme 7.34).

The kinetics of reaction of DABCO (7.66) and nicotinic acid (7.67; R = COOH) with the aminochlorotriazine dye CI Reactive Red 3 (7.2) were studied under neutral conditions at temperatures in the range 100–130 °C. Quaternisation by DABCO was much more rapid than by nicotinic acid under these conditions. Neutral exhaust dyeing tests at 130 °C using the bis(aminochlorotriazine) analogue CI Reactive Red 120 (7.48; X = Cl) with the two catalysts confirmed these trends, in that the degree of fixation was greatly increased by DABCO but nicotinic acid showed no appreciable catalytic effect [60]. This difference may be attributable to steric strain of the C–N^+ bond in the quaternised triazine structure by the non-planar DABCO substituent.

Nicotinic acid (7.67; R = COOH) is a component of the Vitamin B complex that is essential to the mammalian diet, a deficiency causing pellagra. As a dye intermediate it offers relatively low cost and environmental acceptability. When used as a leaving entity it readily dissolves in the dyebath, a significant practical advantage over the tertiary amines with lower solubility and unpleasant odours. This was recognised at ICI in 1979 when the bis(aminonicotinotriazinyl)-substituted triphenodioxazine dye Procion Blue H-EG (CI Reactive Blue 187) was introduced for exhaust dyeing at 80 °C with the other



7.68



Scheme 7.34

bis(aminochlorotriazine) members of the range. Although this product enjoyed some commercial success it was more reactive than typical Procion H-E dyes, rendering it somewhat incompatible in terms of dyeing behaviour. Indeed, it was evident that fixation to cellulose commenced prior to the addition of alkali to the dyebath [8]. Procion Blue H-EG was eventually superseded by the more conventional bis(aminochlorotriazinyl)-substituted analogue Procion Blue H-EGN (CI Reactive Blue 198).

The observation that alkali was not essential for the fixation of nicotinotriazines was exploited by Nippon Kayaku in 1983. A full range of bis(aminonicotinotriazine) dyes was introduced under the Kayacelon React (KYK) brandname, an example being CI Reactive Red 221 (7.48; X = nicotino) [60]. All three possible arrangements of the two reactive systems are represented in the range, these being described as the two-step, one-arm (7.56), linkage (7.57) and two-arm (7.58) types [61]. Most of the commonly encountered chromogens have been patented in this way, including monoazo, disazo, metal-complex azo, copper formazan and copper phthalocyanine [8]. Exhaust dyeing from a neutral bath at 130 °C is recommended, making these dyes particularly suitable for the one-bath dyeing of polyester/cellulosic blends in conjunction with disperse dyes. By operating under these conditions, the diffusion problems anticipated with such large molecules are minimised.

In spite of the anomalous ring-opening decomposition of nicotinotriazine compounds under conditions of alkaline hydrolysis (Scheme 7.34), the product of reaction of a bis(aminonicotinotriazine) dye with cellulose is the same as that from the analogous bis(aminochlorotriazine) dye in terms of hue, colour fastness and stability of the dye–fibre bond. If desired, these bis(aminonicotinotriazine) dyes can be applied satisfactorily at 80 °C and pH 11, as was evident for CI Reactive Blue 187. They have slightly higher reactivity

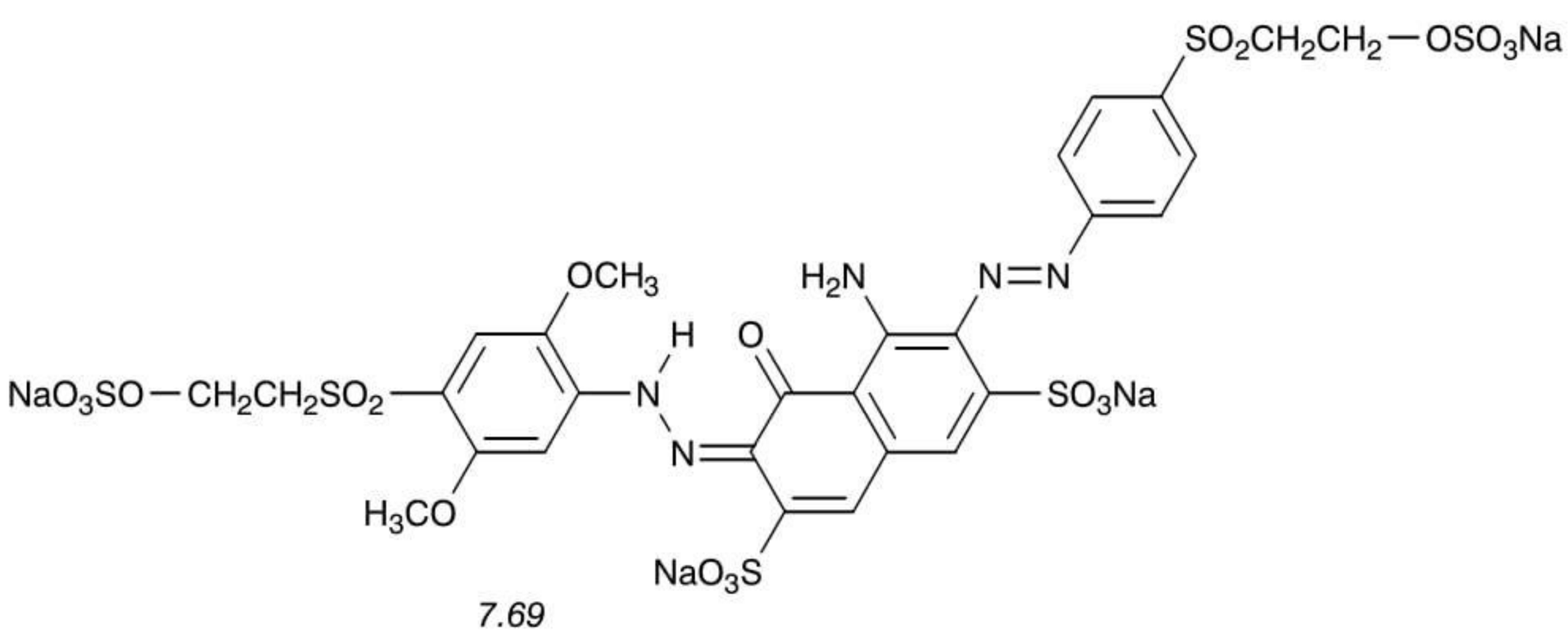
than vinylsulphone or chlorodifluoropyrimidine dyes, but are less reactive than dichlorotriazine or dichloroquinoxaline systems [62].

Six bis-quaternary derivatives of C.I.Reactive Red 120 (7.48; X = Cl) were synthesised using trimethylamine (7.64), DABCO (7.66), pyridine (7.67; R = H), nicotinamide (7.67; R = $CONH_2$), nicotinic acid (7.67; R = COOH) and isonicotinic acid (4-carboxypyridine) as the tertiary amines, the nicotinic acid derivative (7.48; X = nicotino) representing the control dye CI Reactive Red 221. The conditions required to achieve at least 90% conversion to the bis-quaternary species were 2 hours at 70 °C and pH 6.5 for DABCO and trimethylamine. The less reactive pyridine and its analogues required 2 or more hours at 90 °C for completion of this reaction. In exhaust dyeing tests on cotton, all six dyes showed similar levels of fixation at neutral pH, irrespective of dyeing temperature. At alkaline pH, however, fixation of the nicotinamide derivative declined from about 70% at pH 7 to 40% at pH 9. Values of exhaustion for this dye also decreased steadily as the dyebath temperature rose from 100 to 130 °C. These poor results were attributed to ring-opening decomposition of the pyridine-3-carbonamide system (as in Scheme 7.34) with formation of the aminotriazine under these adverse conditions [63].

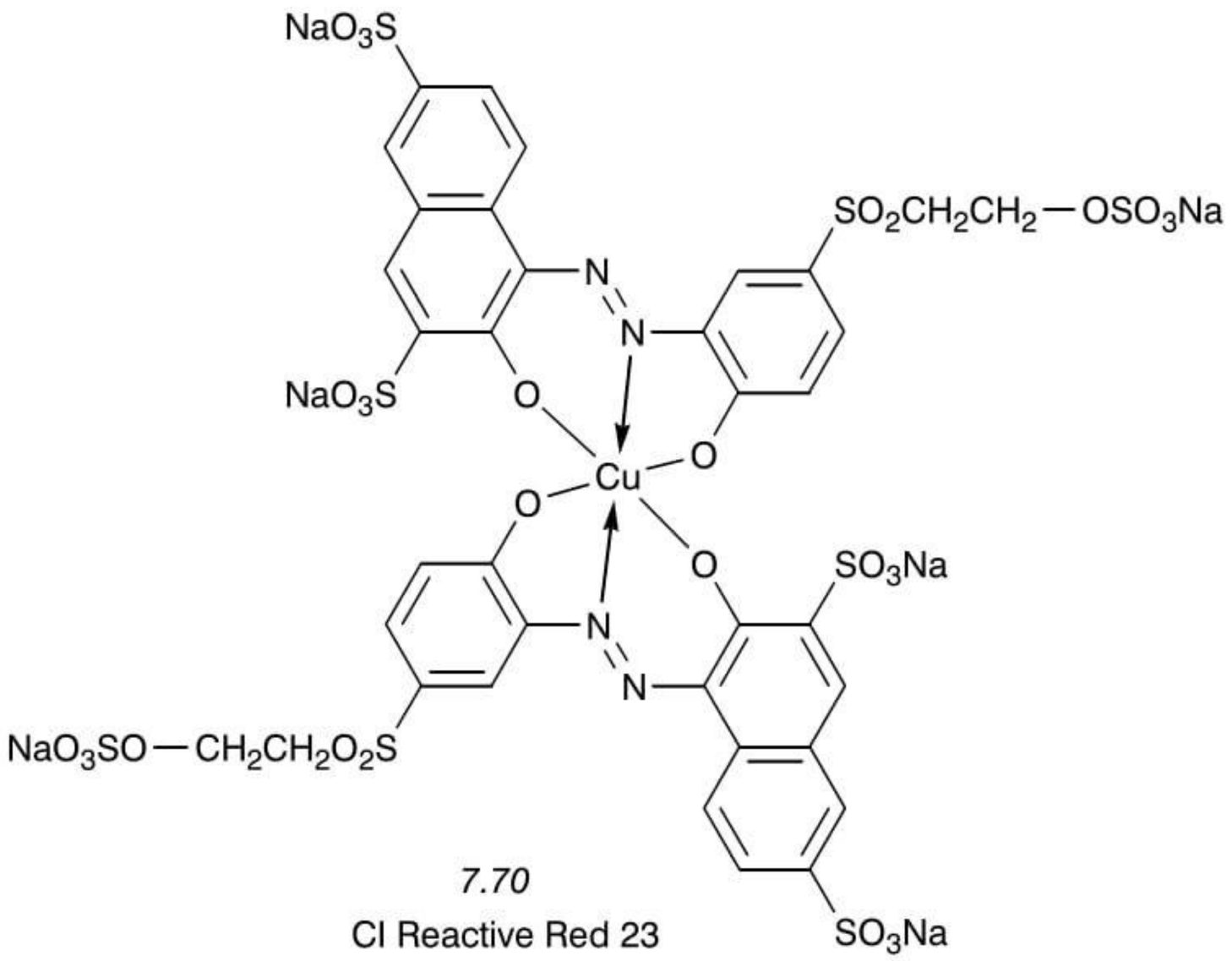
7.4.3 Bis(sulphatoethylsulphone) dyes

The most commercially successful reactive dye of all, CI Reactive Black 5 (7.36) contains two sulphatoethylsulphone precursor groups that contribute markedly to its initial solubility. When these are hydrolysed in alkali to release the reactive bis(vinylsulphone) form, the considerable increase in substantivity (Table 7.3) leads to highly efficient fixation. Further hydrolysis of the vinylsulphone groups to give the inactive bis(hydroxyethylsulphone) derivative, however, lowers the substantivity and hence contributes to favourable wash-off performance.

A dimethoxy analogue of Black 5 has also been marketed but this (7.69) has not been so successful as it is more expensive to make, greener in hue and thus less suitable as a basis for black. Structures of the bis(sulphatoethylsulphone) type have been commercialised in other sectors of the colour gamut, including the bluish red 1:2 metal-complex CI Reactive Red 23 (7.70), anthrquinone blues such as the symmetrical structure 7.71 and phthalocyanine blues similar to 7.72.

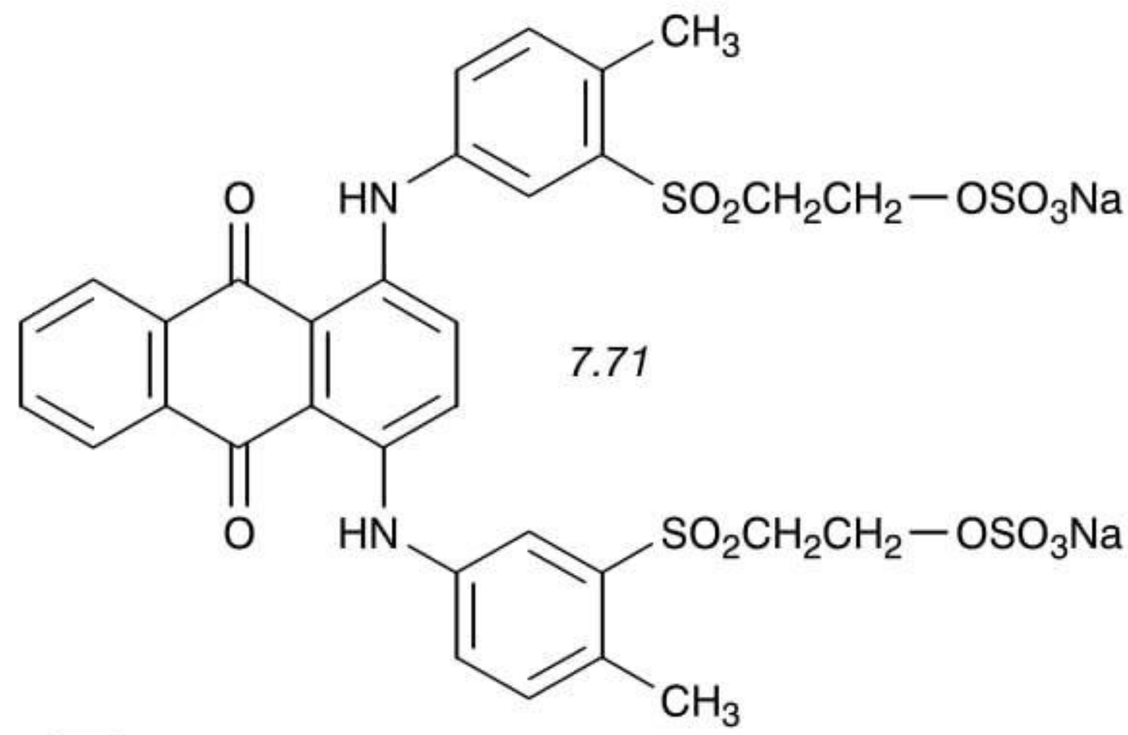


7.69

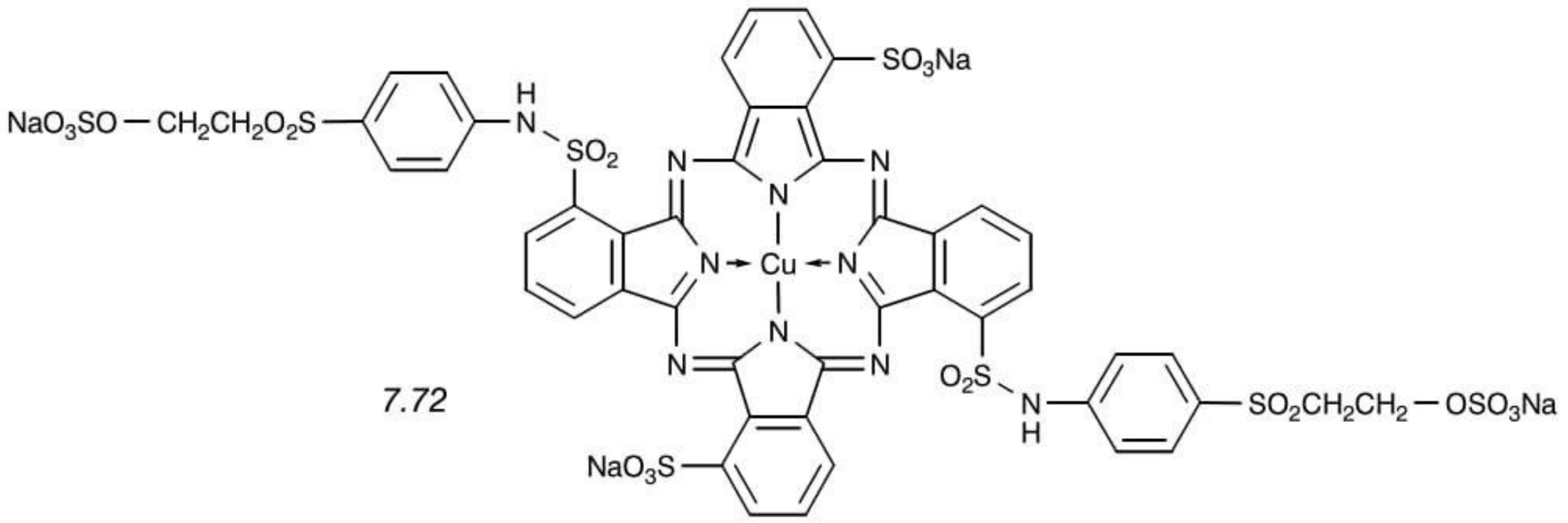


7.70

CI Reactive Red 23

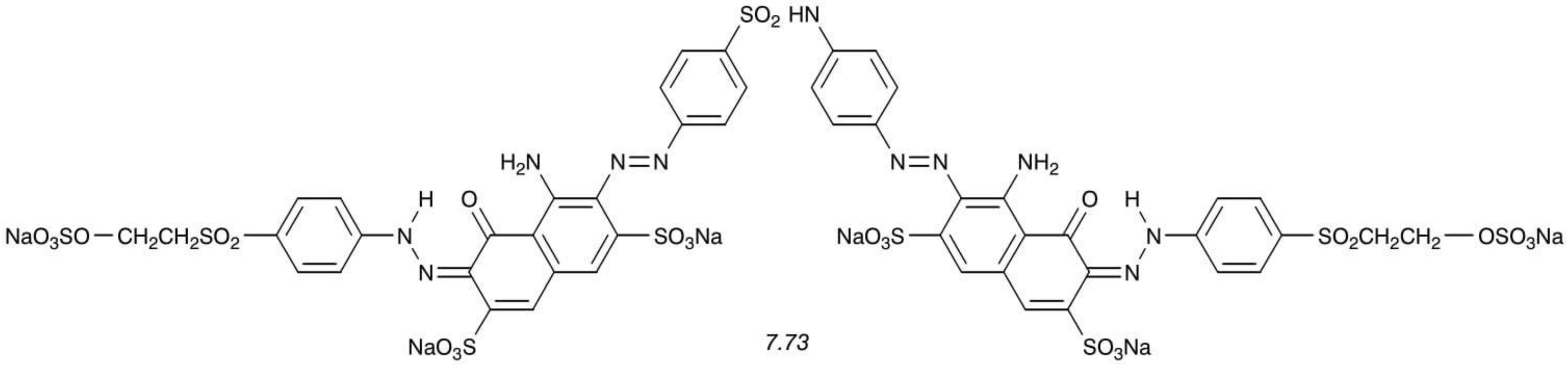


7.71

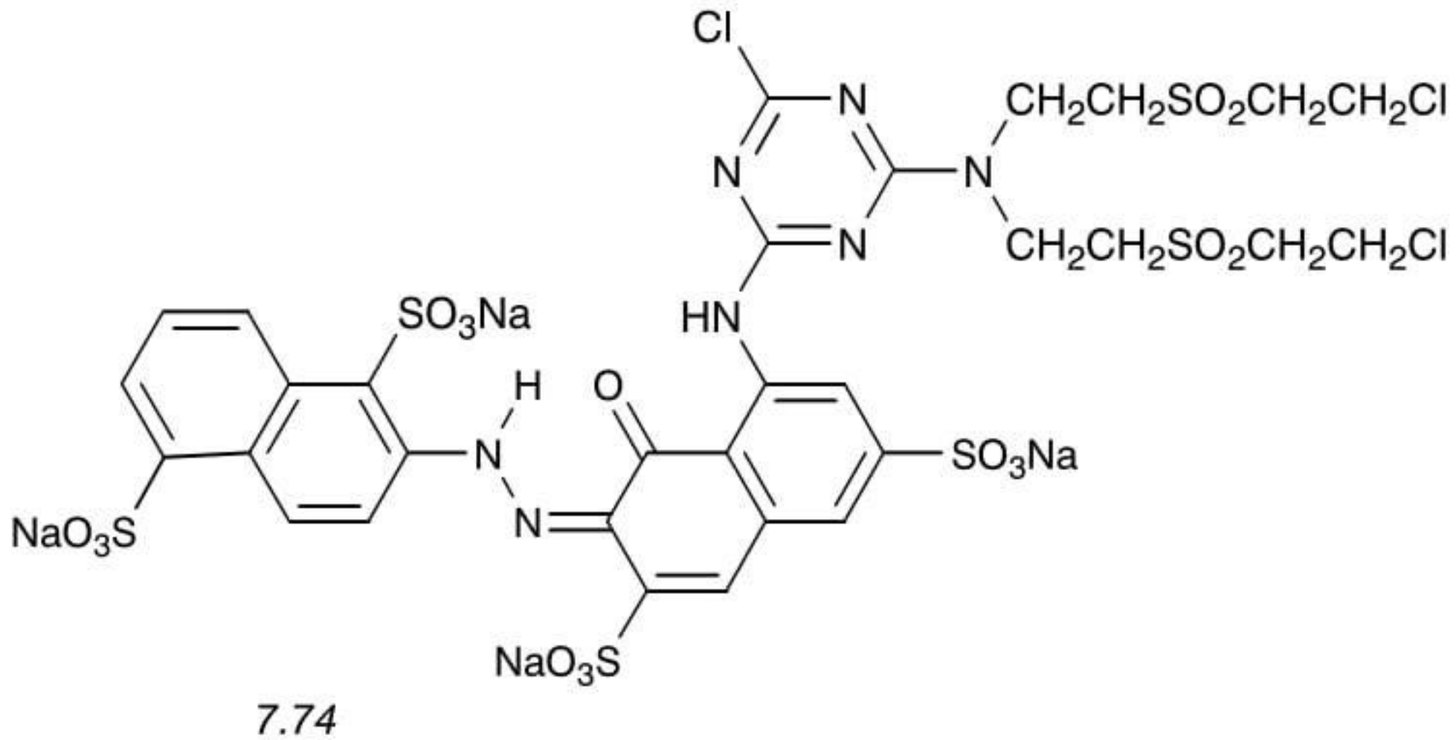


7.72

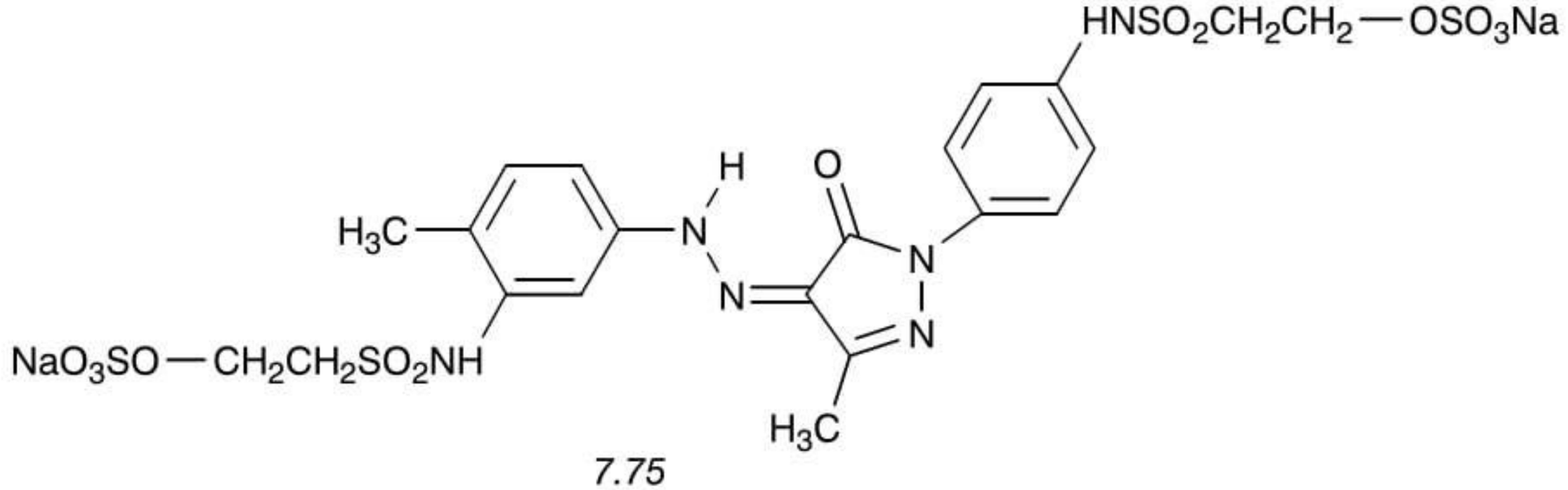
A highly substantive bluish red bis(sulphatoethylsulphone) structure (7.73) has been patented recently [29]. In a kinetic study using the t.l.c. double-scanning method, the condensation reactions between the bis(aminochlorotriazine) dye CI Reactive Red 120 (7.48; X = Cl) and the two isomeric sulphatoethylsulphone anilines 7.38 and 7.39 to yield the two corresponding bis(sulphatoethylsulphone) isomeric dyes were compared. The rate constant of the reaction between Red 120 and the *meta* isomer 7.39 was about ten times as large as that for the *para* isomer 7.38 [64].



7.73



7.74



7.75

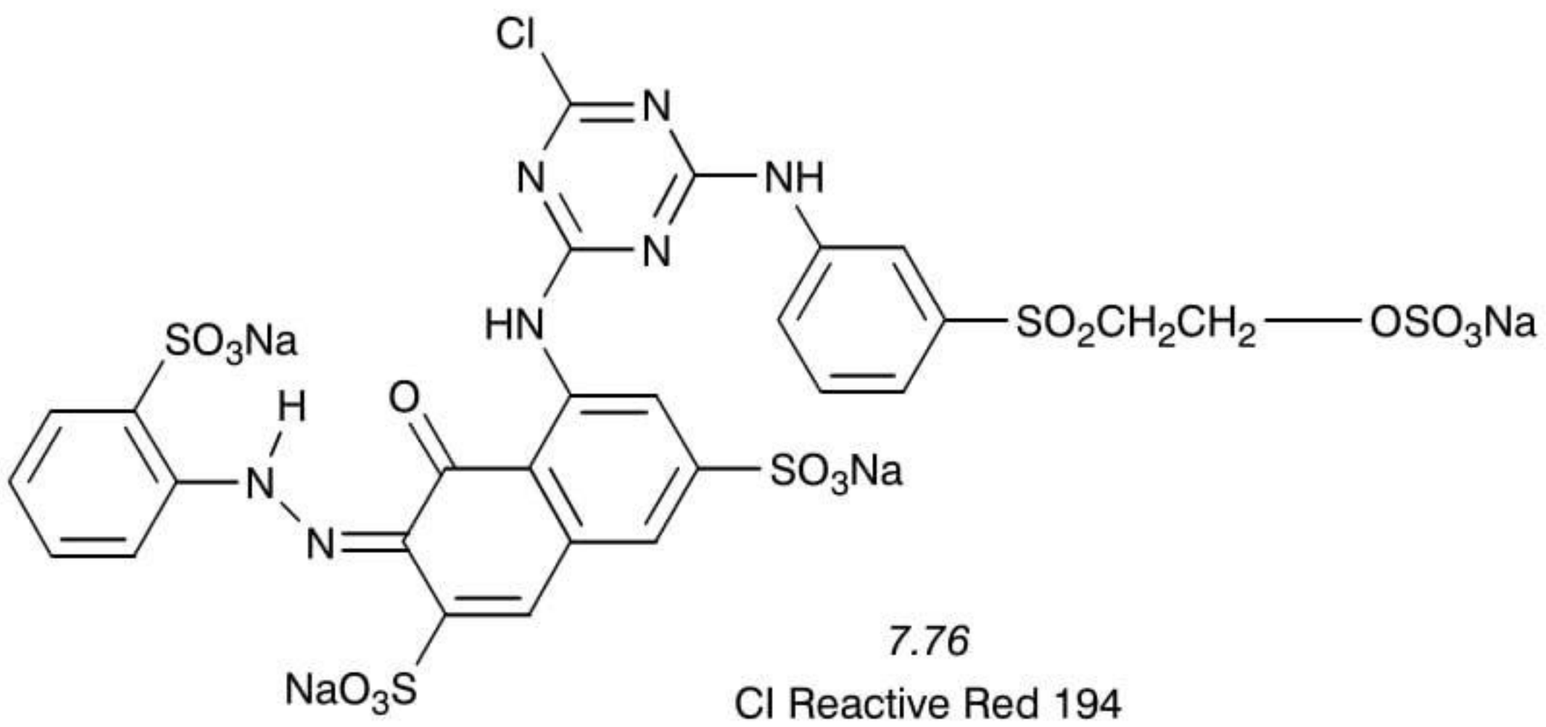
Not all homobifunctional reactive dyes that react with cellulose by the nucleophilic addition mechanism are marketed as sulphatoethylsulphones. Thus the bluish red structure 7.74 contains two chloroethylsulphone precursor groups attached via a diethylamine residue and an activated chlorotriazine grouping to the H acid coupling component. The azopyrazolone yellow structure 7.75 depends for its reactivity on sulphatoethylsulphonamide precursor groups located separately at the diazo and coupler extremities of the molecule.

7.4.4 Aminochlorotriazine-sulphatoethylsulphone dyes

Reaction of a dichloro-s-triazine dye with an anilino intermediate containing a 2-sulphatoethylsulphone substituent, such as 7.38 or the more nucleophilic 7.39, is the preferred route to heterobifunctional reactive dyes of the Sumifix Supra (NSK) class introduced by Sumitomo in 1980. Rate constants for the reactions between two vinylsulphonylaniline isomers and a model dichlorotriazine dye have been determined in DMF by the t.l.c. scanning method. As expected, the *meta* isomer reacted more quickly than *para*-vinylsulphonylaniline [65]. The Sumifix Supra dyes are capable of reacting with cellulose via either the monochlorotriazine moiety or the vinylsulphone group released by the precursor sulphate ester. A typical structure is that of the monoazo H acid dye shown (7.76) [66]. Notable features are the high substantivity contributed by the triazine bridging nucleus and the capability this gives to link the two reactive centres to a wide variety of chromogens.

The marked differences in substantivity between the various forms of monofunctional vinylsulphone dyes (section 7.3.8) recur to a moderated extent in the Sumifix Supra dyes because of the influence of the substantive triazine ring. The scarlet chromogen (7.77) linked via a chlorotriazine unit to the three variants of the vinylsulphone grouping showed similar trends (Table 7.4) to those already seen for those of CI Reactive Red 22 tested under the same conditions (Table 7.3). The rate of secondary exhaustion will be easier to control in this instance because of the lower difference in substantivity between the precursor and the vinylsulphone form [37].

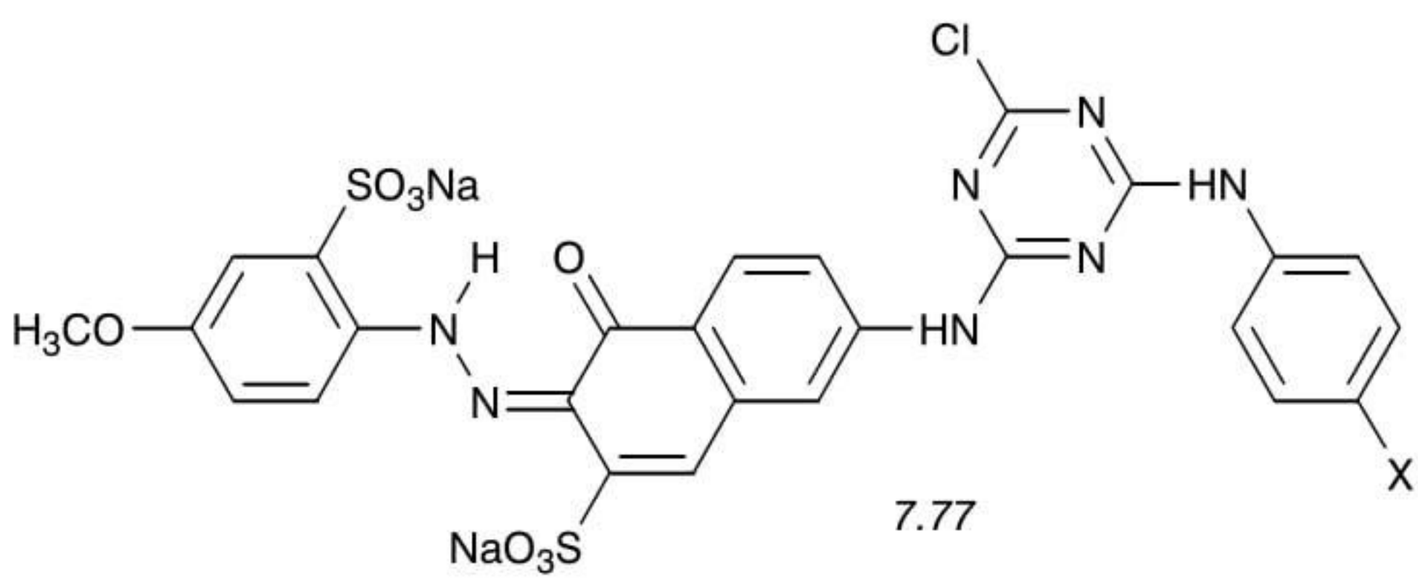
Rate constants and the products formed in the hydrolysis of CI Reactive Red 194 (7.76) at 50 °C and pH values in the 10–12 region were determined by high-pressure liquid chromatography. In addition to the normal hydrolysis of the two reactive systems, the imino link between the triazine and benzene nuclei was also hydrolysed [67]. The heterobifunctional copper formazan dye CI Reactive Blue 221 and two blue anthraquinone monofunctional reactive dyes of the bromamine acid type, namely the aminochlorotriazine Blue 5 and the sulphatoethylsulphone Blue 19, were compared in terms of their sensitivity to



7.76
CI Reactive Red 194

Table 7.4 Relationship between substantivity and nature of the reactive group for heterobifunctional dyes [37]

Reactive group X	Primary exhaustion (%)
$-SO_2CH_2\ CH_2OSO_3Na$	43
$-SO_2CH=CH_2$	82
$-SO_2CH_2\ CH_2OH$	63



7.77

hydrolysis over a wide range of pH (1–12). Three main products of hydrolysis were isolated from Blue 221 by dialysis and thin-layer chromatography. It was confirmed that most of the fixation of Blue 221 to cotton cellulose in exhaust dyeing at 60 °C occurs via the vinylsulphone group [68].

The presence of two reactive groups that differ in reactivity gives dyes that are less sensitive to exhaust dyeing temperature than any of the typical monofunctional reactive systems. They can be applied over a wider range of temperatures (50–80 °C) and reproducibility of hue in mixture recipes is improved. Moreover, they show minimal sensitivity to electrolyte concentration and are less affected by changes in liquor ratio [69]. Low dyeing temperatures favour reaction via the vinylsulphone group, whereas at higher temperatures the contribution of the chlorotriazine system to fixation becomes more important [70]. This was demonstrated by controlled enzymatic degradation of a mechanically milled cotton fabric that had been exhaust dyed at 60 °C, generating the following conclusions after analysis of the products isolated [71]:

(1) About 80% of the vinylsulphone groups had reacted with hydroxy groups in cellulose
(2) About 50% of the chlorotriazine groups had not reacted and only about half of these had been hydrolysed to the hydroxytriazine
(3) A considerable proportion of the dye molecules had formed crosslinks by reacting via both reactive systems.

For further studies of this kind a scarlet monoazo dye of this type was synthesised containing three ^{13}C-labelling atoms in the triazine ring. Enzymatic digestion of cotton dyed by four different exhaust methods yielded various dye-sugar derivatives that were estimated quantitatively using ^{13}C-NMR liquid spectroscopy. As well as crosslinking through both groups, monofixation can occur via either group with the other either hydrolysing or remaining intact. Distribution patterns between these five modes of fixation to cellulose were elucidated for all four dyeing methods. In isothermal dyeing at 50, 60 or 80 °C, the proportion of fixation via the chlorotriazine group increased at the expense of vinylsulphone

fixation and crosslinking. Crosslinking could be optimised by neutral exhaustion at 40 °C followed by two-step fixation at 60 °C and 80 °C [72].

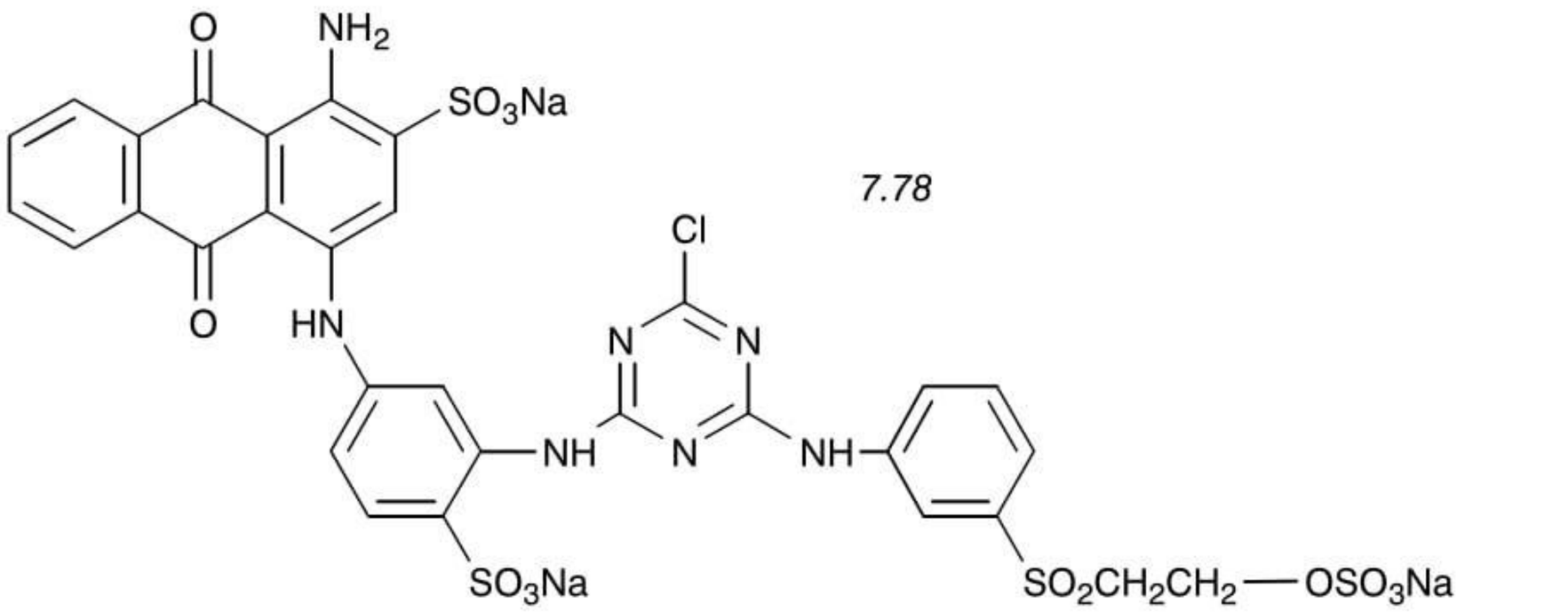
The levelling properties of CI Reactive Red 194 (7.76), a twice-coupled H acid blue dye containing the same heterobifunctional system, the bis(sulphatoethylsulphone) dye CI Reactive Black 5 (7.36) and six monofunctional sulphatoethylsulphone dyes were compared recently in considerable detail. The results confirmed that those anthraquinone blue dyes of the bromamine acid type that rely only on the 2-sulphonate group and the precursor sulphatoethylsulphone substituent for aqueous solubility, such as CI Reactive Blue 19 (7.37), are especially prone to unlevel dyeing. These relatively hydrophobic characteristics promote aggregation in salt solution at relatively low dyeing temperatures [73]. Premature loss of the sulphate ester group should be avoided and such dyes should be applied at the lowest salt concentration and highest temperature that are consistent with the attainment of acceptable exhaustion and fixation performance.

The incorporation of two different reactive systems and the high substantivity of heterobifunctional dyes favour the achievement of unusually high fixation. Although this leads to better utilisation of the dyes applied, with less of the hydrolysed by-products to colour the effluent, removal of these unfixed dyes at the washing-off stage may present difficulties because of their high intrinsic substantivity [8]. The formation of two different types of dye–fibre bond has beneficial consequences for fastness performance. Heterobifunctional dyes show superior fastness to acid storage compared with dichlorotriazine or dichloroquinoxaline systems and better fastness to peroxide washing than difluoropyrimidine or dichloroquinoxaline dyes [53].

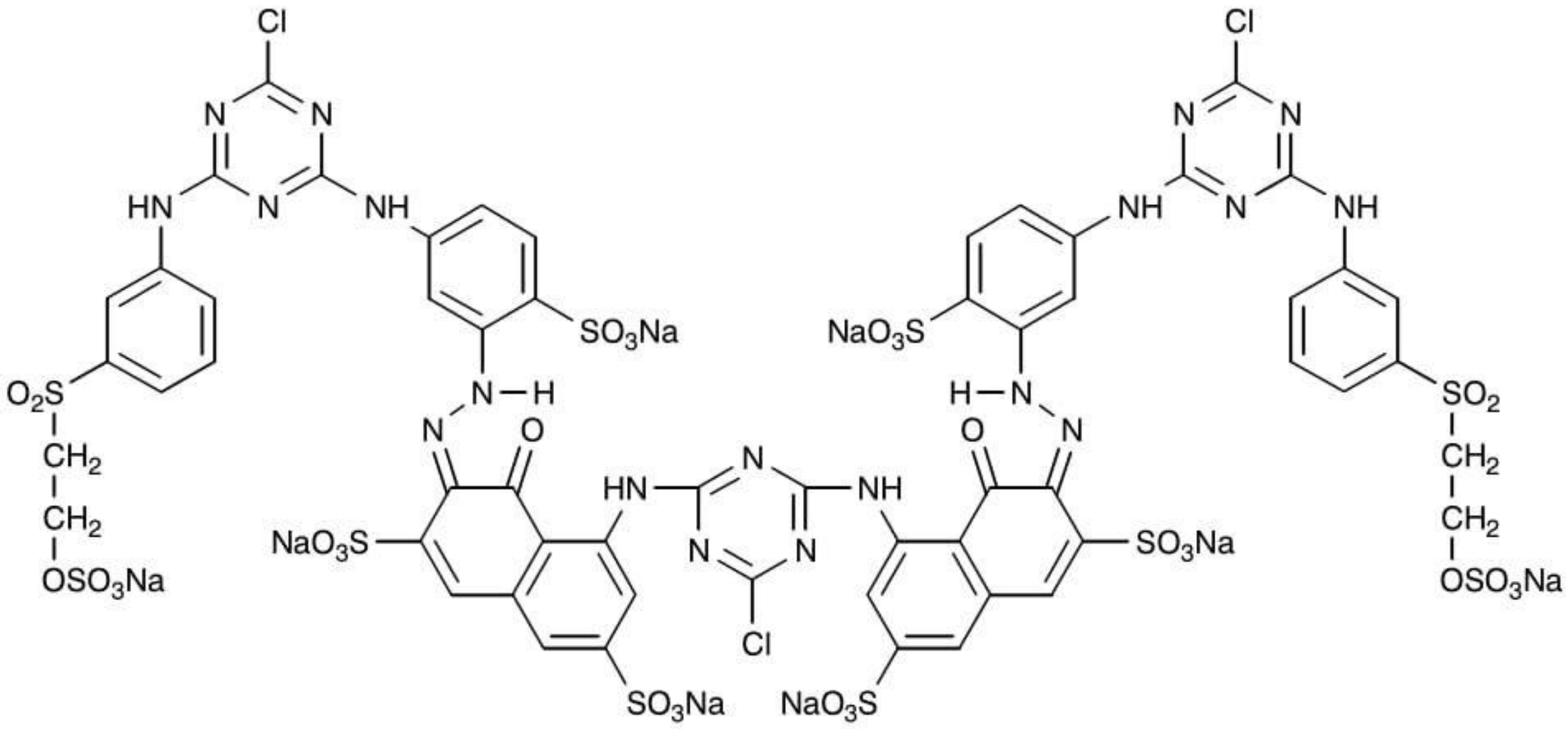
In a detailed investigation, the dye–fibre bond stabilities of exhaust dyeings on cotton of the orthodox heterobifunctional dye CI Reactive Red 194 (7.76) and two monofunctional control dyes were compared. Both were analogues of Red 194, one having a hydroxytriazine group instead of the normal chlorotriazine and the other a hydroxyethylsulphone group instead of the normal sulphate ester. As expected, in acidic buffer solutions the orthodox dye 7.76 showed higher stability than the hydroxytriazine-vinyisulphone analogue, which was itself more stable than the chlorotriazine-hydroxyethylsulphone dye. Under alkaline conditions the hydroxytriazine-vinylsulphone dye was much less stable than the two dyes with an active chlorotriazine group [74].

Two unorthodox heteromultifunctional dyes were also included in this investigation, neither being of commercial interest. The anthraquinone blue dye 7.78 containing the same heterobifunctional reactive system as Red 194 exhibited surprisingly low fixation. This was attributed to the non-planar conformation of bromamine acid derivatives of this kind [74]. All three imino groups linking together the phenyl-triazine-phenyl-anthraquinone series of nuclei in this structure have a twisting effect on the aryl systems on both sides of each NH link. Thus the triazine ring is twisted through about 90 degrees relative to the plane of the anthraquinone chromogen. Another multifunctional dye that gave disappointingly low fixation was the symmetrical structure 7.79, even though there were no less than five reactive systems linked together with two red monoazo H acid chromogens. Apparently this exceptionally large dye molecule is absorbed so gradually and diffuses so slowly that adequate fixation cannot be attained within an acceptable dyeing time [74].

Another comprehensive evaluation of cotton dyeing parameters has been carried out for eighteen isomeric monoazo H acid red dyes containing aminochlorotriazine and



7.78



7.79

sulphatoethylsulphone (Z) reactive groups [66]. Representative results for the affinity parameter, rate of hydrolysis and fixation yield are presented in Table 7.5. Three commercially available dyes are represented in the series (CI Reactive Reds 194, 198 and 227). Substitution in the *o*-position usually lowers the affinity parameter by sterically hindering the coplanarity of the aryl nuclei. Thus the two dyes with *ortho* substituents in both rings have the lowest affinity values. Surprisingly, however, the two dyes (Reds 194 and 227) with an *o*-sulpho group in ring A and the reactive system in the *m*- or *p*-position of ring B show the highest affinity values.

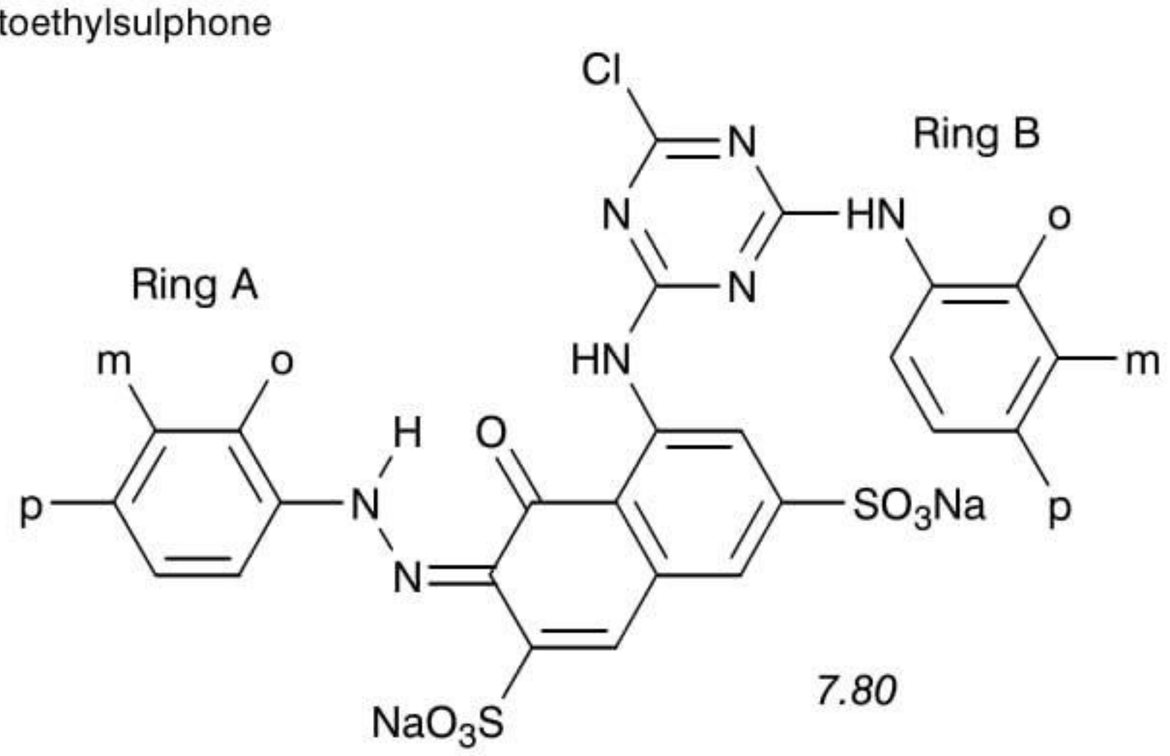
Dyes with the sulphatoethylsulphone group in the *m*-position of ring B are the most reactive, especially Red 194, which hydrolyses about ten times more quickly than those dyes with an *ortho* reactive group in this ring. Two of the commercial products (Reds 194 and 227) achieved the highest fixation values. The combination of a *m*- or *p*-sulpho group in ring A and the reactive group in the *o*-position of ring B leads to poor affinity and the lowest reactivity, resulting in fixation yields less than half those of Reds 194 and 227. In general, dyes like these four with both reactive systems attached via the imino link in the coupling component show more extremes of dyeing behaviour than those in which the sulphatoethylsulphone group is in the diazo component (ring A).

Table 7.5 Affinity parameter, rate of hydrolysis and fixation yield [66]

Substituent in					
Ring A SO_3Na	Ring B Z	CI Reactive	Affinity parameter	Rate of hydrolysis (10^{-2}/min)	Fixation yield (%)
o	o		0.29	1.9	28.4
o	m	Red 194	0.62	15.0	41.8
o	p	Red 227	0.64	4.8	44.8
m	o		0.33	1.1	18.7
m	m		0.50	7.4	37.1
m	p		0.50	2.1	37.8
p	o		0.35	1.3	20.6
p	m		0.52	8.3	34.7
p	p		0.51	2.5	39.1

Substituent in					
Ring A Z	Ring B SO_3Na	CI Reactive	Affinity parameter	Rate of hydrolysis (10^{-2}/min)	Fixation yield (%)
o	o		0.27		
m	o		0.36	4.9	28.3
p	o		0.36	4.6	32.4
o	m		0.46		
m	m		0.58	5.4	34.5
p	m	Red 198	0.54	4.3	37.9
o	p		0.46		
m	p		0.54	3.4	36.3
p	p		0.51	3.0	38.9

Z Sulphatoethylsulphone



7.80

7.4.5 Aminofluorotriazine-sulphatoethylsulphone dyes

In 1988 Ciba launched the Cibacron C range of bifunctional reactive dyes. They contain a new aliphatic vinylsulphone system and either a monofluorotriazine bridging group or an arylvinylsulphone function [75]. Owing to the small size of the fluorine atom, the difluorotriazine precursor reacts more smoothly with an alkylamine carrying the sulphato-

ethylsulphone system such as 7.81 than with an arylamine intermediate such as 7.38 or 7.39. The Cibacron C dyes are designed mainly for pad applications and are characterised by low to moderate affinity, good build-up, ease of washing-off and high fixation (often >90%). Their good stability under padding conditions, high solubility, efficiency of reaction and outstanding fixation make them especially suitable for the pad–batch process [76]. The presence of the vinylsulphonylalkyl group assists solubility and most of these dyes form stable liquids without the addition of urea [36].

$H_2NCH_2CH_2SO_2CH_2CH_2OSO_3Na$

7.81

The stability of the dye–fibre bonds in these dyeings is high to both acid and alkali, compared with monofunctional halotriazine analogues, because of the major contribution of the vinylsulphone function to the fixation mechanism. The fluorotriazine group confers much higher stability to alkali than is shown by monofunctional sulphatoethylsulphone dyes [77]. A characteristic feature of the Sumifix Supra (NSK) heterobifunctional system is the major difference in reactivity between the aminochlorotriazine moiety and the much more reactive vinylsulphone group. There are some practical conditions, notably in pad–batch application, that do not allow full advantage to be taken of both types of reactive group present. The combination of aminofluorotriazine and sulphatoethylsulphone in the Cibacron C (Ciba) synchronised bifunctional system, both groups offering effective fixation under virtually the same conditions, exploits the concept of bifunctionality more effectively.

These factors have been demonstrated elegantly in a detailed evaluation by pad–batch dyeing of cotton with three commercially important copper formazan reactive dyes:

(1) Cibacron Blue F-R (Ciba; CI Reactive Blue 182) with a monofunctional aminofluorotriazine group.
(2) Sumifix Supra Blue BRF (NSK; CI Reactive Blue 221) with a heterobifunctional aminochlorotriazine-sulphatoethylsulphone system.
(3) Cibacron Blue C-R (Ciba) with a synchronised bifunctional aminofluorotriazine-sulphatoethylsulphone system.

Under the relatively mild conditions of pad–batch fixation within 6 hours batching time, the heterobifunctional dye (Blue 221) behaved as if it were a monofunctional sulphatoethylsulphone dye and only the synchronised Cibacron C system showed truly bifunctional performance [78].

Interfibrillar crosslinking induced by a colourless cellulose reactant early in the wet processing sequence can prevent further fibrillation of lyocell fibres. Certain bifunctional reactive dyes exert a similar effect but specific molecular characteristics must be present. These include steric orientation and separation of the reactive groups, degree of reactivity, size of chromogen, molecular flexibility and diffusion properties. Cibacron LS bis(aminofluorotriazine) dyes applied by exhaust dyeing and Cibacron C aminofluorotriazine-sulpatoethylsulphone dyes in the cold pad-batch process largely fulfil these requirements and thus provide control of undesirable post-fibrillation of lyocell during finishing and laundering [79].

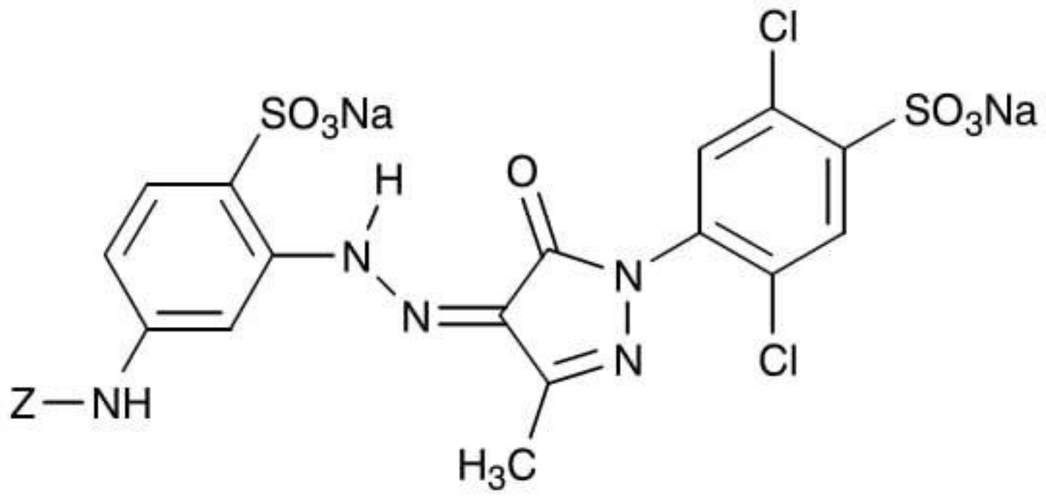
7.5 CHROMOGENS IN REACTIVE DYES

Providing there are enough sulpho groups to ensure adequate solubility in water, the only essential feature of a chromogen needed to build it into a reactive dye molecule of the haloheterocyclic type is a primary or secondary amino group to which the heterocyclic system can be attached. This also applies to the various ranges of bifunctional dyes described in section 7.4, since they all contain this same type of amino-*s*-triazine grouping attached to the chromogen. Only in the case of monofunctional sulphatoethylsulphone dyes is the selection of chromogens more limited by the various ways in which conventional intermediates for these dyes, such as 7.38 and 7.39, can form an integral part of the chromogenic grouping. These intermediates have wide applicability in azo dye structures, since they are conveniently used as diazo components with a variety of orthodox couplers. The *para* isomer (7.38) is less nucleophilic than the *meta*-substituted one (7.39), which is therefore more versatile.

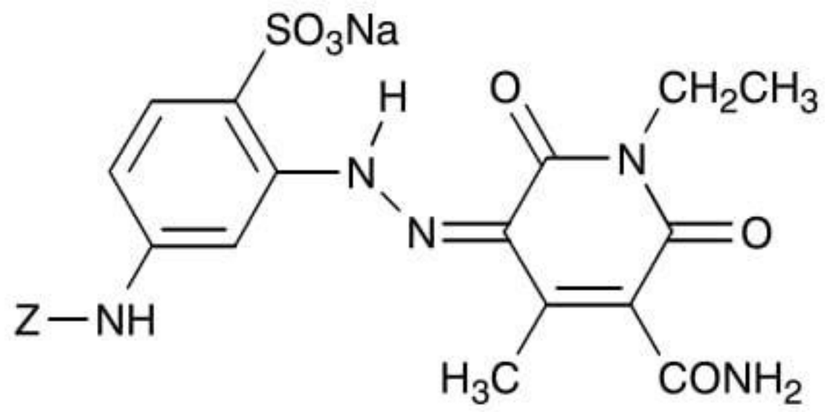
Most ranges of reactive dyes contain examples of monoazo, disazo, metal-complex azo, anthraquinone and phthalocyanine chromogens, with copper formazan or triphenodioxazine blues sometimes also present. Within each sector of the colour gamut it is often possible to find the same specific chromogen being used in various ranges, with individual monofunctional dyes differing only in the nature of the reactive system. These trends are often dictated by the need to consider the ready accessibility of key intermediates. In research centred around the design of novel dye structures, computer-based techniques of molecular modelling and statistical experimental design to reveal structure–property relationships are now common practice [80].

7.5.1 Greenish yellow chromogens

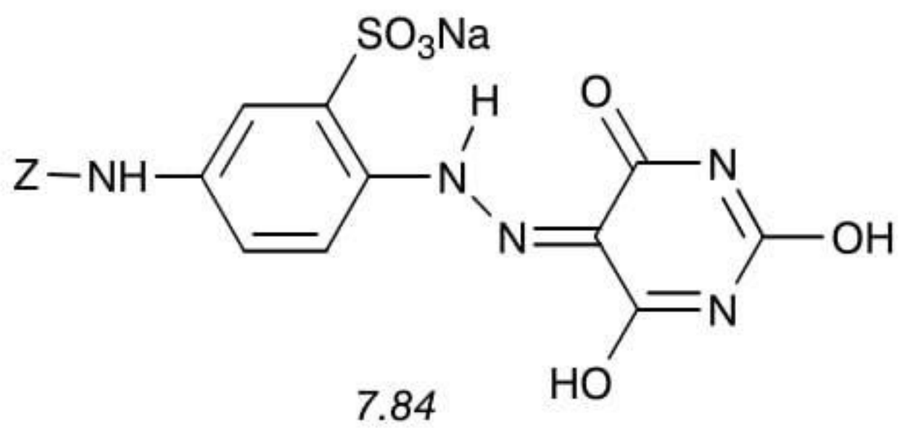
These dyes are invariably monoazo compounds with the reactive system attached to the diazo component, owing to the ready availability of monosulphonated phenylenediamine intermediates. Pyrazolone couplers are most commonly used, as in structure 7.82 (where Z is the reactive grouping), and this is particularly the case for greenish yellow vinylsulphone dyes. Catalytic wet fading by phthalocyanine or triphenodioxazine blues is a characteristic weakness of azopyrazolone yellows (section 3.3.4). Pyridones (7.83), barbituric acid (7.84) and acetoacetarylide (7.85; Ar = aryl) coupling components are also represented in this sector, with the same type of diazo component to carry the reactive function.



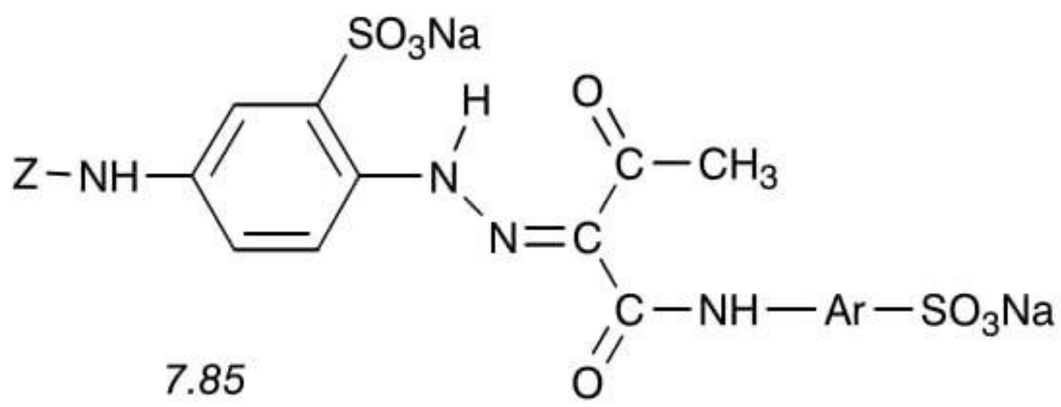
7.82



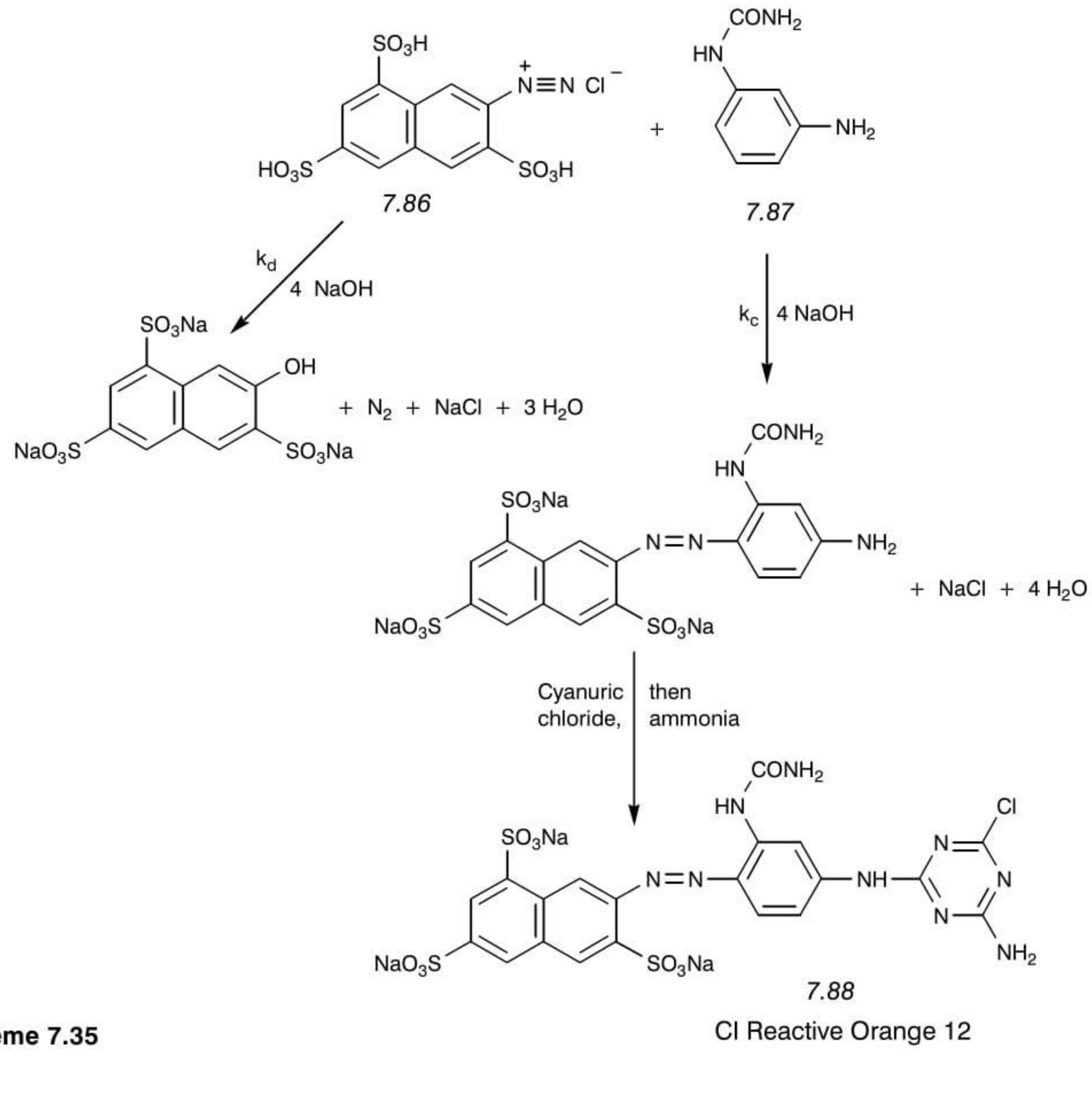
7.83



7.84



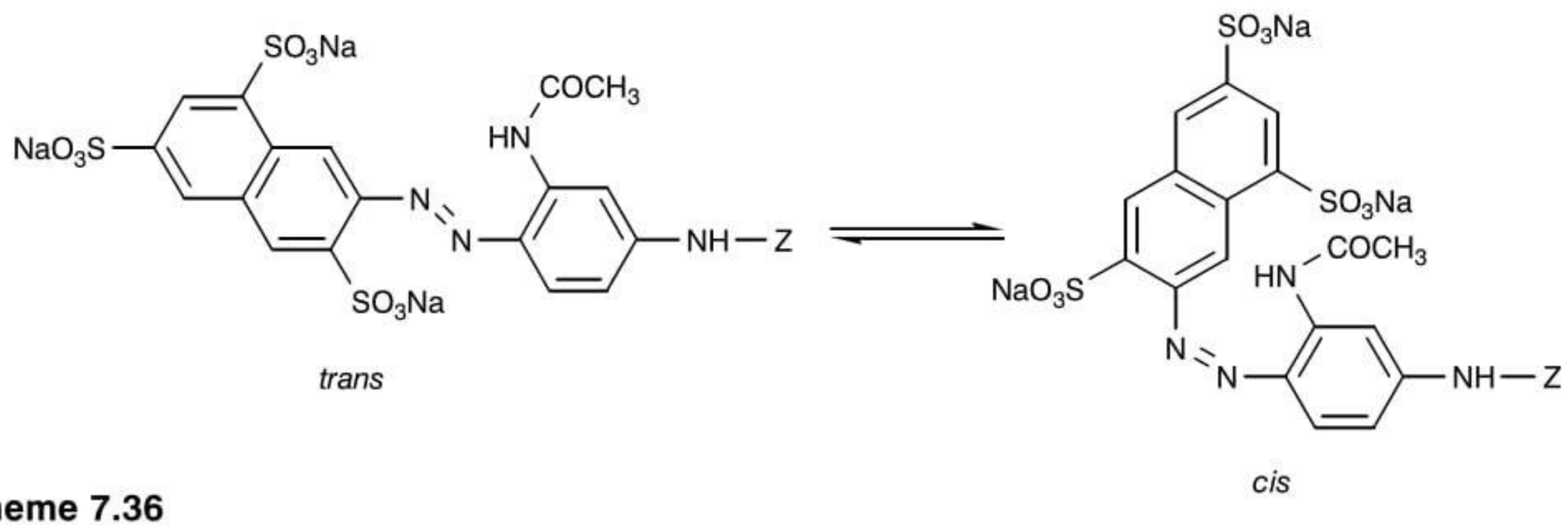
7.85



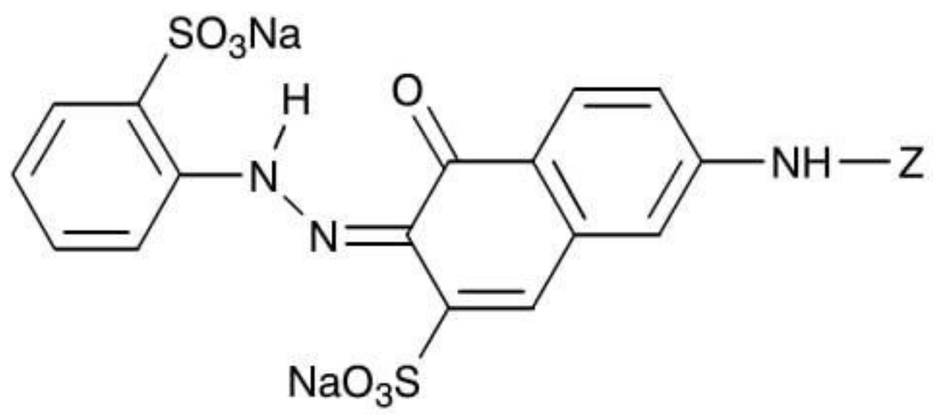
Scheme 7.35

7.5.2 Reddish yellow chromogens

Azo structures covering this sector of the colour gamut are prepared from di- or trisulphonated naphthylamine diazo components and *p*-coupling anilines, such as 3-aminophenylurea as in structure 7.88, 3-aminoacetanilide or cresidine (3-amino-4-methoxytoluene), with the reactive system attached to the terminal amino group. The kinetics of the azo coupling reaction (k_c) to form the Orange 12 chromogen from diazotised 2-naphthylamine-3,6,8-trisulphonic acid (7.86) and 3-aminophenylurea (7.87), as well as the rate of decomposition (k_d) of the diazonium salt (Scheme 7.35), were measured



Scheme 7.36



7.89

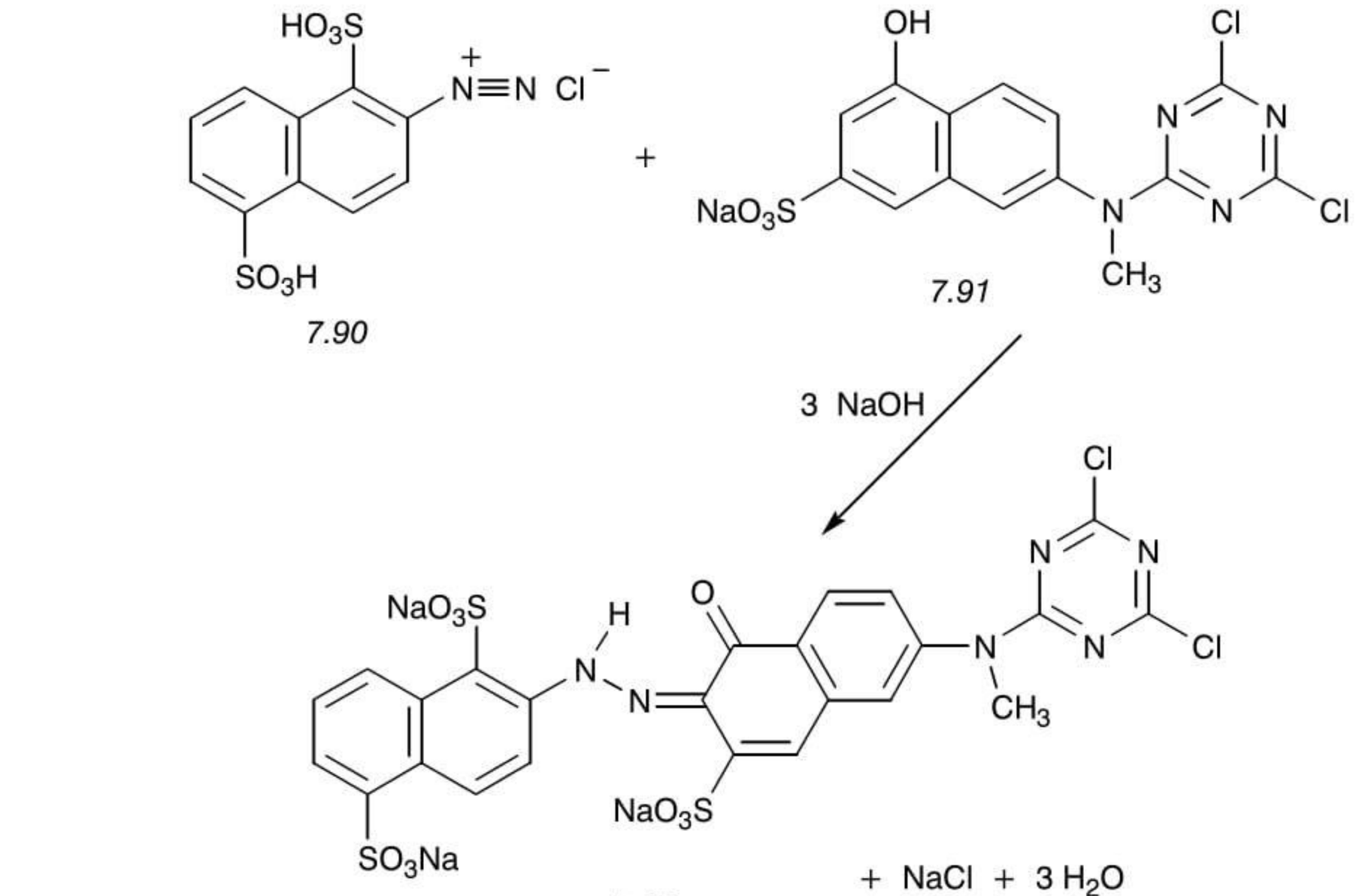
potentiometrically [81]. Stepwise condensations with cyanuric chloride and then with ammonia yield the aminochlorotriazine dye (7.88).

A well-recognised practical problem with arylazoaniline golden yellow dyes of this kind is photochromism. This slight change in hue is attributed to a reversible, photochemically induced transformation from the more stable *trans* to the less stable, less linear *cis* isomer (Scheme 7.36). It occurs very quickly on exposure to light but the thermal reversion from *cis* to *trans* in the dark is a much slower process. Greenish yellow chromogens (7.82–7.85) and orange reactive dyes of the J acid type (e.g. 7.89) do not exhibit this phenomenon. These structures are all derived from *o*-hydroxyazo coupling components that exist predominantly in the ketohydrazone form, so that rotation around the N–N axis is possible and *cis–trans* isomerism cannot occur [82].

7.5.3 Orange chromogens

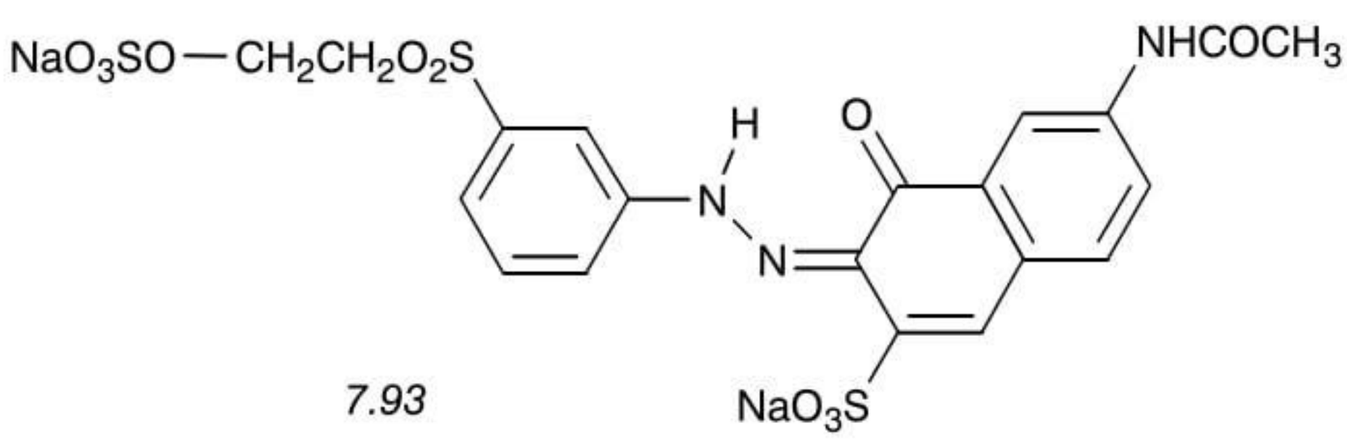
Dye bases for these dyes are obtained from a sulphonated arylamine as the diazo component and J acid as the coupler. Yellowish orange dyes are given by mono- or disulphonated anilines, as in structure 7.89, whereas reddish orange hues result from di- or trisulphonated naphthylamines, structure 7.92 being a typical example. If *N*-methyl J acid is used, as in this instance, the high substantivity that is characteristic of J acid dyes becomes somewhat lower, making it easier to wash-off the unfixed dyes after fixation. In a recent investigation [83], the kinetics of the coupling reaction between diazotised 2-naphthylamine-1,5-disulphonic acid (7.90) and the dichlorotriazinyl derivative of *N*-methyl J acid (7.91) that yields the Orange 4 chromogen (Scheme 7.37) were examined in detail.

In orange dyes of the haloheterocyclic type, the reactive system is invariably attached via the nitrogen of the J acid coupler. In vinylsulphone dyes, on the other hand, it is normally more convenient to use as diazo component an intermediate such as 7.38 or 7.39 bearing the precursor grouping together with an *N*-acetylated derivative of J acid or γ acid as coupler, structure 7.93 being typical.

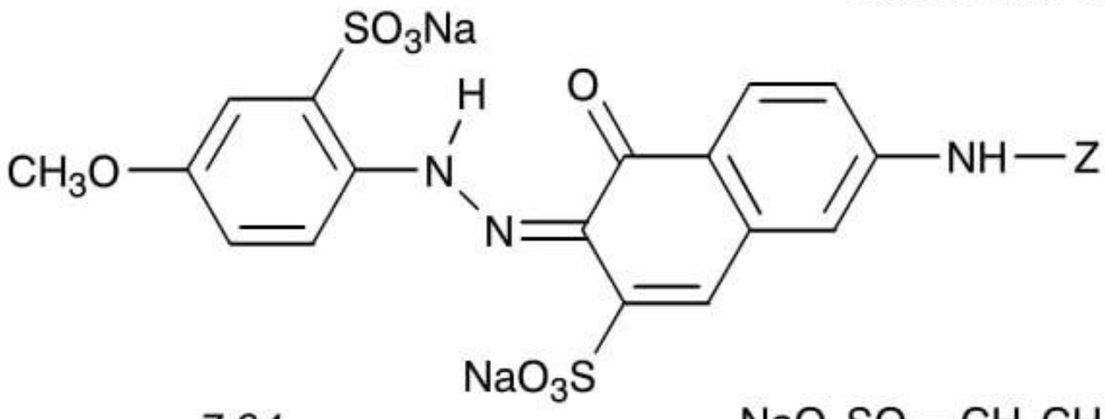


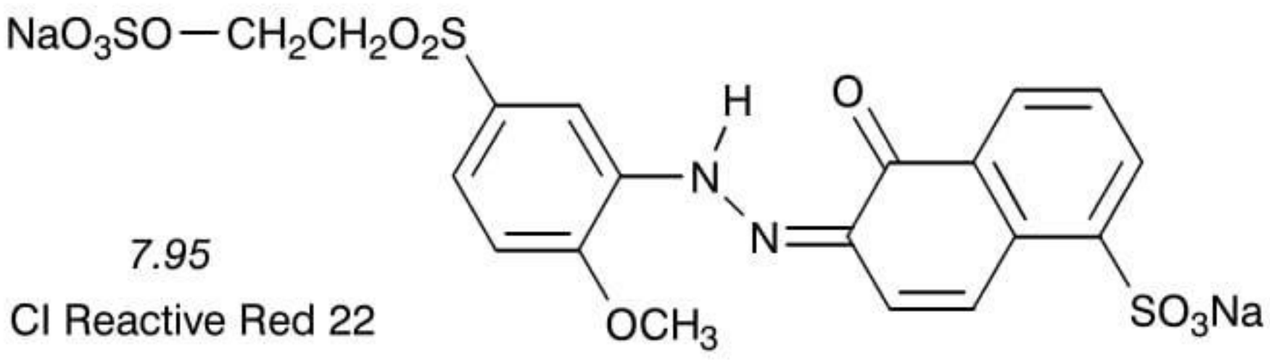
Cl Reactive Orange 4

Scheme 7.37



Cl Reactive Orange 7





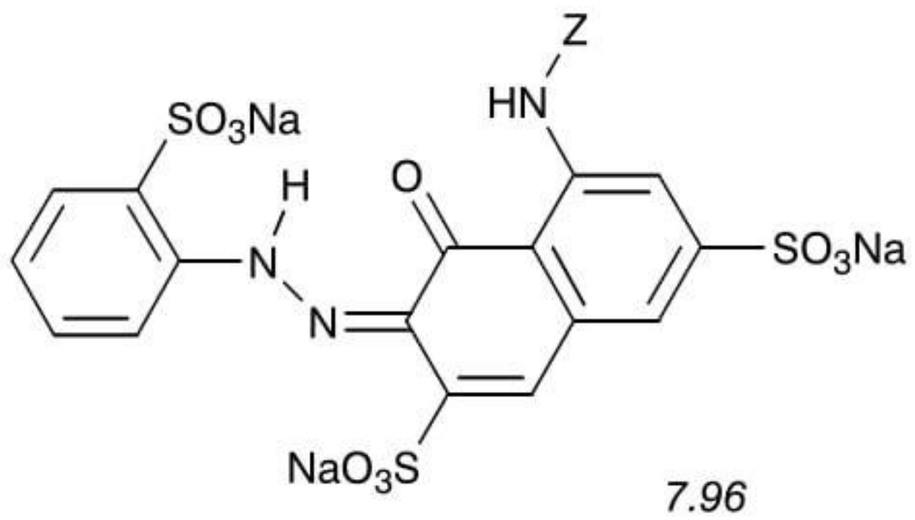
Cl Reactive Red 22

7.5.4 Scarlet chromogens

Dyes in this hue sector are also derived from J acid, *N*-methyl J acid or γ acid but the diazo component is usually a sulphonated 2- or 4-anisidine, as a methoxy substituent has a bathochromic influence. The highly substantive structure 7.94 is found in various haloheterocyclic (Z) dyes. As in the orange region, vinylsulphone dyes have the precursor grouping located on the diazo arylamine, as exemplified by structure 7.95.

7.5.5 Red chromogens

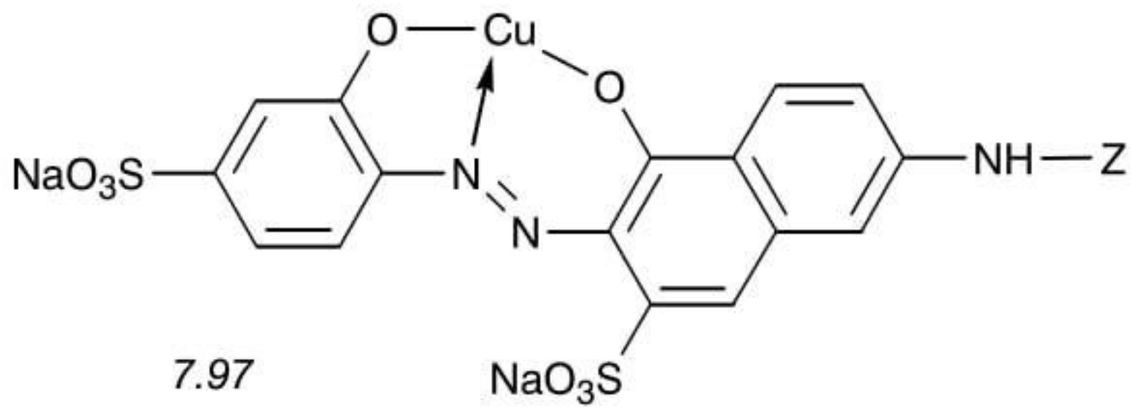
Bluish red reactive dyes are almost totally dominated by H acid as the indispensable coupling component. Various mono- or disulphonated anilines or naphthylamines are suitable diazo components, but the outstandingly important one is orthanilic acid (7.96). As with orange and scarlet dyes, haloheterocyclic (Z) reactive systems are linked via the imino group of the H acid residue but sulphatoethylsulphone substituents are found in the diazo component with *N*-acetyl H acid as the typical coupler. A characteristic problem associated with reactive dyes derived from H acid is their accelerated fading under the simultaneous influence of perspiration and light (section 3.3.4).



7.96

7.5.6 Rubine chromogens

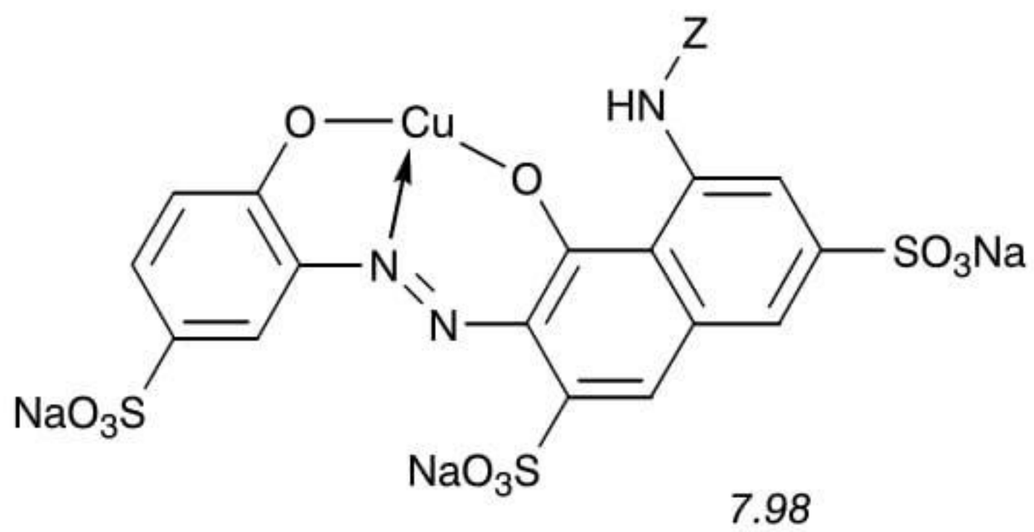
Bordeaux and rubine hues are given by 1:1 copper-complex monoazo structures made from a diazotised aminophenolsulphonic acid and J acid or γ acid, with the haloheterocyclic group (Z) on the coupling component (7.97). As usual in the vinylsulphone series it is more convenient to use a precursor-substituted aminophenol with *N*-acetyl J acid as coupler. In the red–violet–blue zone of the colour gamut the higher light fastness shown by copper complexes compared with their unmetallised analogues is particularly desirable in spite of the sacrifice of some brightness.



7.97

7.5.7 Violet chromogens

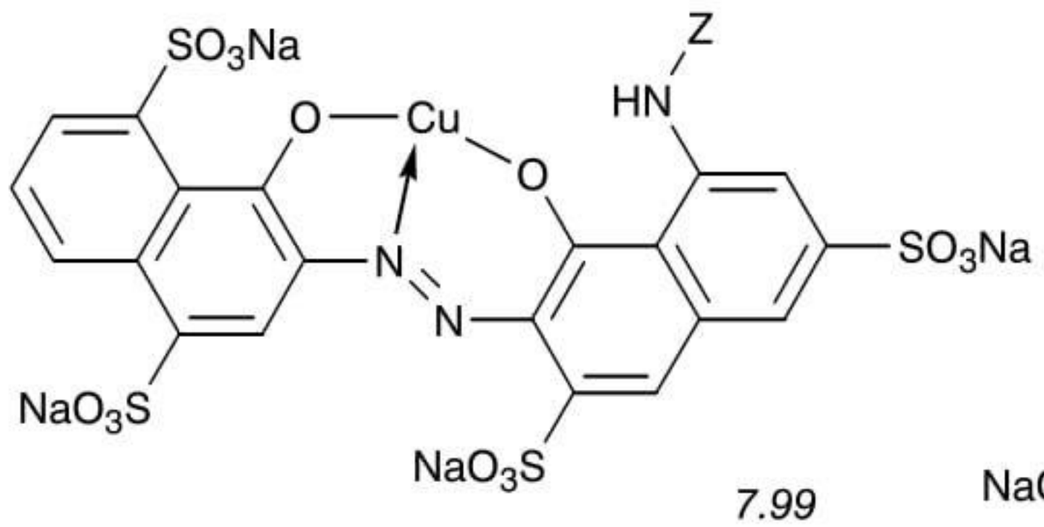
These very much resemble the corresponding rubine dyes but have H acid rather than J acid as the coupling component. This does mean that there is some risk of accelerated fading as a result of the combined effects of perspiration and light. The histidine component of perspiration is able to abstract the copper from some metal-complex azo dyes (section 5.7.2) and the demetallised H acid structure will then be vulnerable to this problem (section 3.3.4). Nevertheless, these copper-complex violet dyes are much less sensitive than the unmetallised bright bluish reds in this respect. Examples of typical structures include those with a haloheterocyclic (Z) group on the H acid residue (7.98) and those such as CI Reactive Violet 5 (7.34) with a sulphatoethylsulphone group in the diazo component.



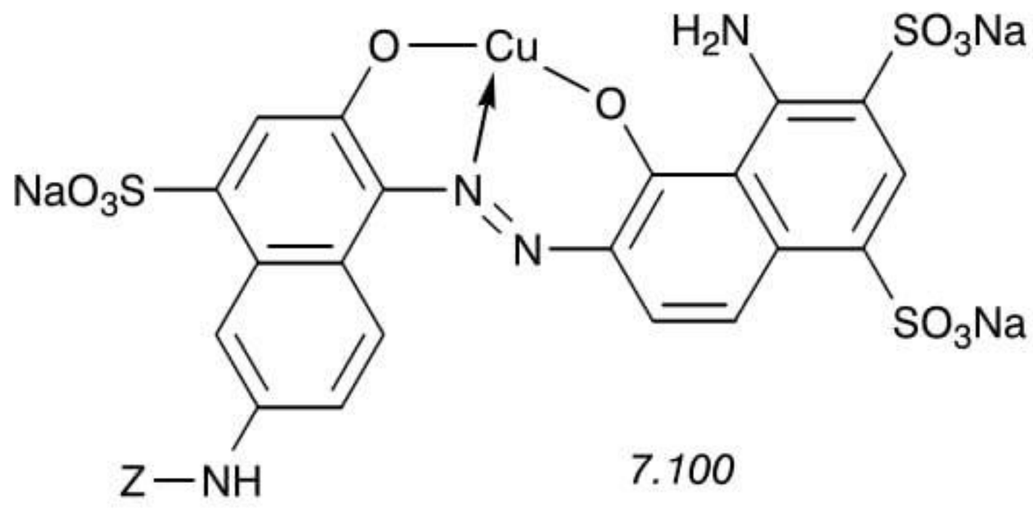
7.98

7.5.8 Dull blue chromogens

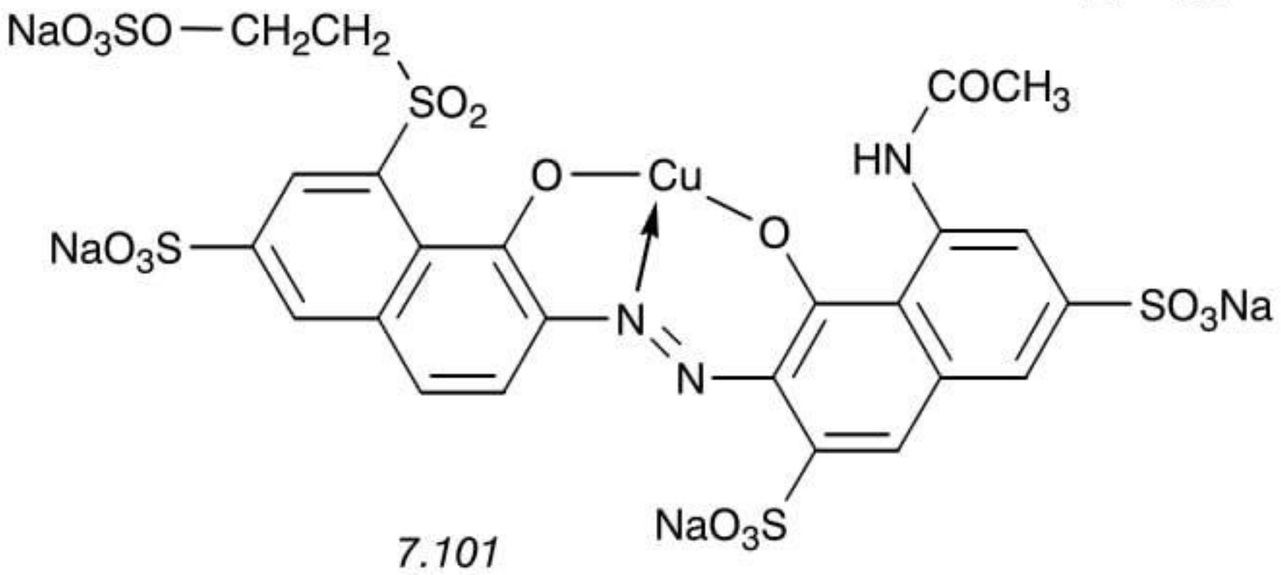
These are reddish blue 1:1 copper-complex monoazo dyes derived from a 2-naphthylamine- or 2-aminonaphtholsulphonate as diazo component and another aminonaphtholsulphonate as coupler. Often such dyes are more easily prepared using a 2-naphthylaminesulphonate and oxidatively coppering the resulting monoazo dye (section 5.5.3). In orthodox structures the imino link of H acid carries the reactive system (7.99), but in other instances the naphthylamine diazo component provides the site of attachment of a haloheterocyclic (7.100) or sulphatoethylsulphone (7.101) grouping.



7.99



7.100

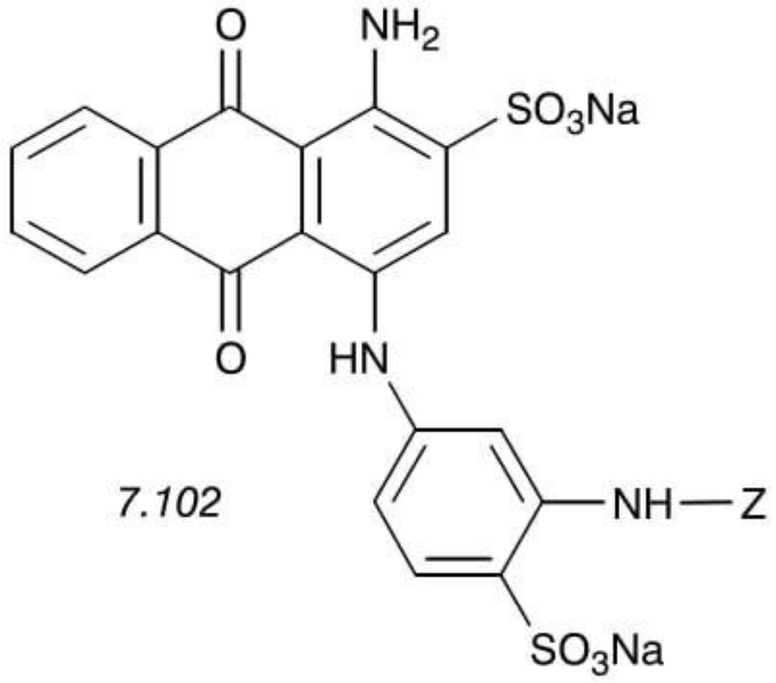


7.101

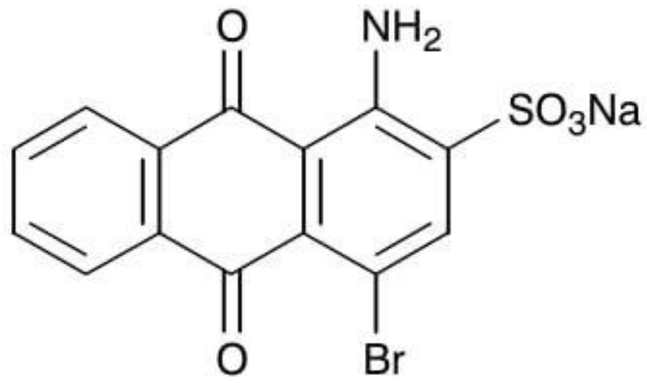
7.5.9 Bright blue chromogens

Two different chemical classes contribute to this sector. Initially it was entirely dominated by anthraquinone dyes typified by structure 7.102. The dye bases for attachment of haloheterocyclic (Z) systems are prepared by condensing bromamine acid (7.103) with various phenylenediamines. The outstandingly successful CI Reactive Blue 19 (7.37) is the

condensation product of bromamine acid with the precursor arylamine 7.39. More recently, bright blue symmetrical structures of the triphenodioxazine class (7.104; –NH–R–NH– = alkylenediamine, Z = haloheterocyclic system) have been developed. These are tinctorially much more intense than anthraquinone chromogens and thus offer economic advantages. The marketing of a bis(aminonicotinotriazine) dye of this class (CI Reactive Blue 187) had an important influence on the subsequent development and success of the Kayacelon React (KYK) range of dyes containing this bis-quaternary system (section 7.4.2).



7.102

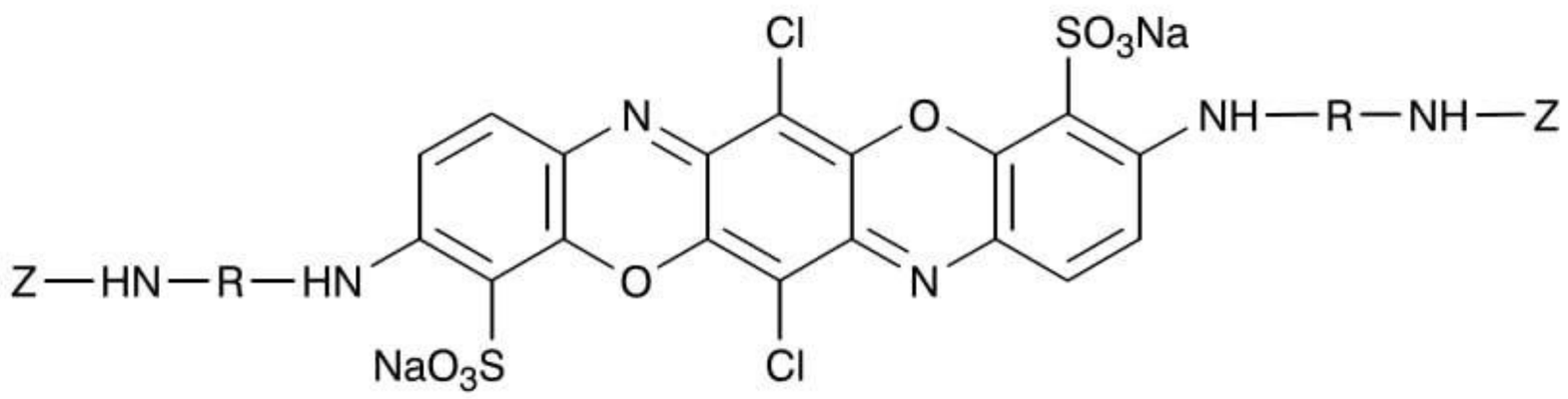


7.103

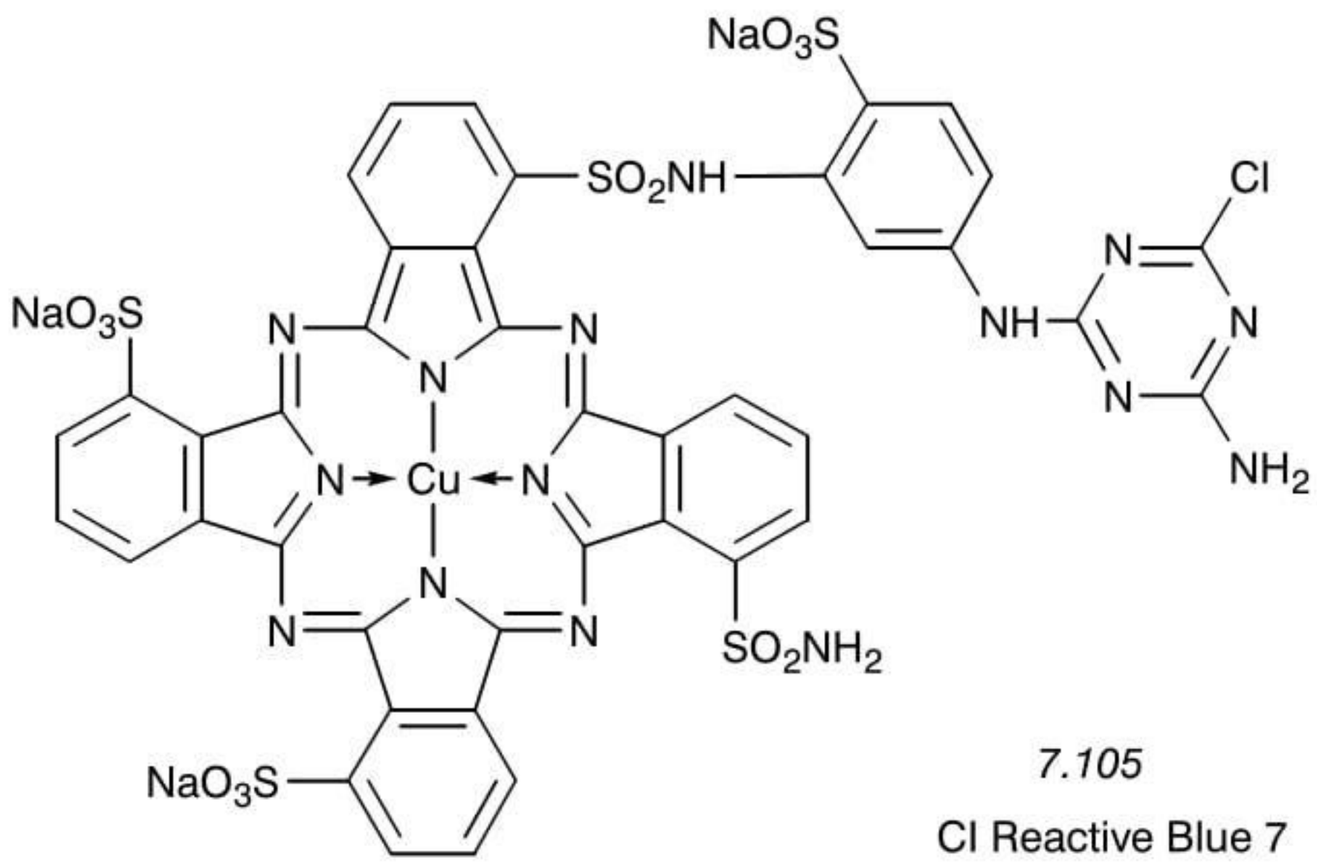
Bromamine acid

7.5.10 Turquoise chromogens

This colour makes an important contribution to the appeal of reactive dyeings and prints. It is totally dominated by dyes derived from copper phthalocyanine (section 5.4.3). A notable early example is structure 7.105, made from copper phthalocyanine by chlorosulphonation of all four 3-positions, partial reaction with phenylene-1,3-diamine-4-sulphonic acid and ammonia, hydrolysis of the remaining chlorosulphonyl groups, then finally introduction of the reactive system using cyanuric chloride and ammonia. Such products are inhomogeneous mixtures of slightly different components, the overall balance of substituents totalling four per molecule as shown in formula 7.105. Solubility and dyeing properties of these dyes can be modified by varying the proportion of 3-sulphonamide (polar) to 3-sulphonic acid (hydrophilic) groups, as well as selection from a variety of phenylenediamines. An important dye of this class is CI Reactive Blue 21, in which the reactive function is provided by a 3-$SO_2NHPhSO_2CH_2CH_2OSO_3Na$ grouping.



7.104

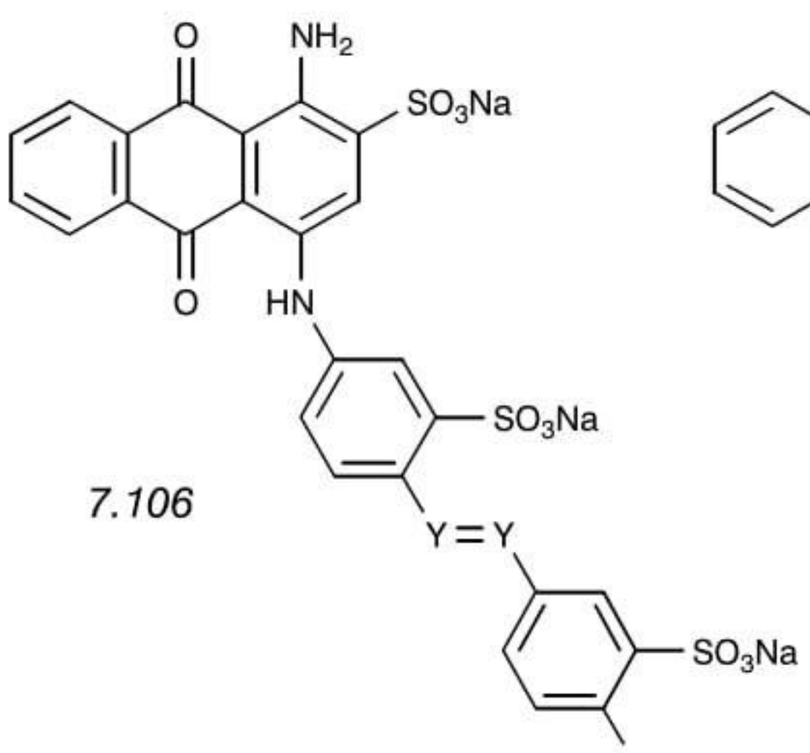


7.105

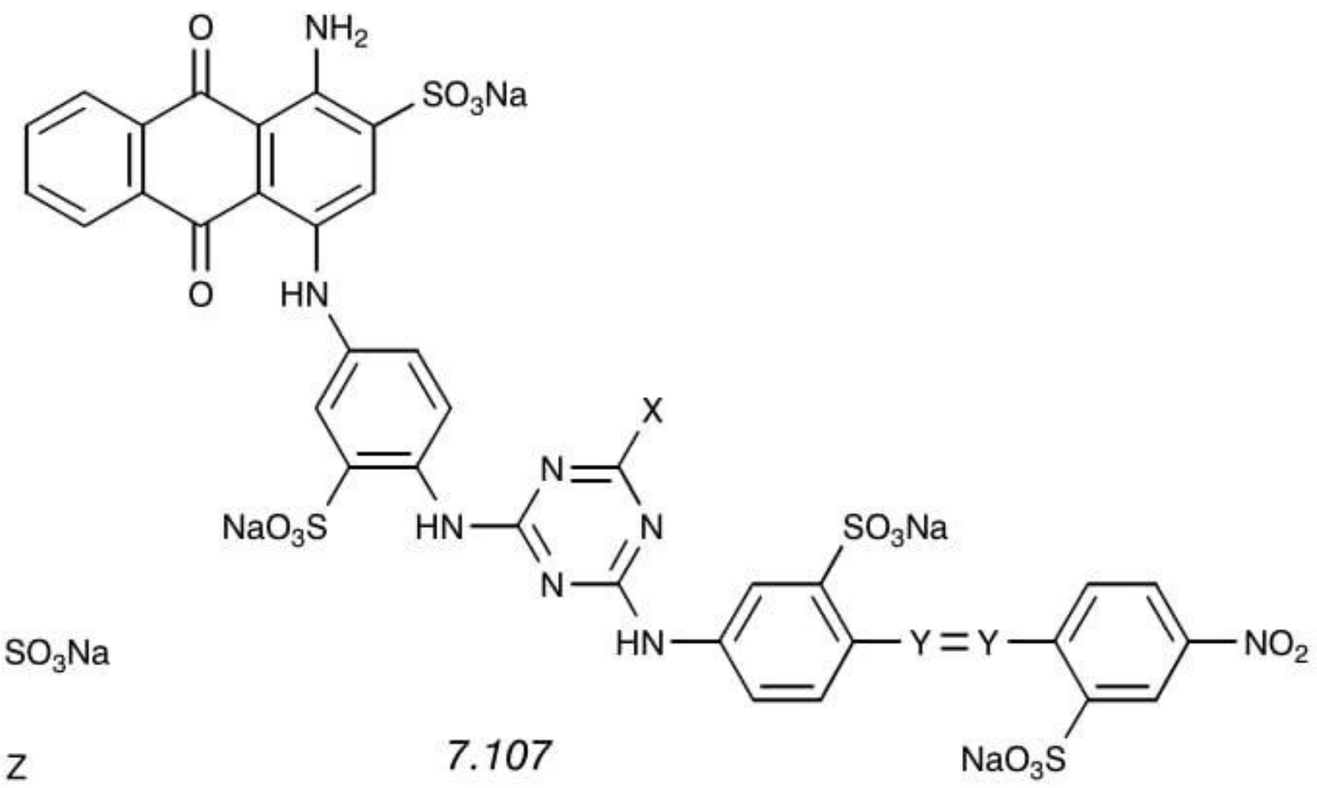
CI Reactive Blue 7

7.5.11 Green chromogens

Only relatively few green reactive dyes have been marketed and most of them have been designed by linking up separate blue and yellow chromogens. The most important approach has been to attach a yellow monoazo (Y = N) or stilbene (Y = CH) chromogen to a bromamine acid residue, either directly (7.106) or via a phenylenediamine linking group and an aminohalotriazine system (7.107; X = Cl or F). Another possibility is to incorporate a yellow chromogen together with the reactive grouping of a copper or nickel phthalocyanine, but such dyes have unattractive dyeing properties because of the length of this extended substituent. In a few instances, dull bluish greens can be achieved from twice-coupled H acid structures if the two diazo components are correctly chosen, as in the bis(aminochlorotriazine) dye CI Reactive Green 19.



7.106

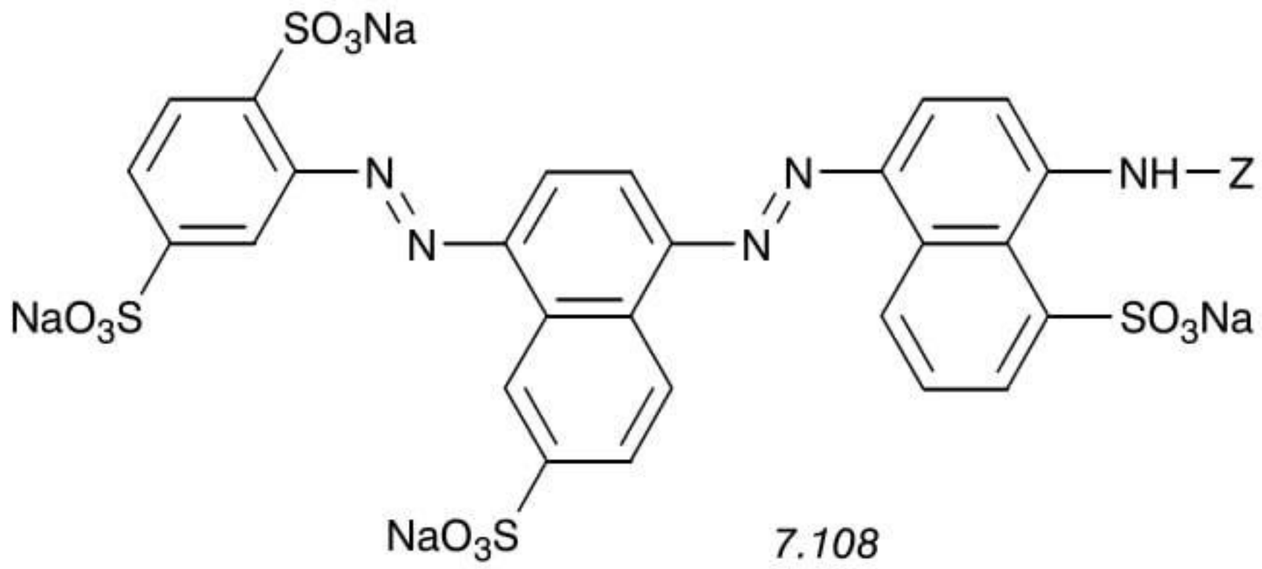


7.107

7.5.12 Brown chromogens

Unmetallised disazo dyes of the type A→M→E in Winther symbols (section 4.7) dominate this sector. The A component is usually a disulphonated aniline or naphthylamine. Orthanilic acid or *p*-xylidine (2,5-dimethylaniline) for yellow browns, or a variety of monosulphonated 1-naphthylamines for redder browns, are selected as the M and E components. The terminal amino group provides the site for attachment of the reactive

system (Z). Structure 7.108 illustrates a typical reddish brown. Monoazo J acid, γ acid or pyrazolone ligands have been used in unsymmetrical 1:2 cobalt or chromium complexes with a reactive group in each ligand to give brown dyes of high fastness to light and wet treatments.



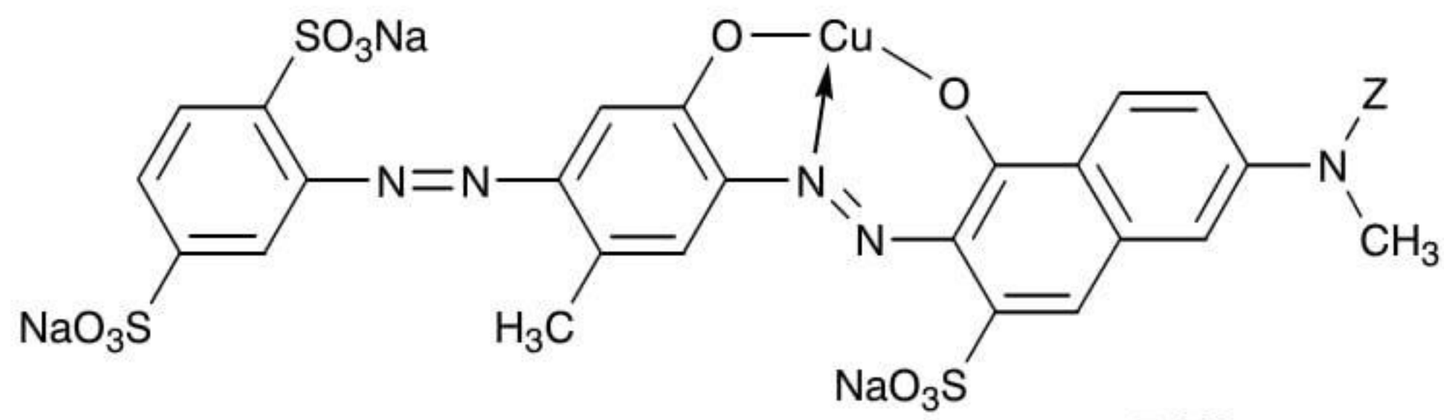
7.108

7.5.13 Navy blue chromogens

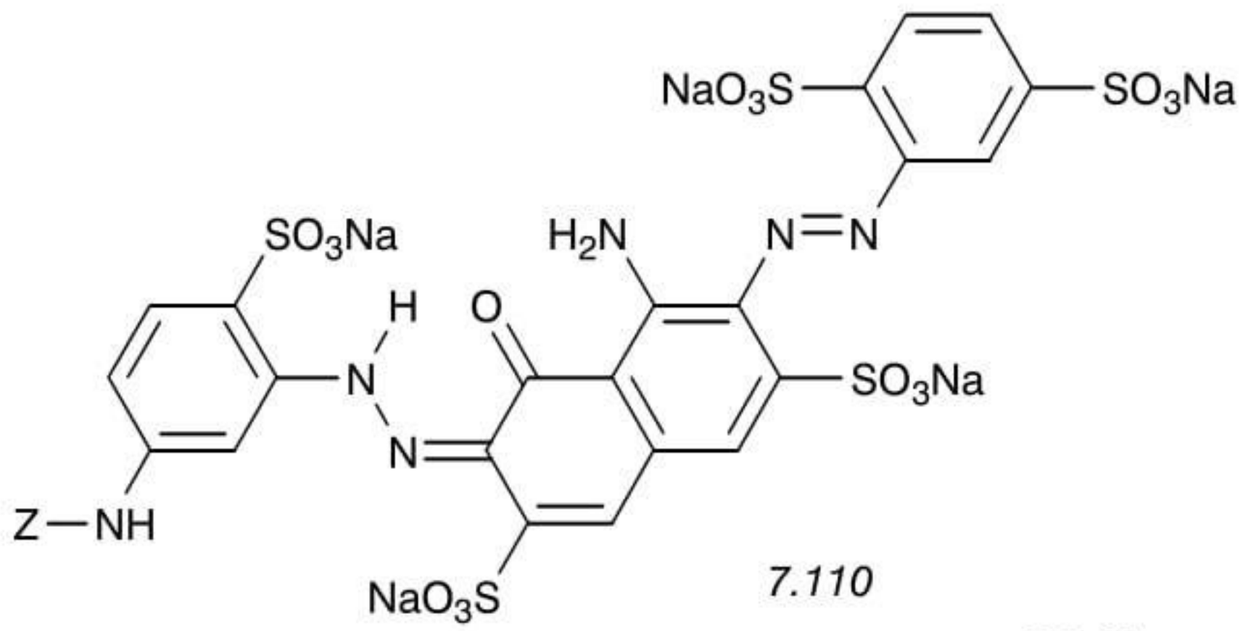
Three major approaches have been followed to provide reactive dyes in this important sector. One category is closely related to the reddish blue monoazo 1:1 copper complexes already described (section 7.5.8). To provide the higher substantivity and deeper intensity for build-up to navy blue shades, a second unmetallised azo grouping is introduced. As with the brown dyes, the A→M→E pattern is adopted for their synthesis. Component A is normally a sulphonated aniline, M an aminophenol or aminocresol and E a sulphonated naphthol or aminonaphthol. The reactive system (Z) is usually, but not invariably, located on the E component and the copper atom always coordinates with an o,o′-dihydroxyazo grouping provided by the M and E components (7.109).

This hue sector is dominated, however, by the more economical unmetallised twice-coupled H acid derivatives. In these dyes the amino group in the H acid molecule is not used to attach the reactive system because that would prevent conjugation between the two azo groups. As in structure 7.110, the diazo components are almost always aniline-2,5-disulphonic acid and a sulphonated phenylenediamine. Usually the former is attached by acid coupling *ortho* to the amino group and the latter, which provides the site for the haloheterocyclic (Z) group, by alkaline coupling *ortho* to the hydroxy group. In monofunctional vinylsulphone dyes of this type, a precursor-bearing intermediate such as 7.38 or 7.39 is introduced by alkaline coupling to the hydroxy side of the H acid residue.

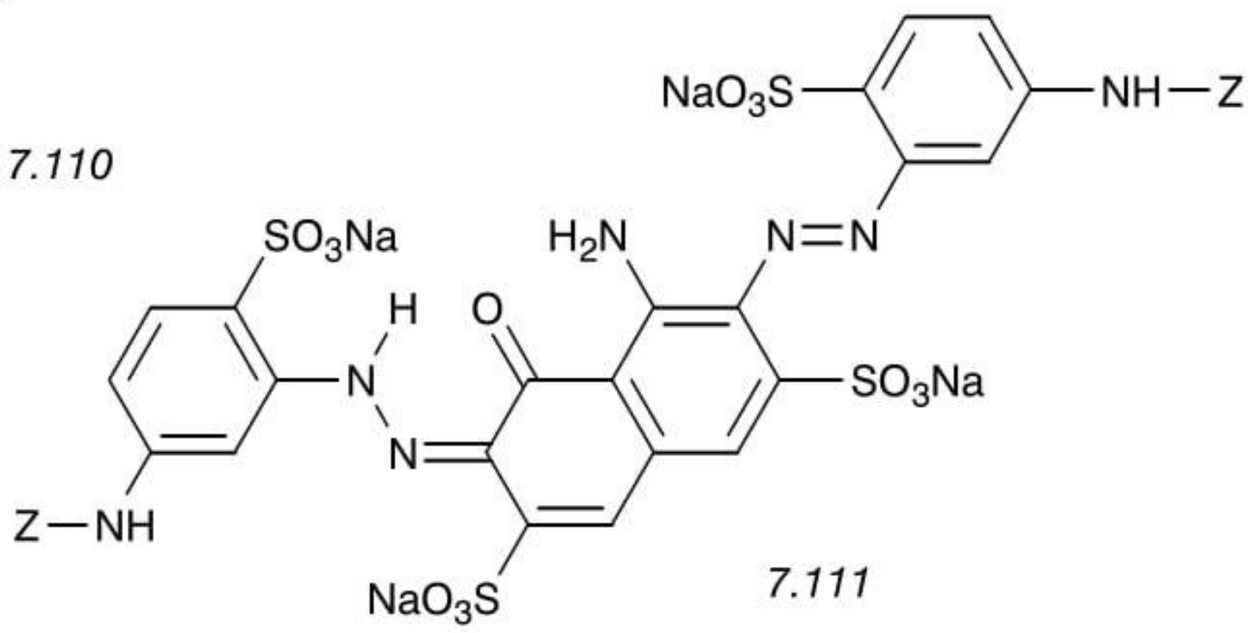
In the outstandingly successful CI Reactive Black 5, two such precursor-bearing units are used in the synthesis of this near-symmetrical bifunctional structure (7.36). Following this precedent, competing bifunctional dyes of analogous structure were designed with two phenylene-1,3-diamine-4-sulphonate groupings to accommodate the reactive systems



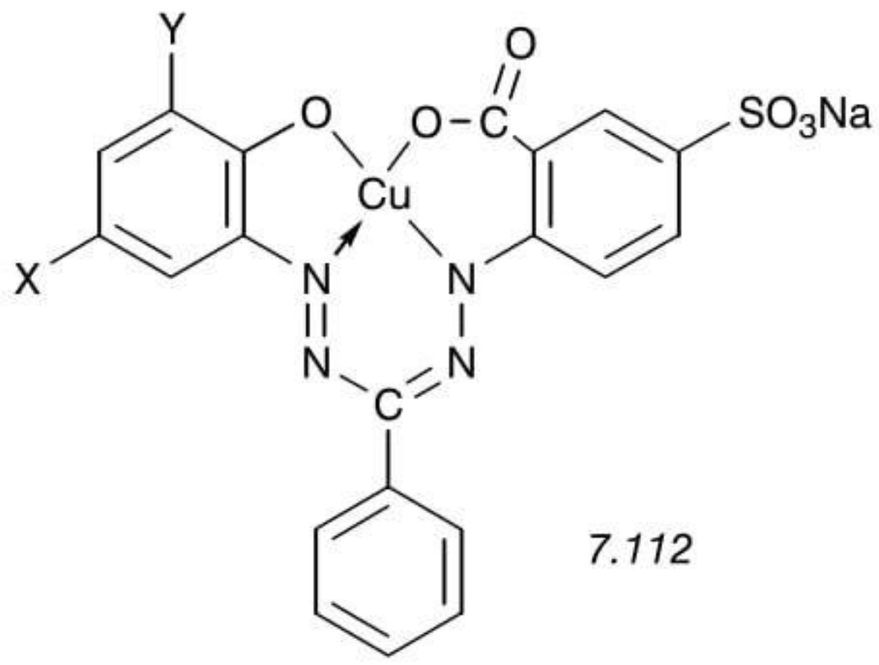
7.109



7.110



7.111



7.112

(7.111). Navy blue reactive dyeings that meet exceptional levels of fastness to light and wet treatments can be achieved (at a price) by turning to copper formazan complexes (7.112). In those dyes with a haloheterocyclic reactive system, this is normally attached through an imino link at position Y and X is a sulpho group. Conversely, in vinylsulphone analogues Y is sulpho and X is the sulphatoethylsulphone precursor.

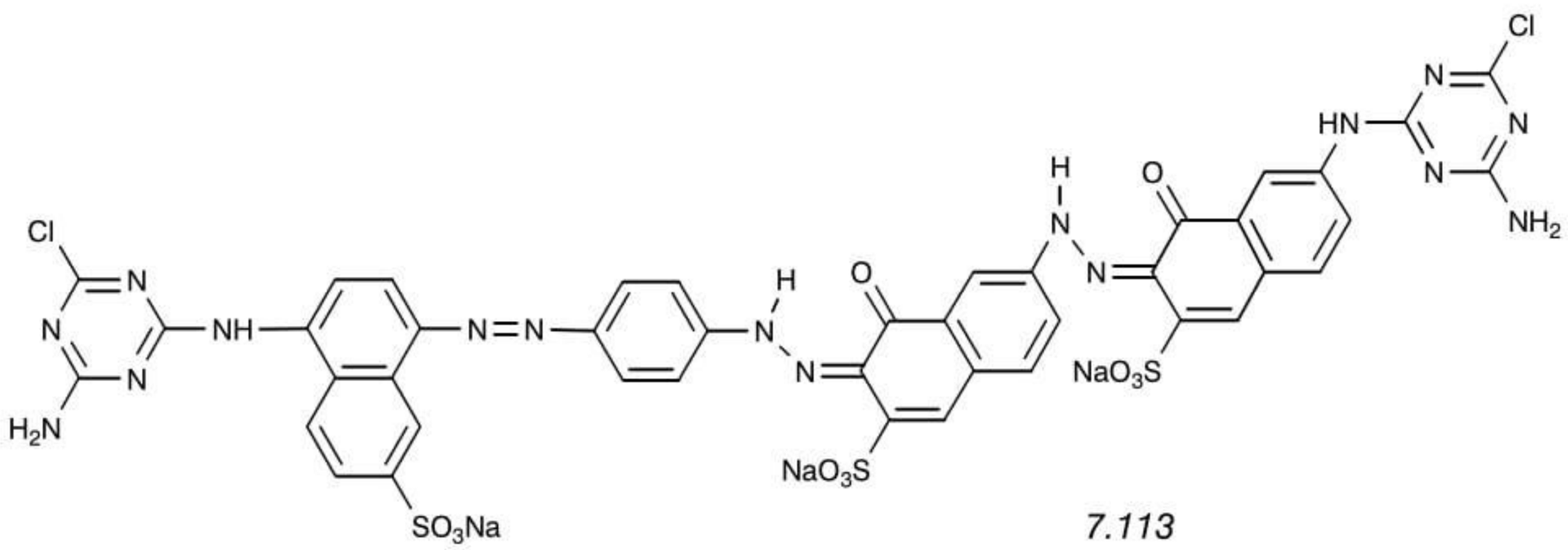
7.5.14 Black chromogens

This is almost a contradiction in terms for reactive dyes. As in the green sector, it is difficult to design a homogeneous reactive dye that will yield deep black dyeings without shading. The economically attractive twice-coupled H acid dyes build up well but even those described as blacks, such as CI Reactive Black 5, are really dark navy blues. Dyes of this kind are readily shaded with low-cost browns of the A→M→E type (section 7.5.12), or with smaller amounts of yellow and red shading components, to give general-purpose black mixtures of considerable versatility. Copper-complex navy blues can be used in a similar way with shading components of high light fastness for more demanding outlets.

Mixed cobalt/chromium complexes of the symmetrical 1:2 type in which each ligand contains a low-reactivity system linked to the coupling component (section 5.5.2) have been widely used for continuous dyeing and printing. They offer high light fastness and the

unfixed dye is more readily washed-off because such structures tend to be less substantive to cellulose than the unmetallised disazo dyes designed principally for exhaust dyeing.

Homogeneous black chromogens are well represented among direct dyes, where highly substantive trisazo or tetrakisazo structures are often encountered. Quite often these contain primary amino groups as auxochromes and hydrogen bonding sites positioned at each end of the molecule. It would not be difficult to convert the typical trisazo dye CI Direct Black 80, for example, into its bis(aminochlorotriazine) derivative (7.113). This hypothetical structure, however, would possess such a high substantivity and such a slow rate of diffusion that undesirable characteristics of poor levelling, inadequate penetration and inefficient fixation would be likely, together with great difficulty at the washing-off stage. This performance profile is reminiscent of that shown by the pentafunctional red dye (7.79) described in section 7.4.4 [74].

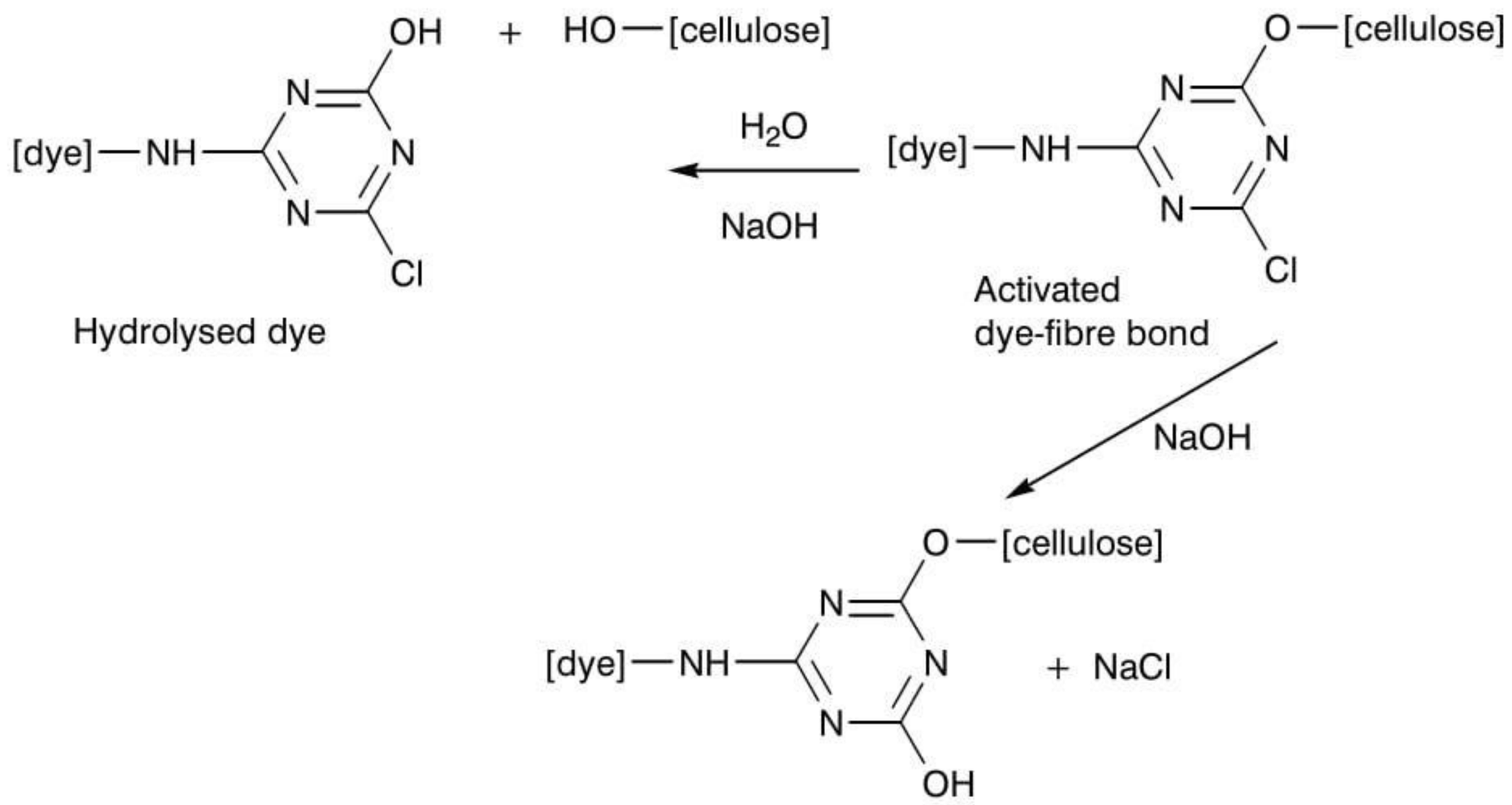


7.113

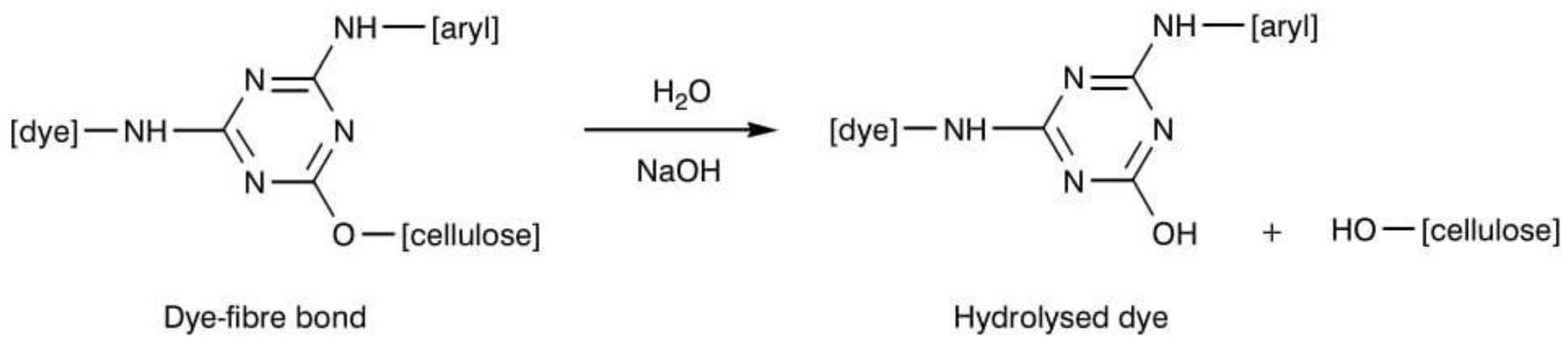
7.6 STABILITY OF DYE–FIBRE BONDS

The chromogens used to synthesise reactive dyes normally exhibit poor wet fastness in the unfixed state. The high wet fastness of reactive dyeings depends almost entirely on the resistance of the dye–fibre bonds to the agencies characteristic of wet fastness tests, including pH, temperature, surfactants and oxidants. When the dye–fibre reaction product is formed during the fixation process (Schemes 7.8 and 7.25), many of the factors responsible for the susceptibility of the reactive system to hydrolysis remain operative and may play a decisive part in determining the wet fastness attainable [10]. Thus when a dichlorotriazine dye reacts with a cellulosate anion, one of the chloro substituents is replaced by an electron-releasing cellulosyl grouping that is less electronegative. The other electronegative chlorine and three nitrogen atoms remain, however, activating the substituents on the heterocyclic ring to hydrolytic attack (Scheme 7.38). This can result in either stabilisation or rupture of the dye–fibre bond.

A somewhat different balance exists with the less reactive aminochlorotriazine dyes. Since an arylamino group is more strongly electron-releasing than the cellulosyl grouping, the electronegative influence of the three nitrogen atoms in the ring predominates and only the activated cellulosyl ether bond is subject to hydrolytic attack (Scheme 7.39). For this reason, therefore, such dye–fibre linkages will be marginally less stable under alkaline conditions than those formed by the reaction of cellulose with a dichlorotriazine dye. The marginal differences in dye-fibre bond stability between aminochlorotriazine, bis(amino-chlorotriazine) and bis(aminofluorotriazine) dyes were examined by treating cotton dyeings



Scheme 7.38



Scheme 7.39

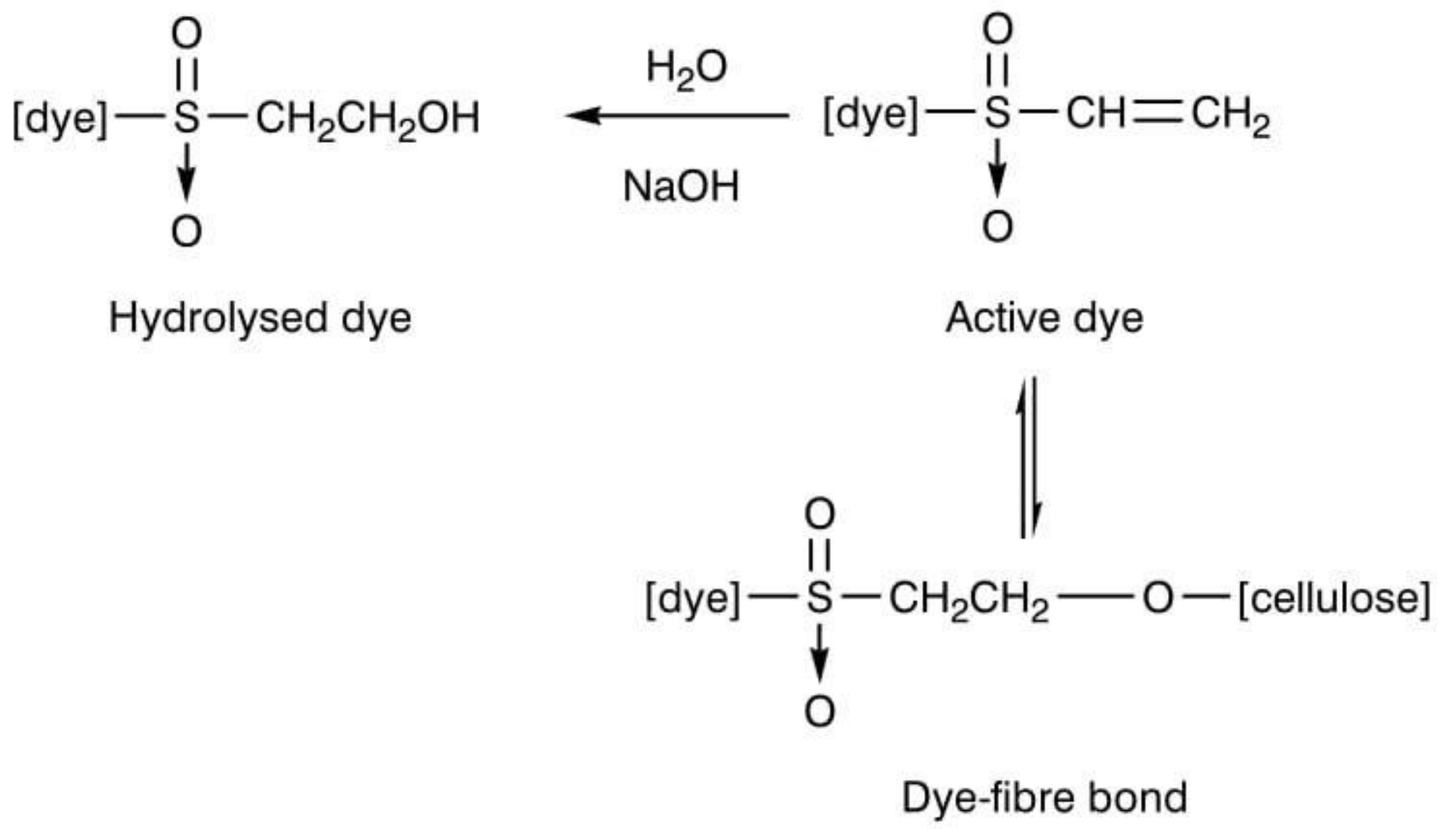
in buffer solutions (pH 10 or 12) at various temperatures (60, 85 or 98 °C). The results were expressed in terms of the percentage of hydrolysed dye released [84].

If a pyrimidine ring forms the basis of a chloroheterocyclic reactive system, the effects are similar to those for chlorotriazine analogues but the activation by only two ring nitrogen atoms is much less marked (Figure 7.1). Thus pyrimidine dye–fibre linkages are more stable to alkali than either of the corresponding chlorotriazine systems. The rate-determining step for acidic hydrolysis of haloheterocyclic systems is nucleophilic attack of the protonated heterocyclic ring by water molecules.

The relative fixation given by various haloheterocyclic dyes on cotton and the stability of their dye–fibre bonds under acidic and alkaline conditions have been compared. Among the triazines, the highest relative fixation (70%) was shown by 2-arylamino and 2-heterylamino derivatives. Among the pyrimidines, the 5-cyano-2,4-dichloro derivatives gave 73% but the 5-chloro-2,4-difluoro derivatives achieved 84%. The latter system also yielded the most stable dye-fibre bonds in acidic as well as alkaline media [85]. A series of quantum mechanical calculations for cellulosic dyeings prepared with analogous dyes representing twelve different reactive systems containing either a pyrimidine or an s-triazine ring provided rate constants for hydrolysis under acidic and alkaline conditions [86].

When fixation to cellulose is achieved by a nucleophilic addition mechanism (Scheme

7.25), an important factor is the reversibility of formation of the dye–fibre bond. Severe alkaline treatments are capable of rupturing this linkage to regenerate the unsaturated reactive system, which is able to react again either with cellulose or with water (Scheme 7.40). The presence of a less electronegative activating group than sulphone, as in the vinylsulphonamide dyes (7.41), increases the stability of the dye–fibre bond but reduces the reactivity of the dye.



Scheme 7.40

The kinetics of alkaline hydrolysis of a series of eleven vinylsulphone reactive dyes fixed on cellulose have been investigated at 50 °C and pH 11. Bimodal hydrolytic behaviour was observed under these conditions, the reaction rates being rapid at first but becoming slower as the concentration of fixed dye remaining gradually decreased. These results were attributed to differences in the degree of accessibility of the sites of reaction of the dyes within the fibre structure [87].

In an interesting comparison of dye–fibre bond stabilities over the pH range 3.5–10, dyeings of an aminochlorotriazine-sulphatoethylsulphone bifunctional dye were compared with those of two monofunctional analogues of almost identical structure. Under acidic conditions the bifunctional dyeing showed higher stability than the vinylsulphone dyeing, which in turn was more stable than the monofunctional aminochlorotriazine analogue. At alkaline pH, on the other hand, the aminochlorotriazine analogue and the bifunctional dyeing were virtually identical in stability, both being markedly more stable than the monofunctional vinylsulphone [74]. For similar reasons, bifunctional reactive dyeings of the aminofluorotriazine-sulphatoethylsulphone type show better allround stability to acidic and alkaline conditions than analogous monofunctional dyeings based on dichlorotriazine, aminochlorotriazine, aminofluorotriazine or vinylsulphone systems [77].

Reactive tendering refers to the strength loss of reactive-dyed cellulosic garments that can occur during commercial laundering. The effect is attributed to the inductive electron-withdrawing influence of the dye structure on the dye–fibre bond, which accelerates acid hydrolysis of β-1,4-glycosidic linkages in the cellulose chain [88]. Conversion of sodium sulphonate groups in the dye molecule to the free acid form by prolonged rinsing can also contribute to acid tendering.

The hydroxide ion is not the most active nucleophile with which the dye–fibre bonds in reactive dyeings have to contend. Many commercial detergent formulations contain sodium

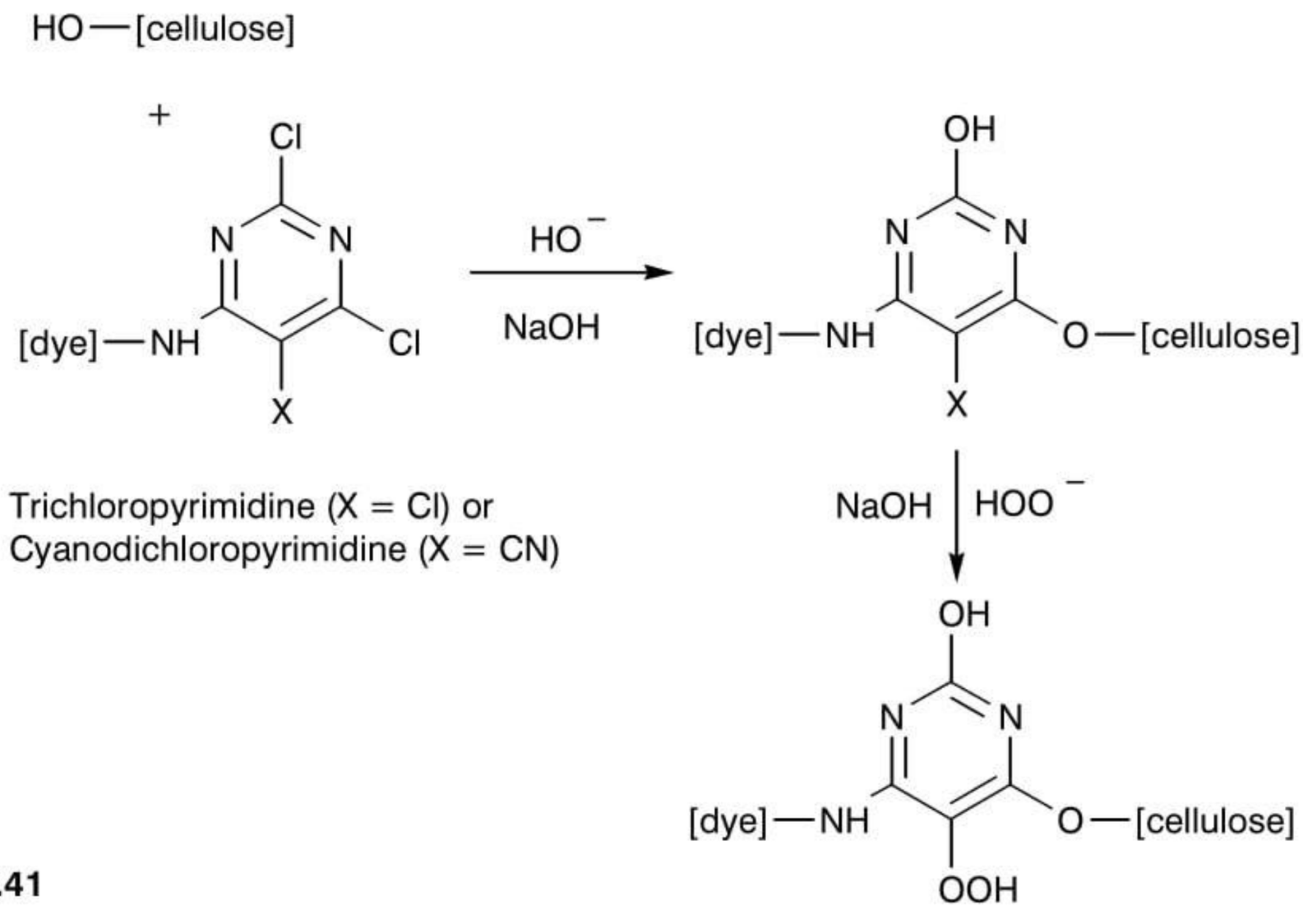
perborate or percarbonate that may release peroxy species in washing treatments. The perhydroxide anion (HOO^-) is an exceptionally powerful nucleophile capable of attacking certain types of haloheterocyclic reactive system to give unstable products. Studies of the reaction of alkaline peroxide solutions with dissolved reactive dyes have shown that reactive chloro substituents are readily displaced. Heterocyclic dyes containing other leaving groups, such as fluoro- or nicotinotriazines, and systems that fix by nucleophilic addition, e.g. vinylsulphone dyes, generally do not show perhydroxide formation.

Surprisingly, however, dyes of the chlorodifluoropyrimidine type readily form a perhydroxide derivative that leads to cumulative damaging effects on dye–fibre bond stability. A comparison between seven different haloheterocyclic systems each attached to the same chromogen (phenylazo H acid) demonstrated several important conclusions [89]:

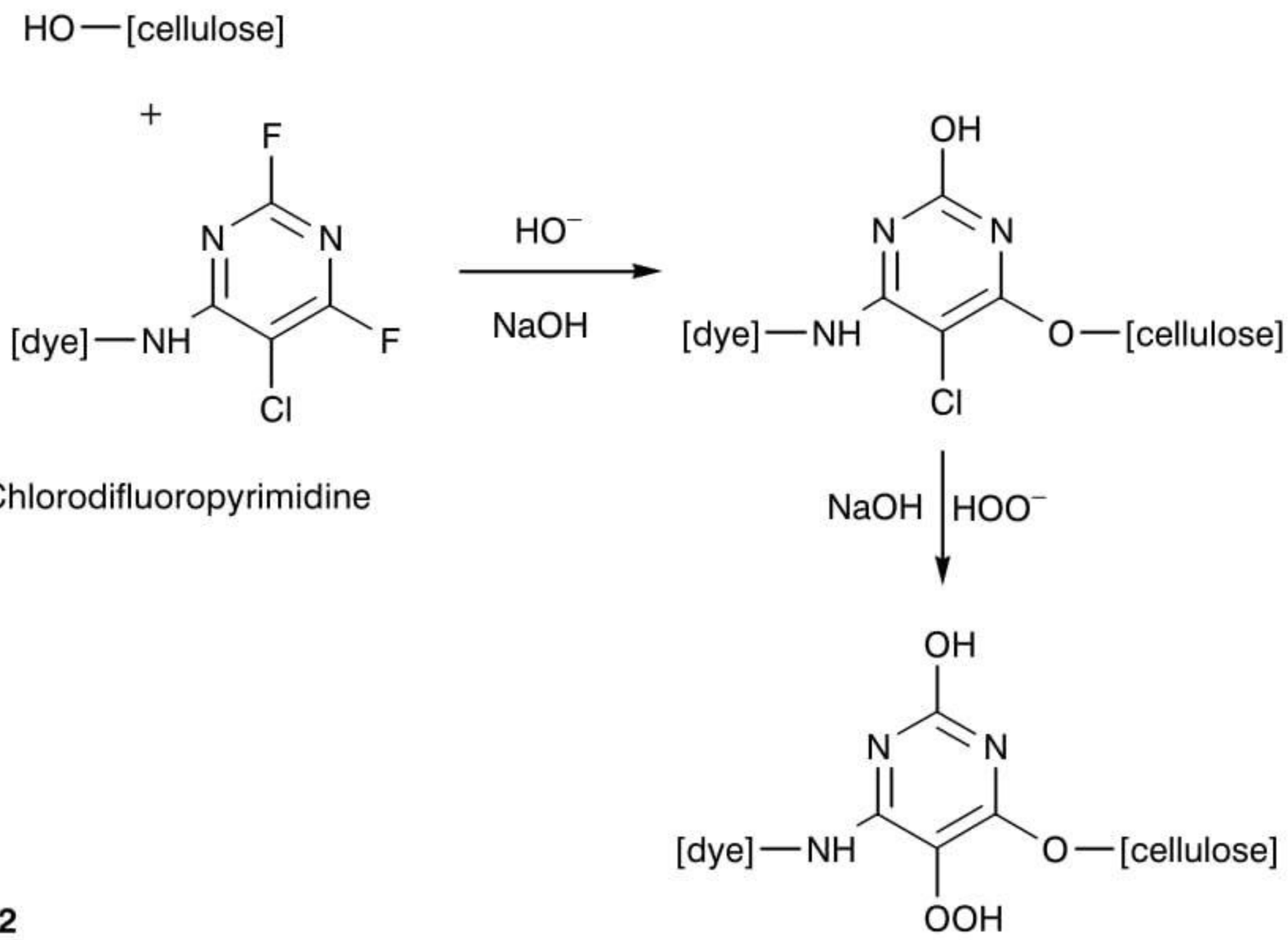
(1) Only dye–fibre linkages that carry on the heterocyclic ring an electronegative substituent that is *ortho* (or *para*) to the dye–fibre bond show both peroxidation (Schemes 7.41 to 7.43) and bond breakage (Scheme 7.44).
(2) Dye–fibre linkages that carry on the heterocyclic ring an electronegative substituent that is *meta* to the dye–fibre bond may show peroxidation (Scheme 7.45) but only slight breakage of bonds.
(3) Dye–fibre linkages with no electronegative substituents on the heterocyclic ring show neither peroxidation nor bond breakage, e.g. aminochlorotriazine, aminofluorotriazine, bis(aminochlorotriazine) and bis(aminonicotinotriazine) dyes.

An amine aftertreatment has been developed recently to protect haloheterocyclic dyes with substituents vulnerable to attack by perborates or other peroxy compounds in detergents. This product displaces such substituents, deactivating the dye–fibre bond system and rendering it resistant to peroxidic attack [90].

The relationship between dye–fibre bonding and light fastness was examined for ten sulphatoethylsulphone reactive dyes on cellulose and it was shown that the stronger the bonding between dye and substrate, the more stable was the dyeing when exposed to light

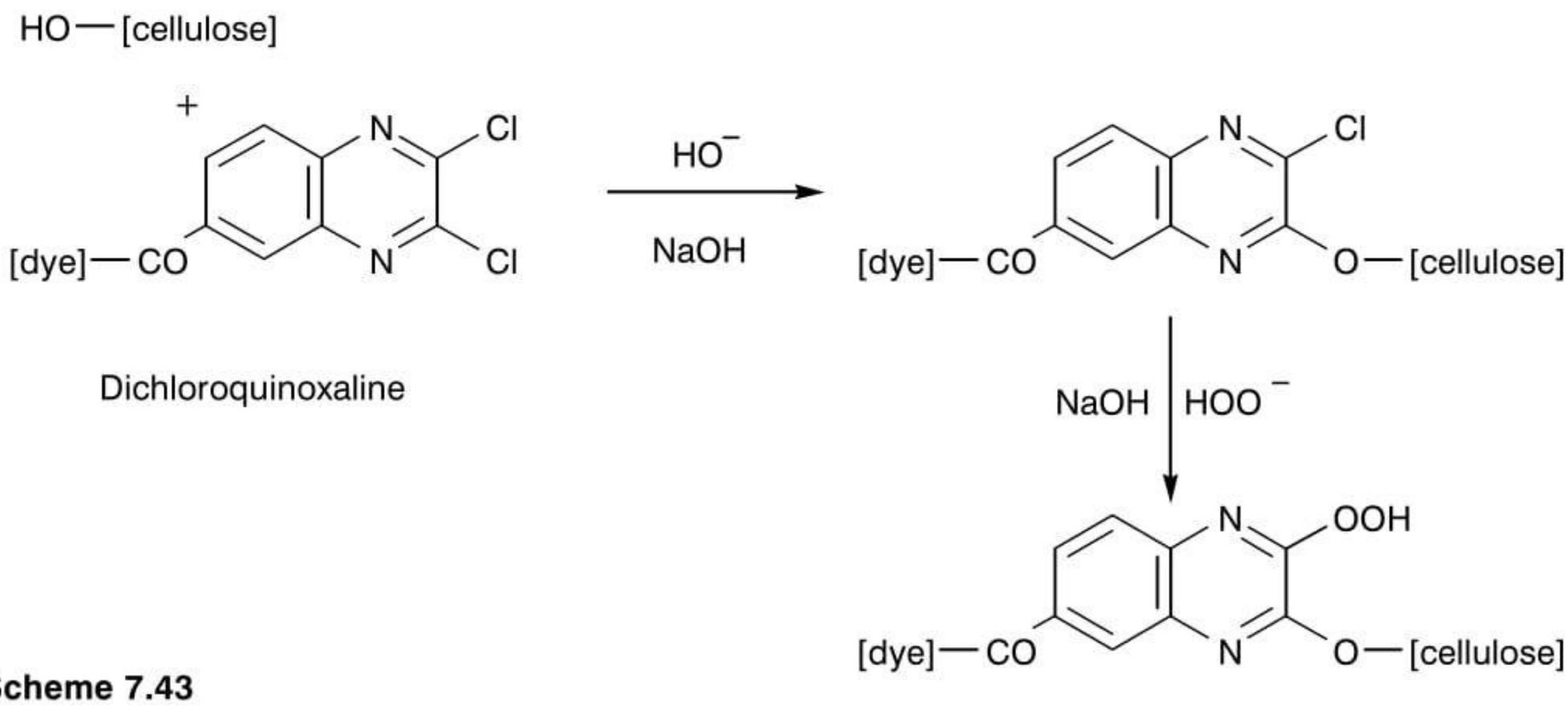


Scheme 7.41



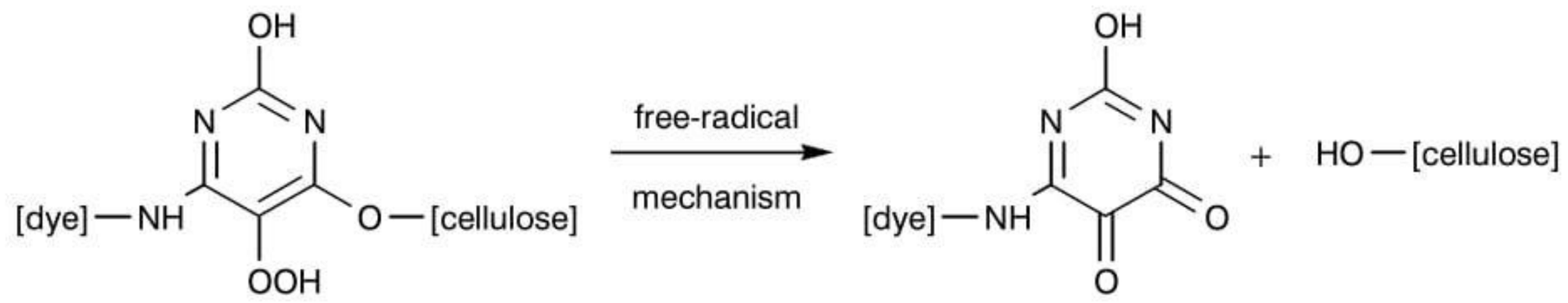
Chlorodifluoropyrimidine

Scheme 7.42



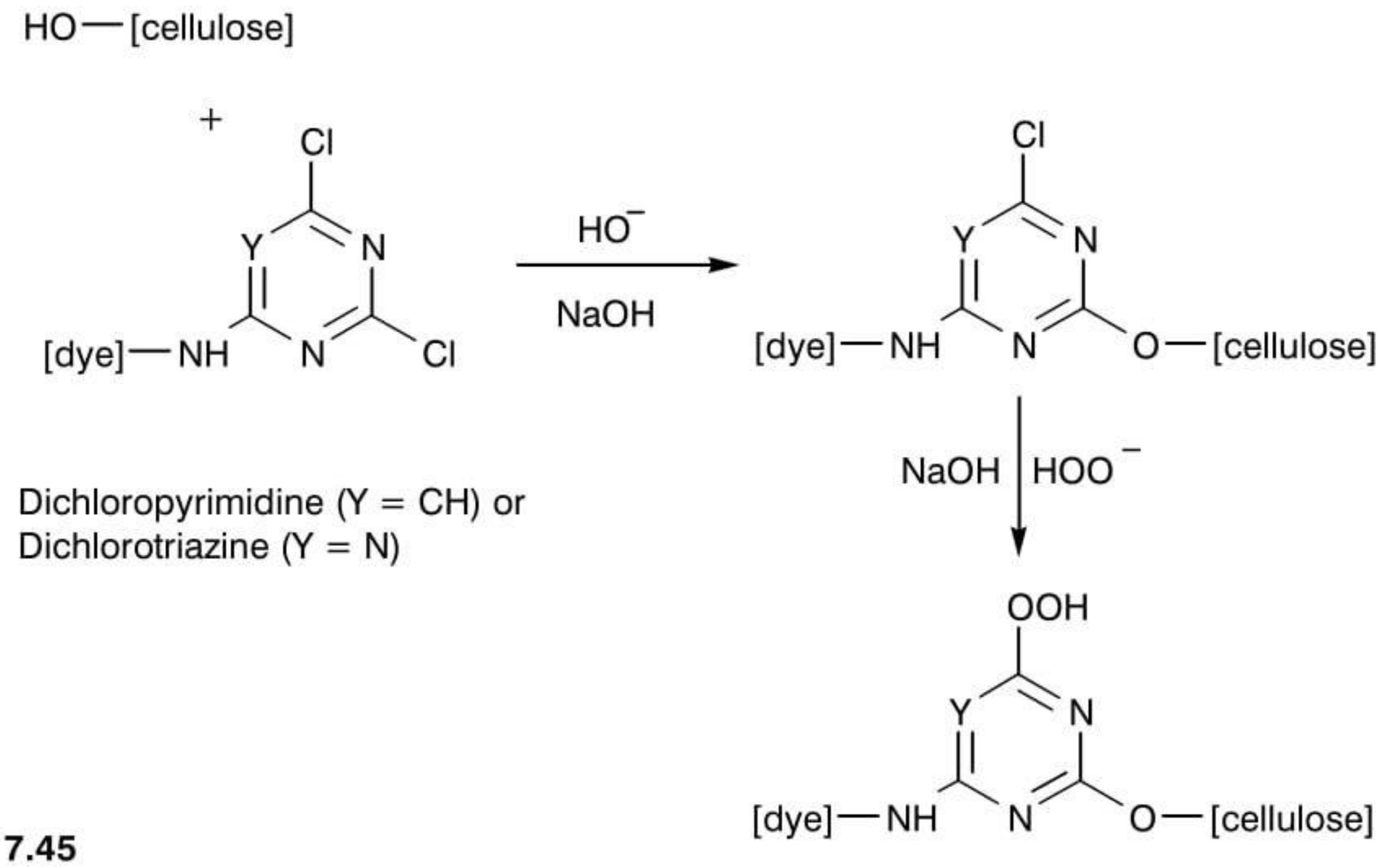
Dichloroquinoxaline

Scheme 7.43

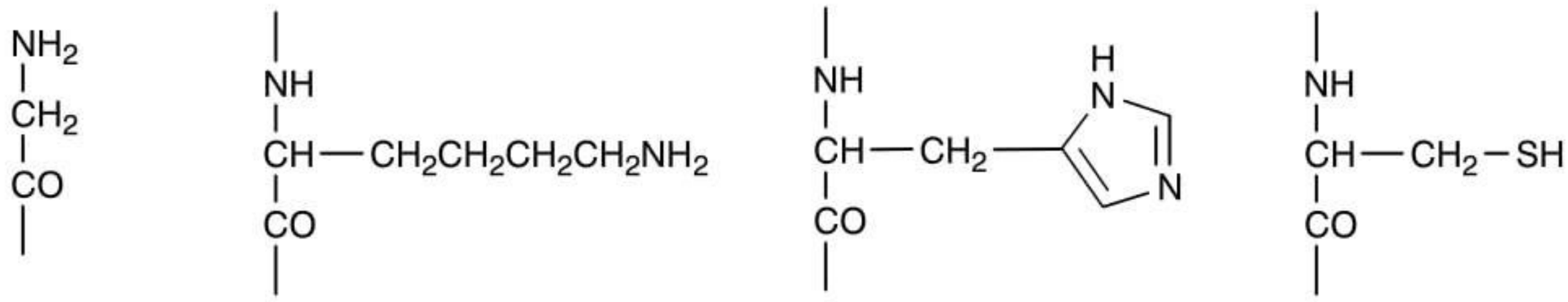


Scheme 7.44

[91]. Light-fading studies on cotton dyeings of five trichloropyrimidine reactive dyes revealed that the rate of photodegradation of the cellulose was influenced by the presence of the dye. Compared with an undyed control, the blue dyeing was degraded more rapidly but the yellow, orange, red and green dyes tested exerted a protective effect [92]. Repeated



Scheme 7.45



N-terminal glycine | Lysine | Histidine | Cysteine

Figure 7.3 Nucleophilic sites in wool keratin for reaction with dyes

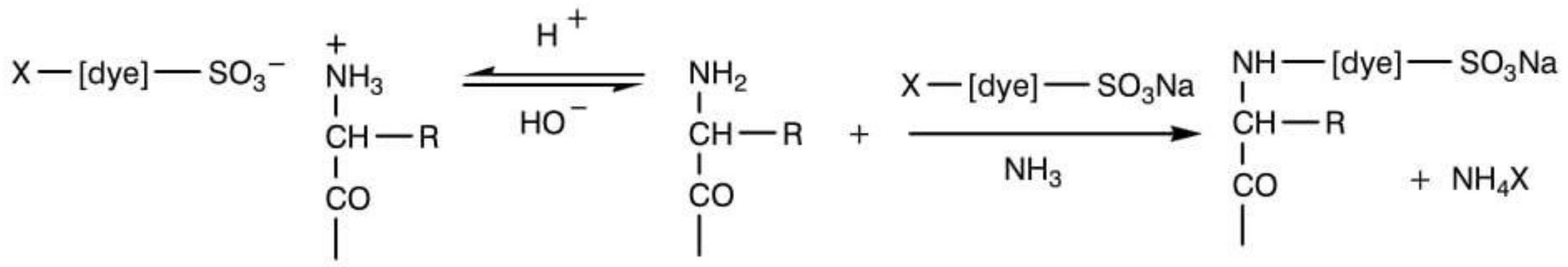
perborate oxidation of dyed cotton and viscose yarns demonstrated increased tendering of dyeings containing metal-complex reactive dyes. Viscose yarns were more significantly affected than cotton, possibly owing to the lower crystallinity, greater accessibility and higher carboxy content of viscose fibres [93].

7.7 REACTIVE DYES ON WOOL

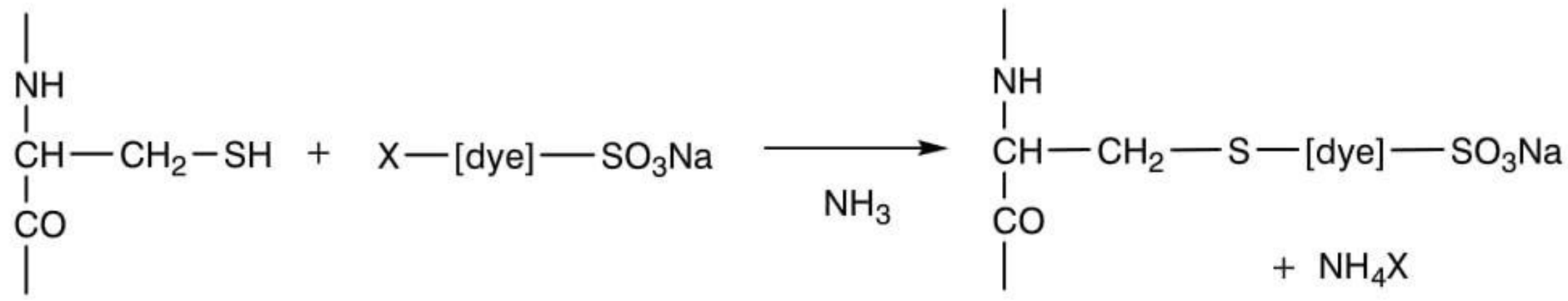
Wool keratin contains several different types of nucleophilic site for reaction with dyes [94-96]. By far the most important ones in intact wool are the amino groups of the *N*-terminal aminoacid residues and the sidechain groups of lysine and histidine (Figure 7.3). These are the same groups that provide positively charged sites under acidic conditions for absorption and electrostatic bonding with reactive or unreactive anionic dyes. A reactive dye with a labile halogen atom (X) will undergo a nucleophilic substitution reaction with one of these amino sites in the uncharged state (Scheme 7.46). The thiol groups of cysteine residues formed by the hydrolysis of cystine disulphide groups in wool provide further sites for reaction with reactive dyes (Scheme 7.47).

The hydrolytic breakdown of the disulphide bonds of cystine liberates some hydrogen sulphide and this can gradually deactivate a vinylsulphone dye by formation of the

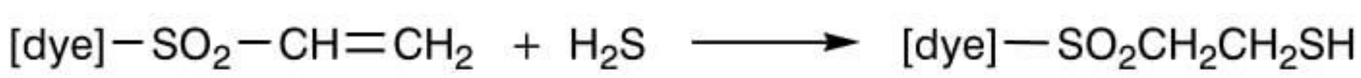
unreactive thioether derivative (Scheme 7.48) [97]. In a similar way, hydrogen sulphide will displace hydrogen bromide from an α-bromoacrylamide reactive system (Scheme 7.49). The thiirane intermediate initially formed is unstable, decomposing to the less reactive unsubstituted acrylamide with the precipitation of sulphur [98]. It is likely that haloheterocyclic reactive dyes are also readily deactivated by hydrogen sulphide, the halo substituent being replaced by a thiol group. The ability of wool reactive dyes to scavenge hydrogen sulphide explains their fibre protective effect when dyeing wool in medium to full depths; damage is related to the extent of the thiol-disulphide interchange or 'setting' reaction, which is promoted by cystine degradation in hot aqueous media [99].



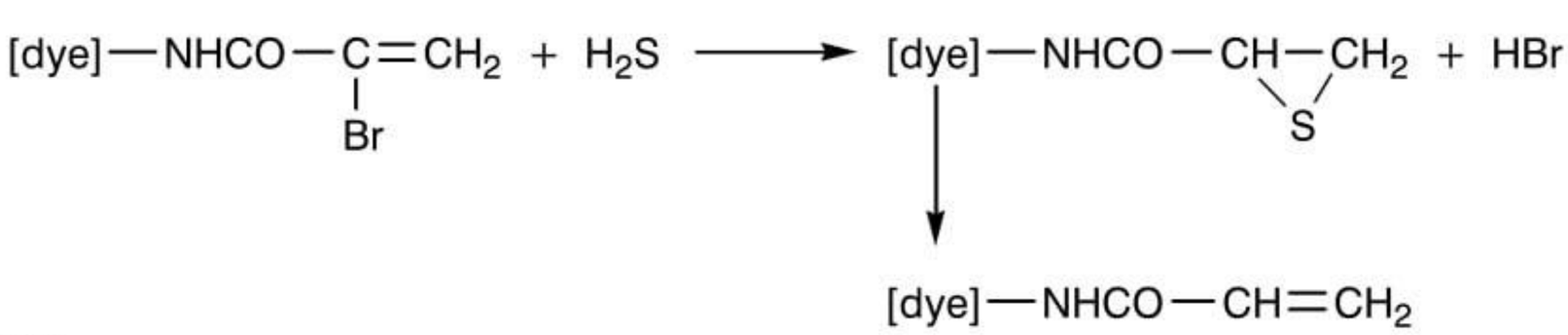
Scheme 7.46



Scheme 7.47



Scheme 7.48



Scheme 7.49

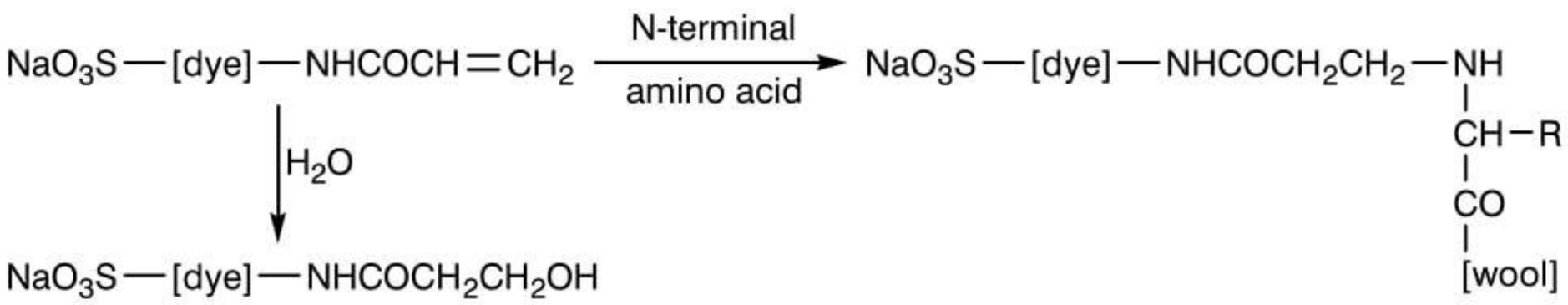
Traditional wool dyeing methods have often involved a rapid unlevel initial strike at low temperature, followed by a prolonged migration treatment at the boil to attain optimum levelness. To fit in with these requirements, ranges of reactive dyes developed for wool needed to react slowly with the fibre and this implied reactive systems with low intrinsic reactivity. One such group that was found to react too slowly for exploitation on cellulosic

fibres was selected for the Procilan (ICI) dyes, the first full range of reactive dyes to be designed for application to wool.

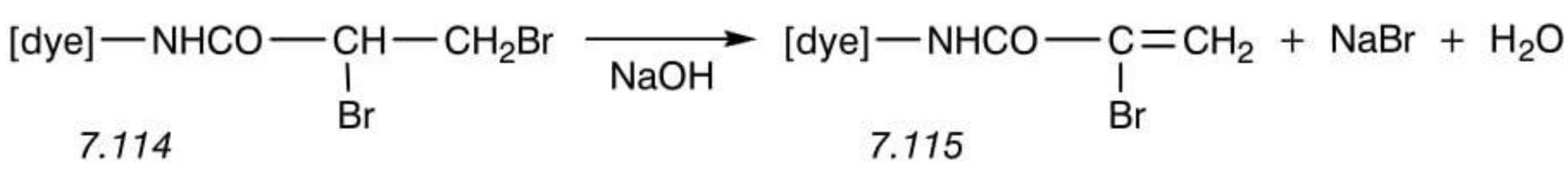
These were unsymmetrical 1:2 chromium complexes of M_r 800–900, derived from different monoazo ligands with one sulpho substituent and one acrylamido reactive group per dye molecule. They were intended for application to wool at the boil, at least an hour being necessary for slow addition of the nucleophilic groups across the activated double bonds of the acrylamide dyes (Scheme 7.50). Like their unreactive analogues (section 3.2.2) these chromium-complex dyes exhibited high neutral-dyeing affinity, but this was a problem from the viewpoint of removal of the unfixed hydroxypropionamide derivative at the washing-off stage. Dullness of hue was another limitation and the range was later extended by adding brighter unmetallised monoazo chromogens of similar M_r with two sulpho groups and an aryloxychlorotriazine reactive system. The technical performance achieved did not justify the relatively high cost of this hybrid range, which was eventually withdrawn.

An important contributory factor was the emergence in 1966 of the most successful range of reactive dyes designed for wool [100,101]. These are the Lanasol (Ciba) α-bromoacrylamide dyes (7.115), usually marketed in the form of their α,β-dibromopropionamide precursors (7.114). In dilute alkaline solution this group readily releases hydrogen bromide to yield the active form (Scheme 7.51). The introduction of acrylamide, α-bromoacrylamide or α,β-dibromopropionamide reactive groups into dye molecules is readily achieved by direct acylation of the dye base [dye]–NH_2 with the appropriate acid chloride Cl–CO–R, where R is –CH=CH_2, –CBr=CH_2 or –CHBr–CH_2Br respectively [36].

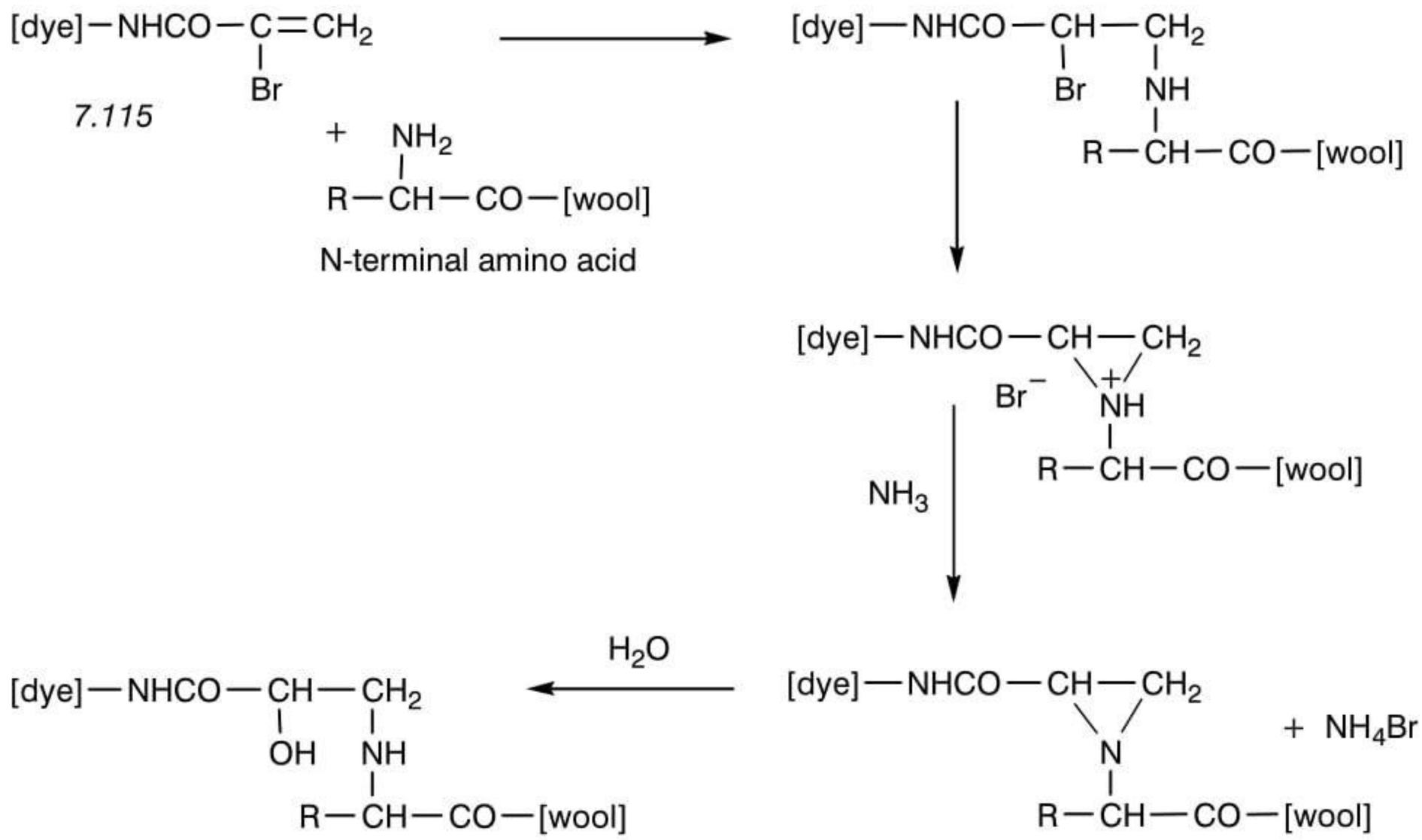
A bromine atom attached to a vinyl group is deactivated towards nucleophilic substitution. The sp^2 hybridisation of the carbon causes the C–Br bond to shorten and become stronger, whilst the delocalisation of the electrons by resonance causes the activation energy for displacement of the bromine to increase [96]. It is now widely accepted that initial reaction with wool involves addition at the double bond [102]. Ring closure to form a three-membered aziridino ring then occurs by intramolecular nucleophilic substitution and this group finally hydrolyses to a β-substituted α-hydroxypropionamide dye–fibre bond (Scheme 7.52). Recent laser Raman spectroscopic studies have provided support for this mechanism and suggest that cysteine thiol groups are particularly important



Scheme 7.50



Scheme 7.51



Scheme 7.52

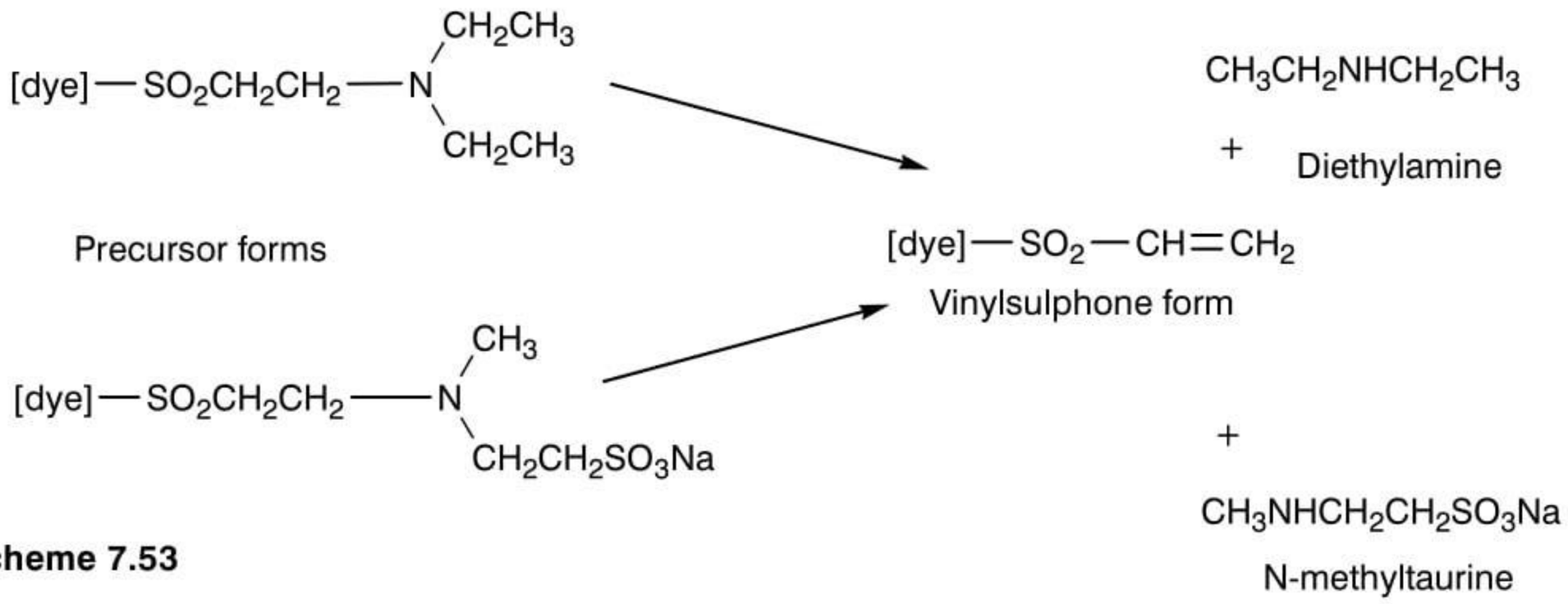
sites for reaction, especially with damaged wool [103]. Further detailed studies using model compounds have confirmed that the reaction with primary amino groups resulting in the formation of aziridine rings is important. Reactions of the α-bromoacrylamide grouping with the imidazole nitrogen of *N*-acetylhistidine and the thiol group of *N*-acetylcysteine were also observed [104].

Although reactive dyes account for only about 5% of total dye usage on wool, no other class can offer such brilliant hues of high fastness to light and wet treatments. Chrome dyes are mainly used for economical navy blue and black dyeings, where reactive dyes in general are particularly costly by comparison. In 1992 Ciba supplemented the Lanasol range with two new dyes, Navy B and Black R, that occupy the shade areas corresponding to chrome navy and black brands. More recently, Lanasol Black PV has been introduced as strong competition for established chrome blacks, even as regards price. It has been designed to give tinctorial strength, shade, metamerism and light fastness close to those of the afterchromed complex from Eriochrome Black PV (CI Mordant Black 9). An amphoteric levelling agent and ammonia aftertreatment are necessary and the fastness to severe wet tests such as potting and cross-dyeing is not quite as high as chrome dyeings [105].

Few of the haloheterocyclic reactive systems that became established for the dyeing of cellulosic fibres have transferred successfully to wool dyeing conditions. The one exception is the 5-chloro-2,4-difluoropyrimidine system (section 7.3.5). This has been utilised in the Drimalan (Clariant) and Verofix (DyStar) ranges of reactive dyes for wool [106]. These are based on conventional reactive dye chromogens (section 7.5) with two or three sulpho groups per molecule and an M_r of 600–800. The dye base usually has an alkylamino substituent (section 7.3.3) for reaction with chlorotrifluoropyrimidine to yield the reactive dye. This is a mixture of two isomers (7.19 and 7.20) and thus gives rise to a variety of different dye–fibre bond structures when fixation to the various nucleophilic sites in wool keratin (Figure 7.3) takes place. The high fixation ratio shown by these dyes has been

attributed to the continuing activity of partially hydrolysed dye, since the reactivity of the second fluorine atom is only slightly decreased by reaction of the first with an amino group in wool [107]. A novel range of heterobifunctional dyes has been introduced recently under the brand name Realan (DyStar). These products contain a 5-chloro-2,4-difluoropyrimidine system and a sulphatoethylsulphone grouping in the same molecule. They are recommended for the dyeing of wool at a mildly acidic pH and of silk under mildly alkaline conditions [108].

Although the first two reactive dyes intended for fixation on wool contained the vinylsulphone reactive system and were marketed by Hoechst as long ago as 1952, it proved difficult to develop a fully compatible coherent range along these lines. Some of the early sulphatoethylsulphone dyes, including the bifunctional Hostalan Black SB (7.36) and the attractive Remalan Brilliant Blue R (7.37), had become highly successful as Remazol equivalents for cellulosic dyeing (section 7.3.8). Various secondary alkylamines, such as diethylamine or *N*-methyltaurine, were exploited as leaving groups in other Hostalan dyes (Scheme 7.53). Under mildly acidic conditions at the boil gradual elimination of the amine took place, allowing the dye to level more effectively before the vinylsulphone form could react with the nucleophilic sites in wool [109]. This assortment of precursor types and the usual need to vary the chromogen considerably (section 7.5) gave rise to marked differences in M_r (600–900) even though most members of the range were disulphonated. This rather incompatible range of products was eventually discontinued in the 1980s.



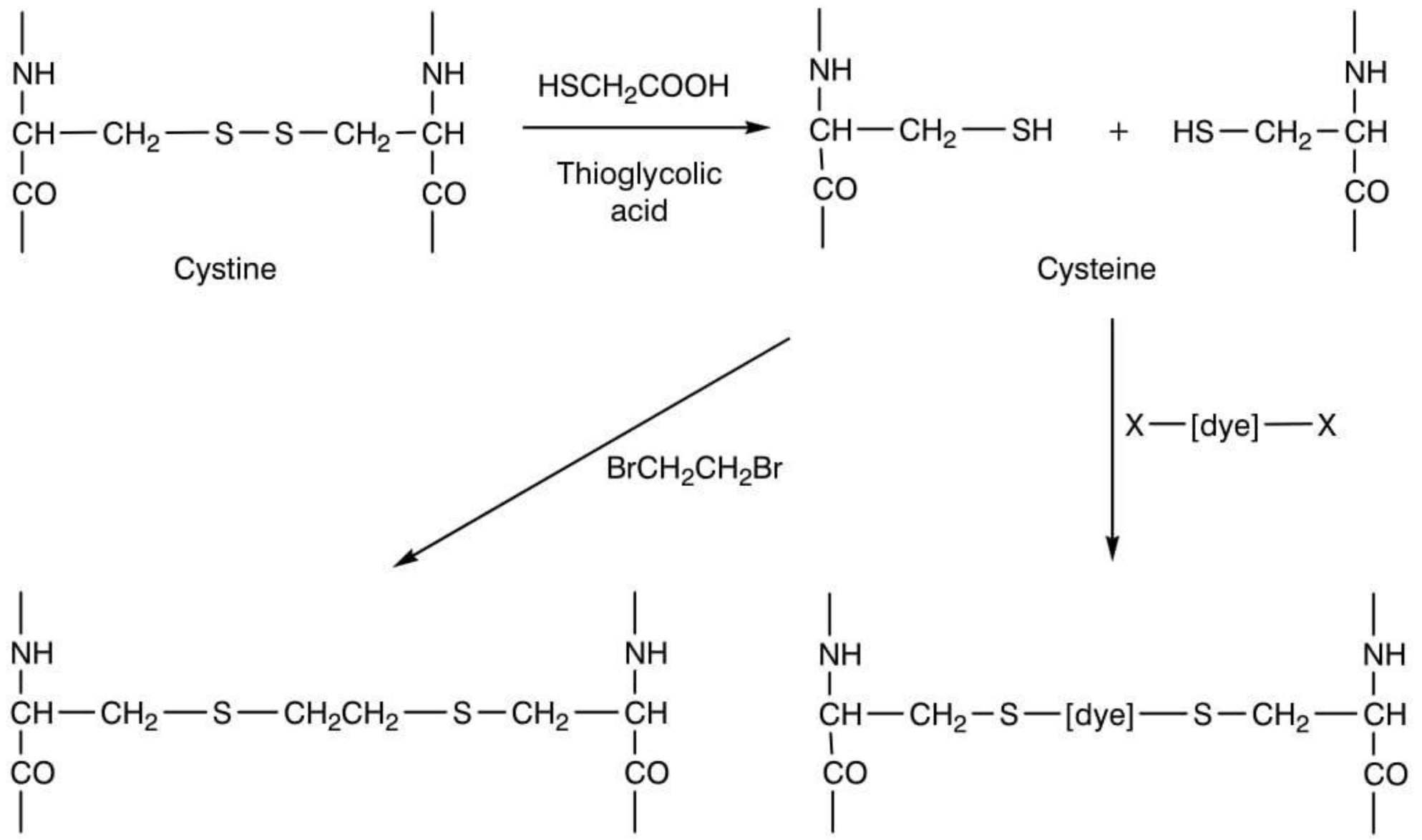
Scheme 7.53

It is widely accepted that reactive dyes protect wool from hydrolytic damage during hot aqueous dyeing processes at pH 3–7. In the dyeing of wool/cotton blends, the wool component is significantly protected if it is first dyed with appropriate wool-reactive dyes before exposure to the strongly alkaline conditions necessary for satisfactory fixation of reactive dyes on cotton [110]. The successful dyeing of severely damaged carbonised wool with the bifunctional sulphatoethylsulphone dye CI Reactive Black 5 (7.36) was attributed to the ability of this product to crosslink the wool keratin chains and thus to exert a protective effect [111].

In a comparison between various reactive dyes for wool and several commercially available colourless fibre-protecting agents, it was shown that reactive dyes in medium and full depths are significantly more effective. Reaction readily occurs between typical reactive dyes and the cysteine thiol groups (Scheme 7.47) released when the cystine disulphide bonds are hydrolysed under dyeing conditions. Such reactions inhibit thiol-disulphide

interchange reactions and thus significantly interfere with the level of set produced in a boiling dyebath. Reactive dyes also react preferentially with non-keratinous proteins in the intercellular material and the endocuticle, thus minimising their tendency to hydrolyse and partially dissolve in the hot aqueous dyebath [112].

The presence of sulphur-containing aminoacids in keratinous fibres seems to have special significance for the clothes moth, which attacks wool and other animal hairs but not silk or other fibre types. An effective method of mothproofing is to reduce the disulphide bonds to thiol groups using thioglycolic acid at pH 7 and 50 °C, followed by an alkylation reaction under similar conditions with an alkylene dihalide (Scheme 7.54). More recently, the possibility of using a bifunctional reactive dye instead of the alkylene dihalide has been explored [113]. The resistance of wool flannel to damage by clothes moth larvae was markedly improved, but the treatment caused adverse effects on physical properties similar to those found with the alkylene bis-thioether crosslinks in wool.



Scheme 7.54

7.8 REACTIVE DYES ON SILK

Silk fibroin contains no cystine and the content of lysine and histidine is also low (about 1% in total), but it does contain tyrosine phenolic (13%) and serine alcoholic (16%) sidechains. Since glycine accounts for 44% of the total aminoacid content, an *N*-terminal glycine residue is reasonably representative of most of the primary amino dyeing sites in silk fibres. Amino acid analysis of hydrolysed reactive-dyed silk indicates that the reaction between fibroin and reactive dyes takes place mainly at the ε-amino group of lysine, the imino group of histidine and the *N*-terminal amino group of the peptide chain. In an alkaline medium, the hydroxy groups of tyrosine and serine also react [114].

Commercial ranges of reactive dyes have not been marketed specifically for silk dyeing, so the more important types of reactive system developed successfully for wool or cellulosic fibres have been evaluated on silk. Apparel made from silk traditionally required dry

cleaning to avoid colour loss, so the high wet fastness offered by reactive dyes has been advantageous. Vinylsulphone dyes in particular provide good dischargeable grounds for printing styles and show excellent fastness to perspiration [115].

Theoretically, all reactive dyes can be used for silk dyeing. However, to achieve the best quality of dyed silk, reactive dyes have to satisfy the following requirements [114]:

(1) Brilliance of hue: this is especially important on mulberry silk. Many dyeings on tussah silk are much duller and the dyed silk shows a lower colour yield because of inferior exhaustion.
(2) High reactivity: silk is damaged in an alkaline medium at high temperature, so reactive dyeing should be carried out in an acidic or neutral dyebath.
(3) Good storage stability: the consumption of dyes for the batchwise dyeing of silk is small, so the dyes should be highly stable to storage.

Silk can be readily dyed with conventional high-reactivity dyes of the dichlorotriazine, dichloroquinoxaline or difluoropyrimidine classes. Exhaust dyeing at 60–70 °C and pH 5–6 gives satisfactory results, especially if a mildly alkaline aftertreatment is given to enhance fixation. Dichlorotriazine dyes can also be applied by pad–batch dyeing with bicarbonate and a batching time of 4–6 hours. The relatively low reactivity of aminochlorotriazine dyes, however, results in moderate to poor build-up on silk. Tertiary amine catalysts such as DABCO (7.66) can be used to accelerate the dye–fibre reaction and increase the fixation substantially [116], but it is difficult to achieve satisfactory compatibility in mixture dyeings by this method (section 7.4.2).

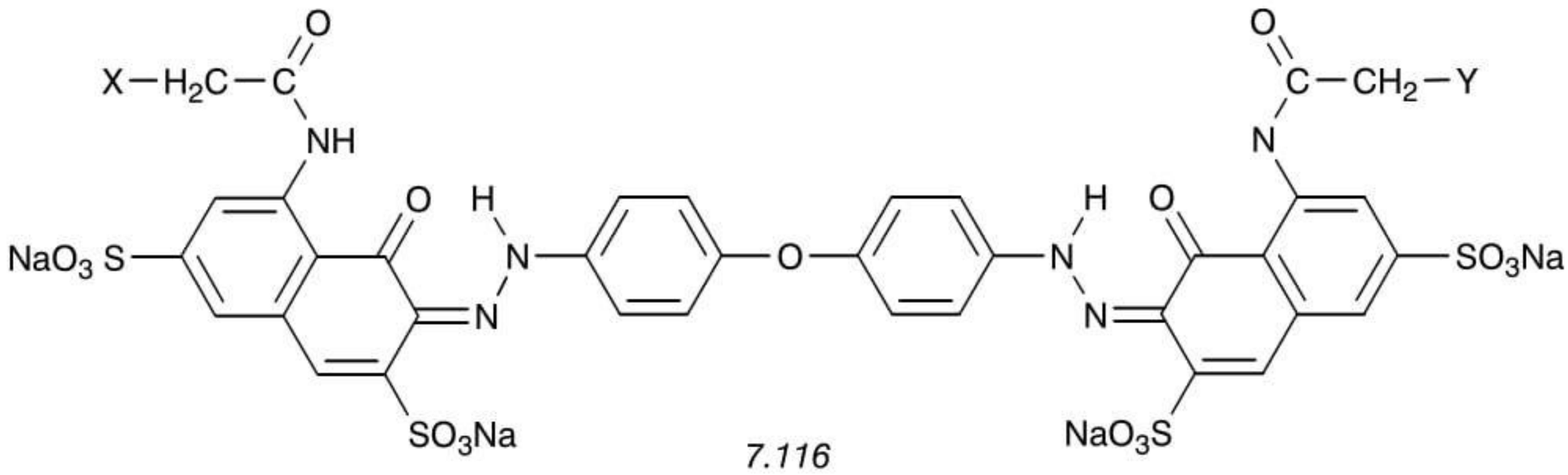
In contrast to cellulosic dyeing with reactive dyes, the fibroin–dye bonds are remarkably stable in aqueous media of pH 4 to 10 [117]. Since there exists only a negligible amount of bond hydrolysis even at high temperature and in a medium of pH 2, the cleavage of the fibroin–dye bond is not a problem in reactive-dyed silk. The stability of these bonds when dyeing with difluoropyrimidine dyes is the highest in both acidic and basic media [118].

Chloroacetyl reactive dyes have occasionally been used for the dyeing of wool but they normally require alkaline fixation for acceptable colour yields. Silk can be damaged by alkaline conditions but research has indicated that certain haloacetyl dyes will give satisfactory performance on silk under mild conditions. Table 7.6 presents selected results from a comparison of mono- and bifunctional dyes containing bromo- or chloroacetyl reactive groups [119]. The exhaustion tended to decrease as the dyebath pH or temperature was increased but the fixation values showed trends in the opposite direction. The two symmetrical bifunctional structures yielded consistently higher exhaustion and fixation than their unsymmetrical monofunctional analogues. An additional bromine atom boosted the exhaustion by about 16%. The most striking difference between the bromoacetyl and chloroacetyl reactive groups was the outstandingly higher reactivity of the bromoacetyl system under mild conditions (pH 7 and 75 °C).

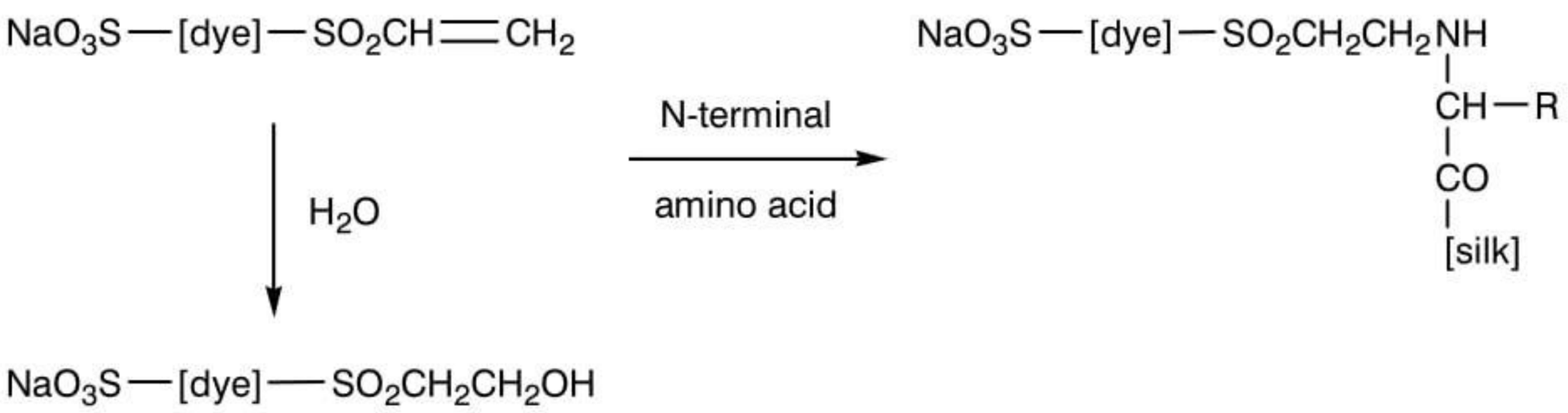
Sulphatoethylsulphone dyes have proved highly suitable for silk, yielding brilliant hues of high wet fastness by application at 80 °C and pH 7–8 in the presence of Glauber's salt, usually followed by an alkaline fixation treatment to ensure optimum fixation [115,120,121]. A new approach to this dyeing system has been explored recently [122], in which the sulphatoethylsulphone dyes were first activated fully by a pretreatment at pH 8 for 5 minutes at the boil (Scheme 7.23). The free vinylsulphone dyes were then applied to silk at 80 °C and pH 4–4.5 in the absence of salt. Under these conditions this highly reactive system

Table 7.6 Exhaustion and fixation of haloacetyl-substituted disazo dyes on silk [119]

Substituents in structure 7.116		Exhaustion (%)			Fixation (%)		
X	Y	75 °C pH 7	90 °C pH 7	90 °C pH 11	75 °C pH 7	90 °C pH 7	90 °C pH 11
Br	Br	94	93	86	94	94	98
Cl	Cl	86	86	94	39	89	98
Br	H	78	76	70	79	76	91
Cl	H	83	80	74	15	38	90



7.116

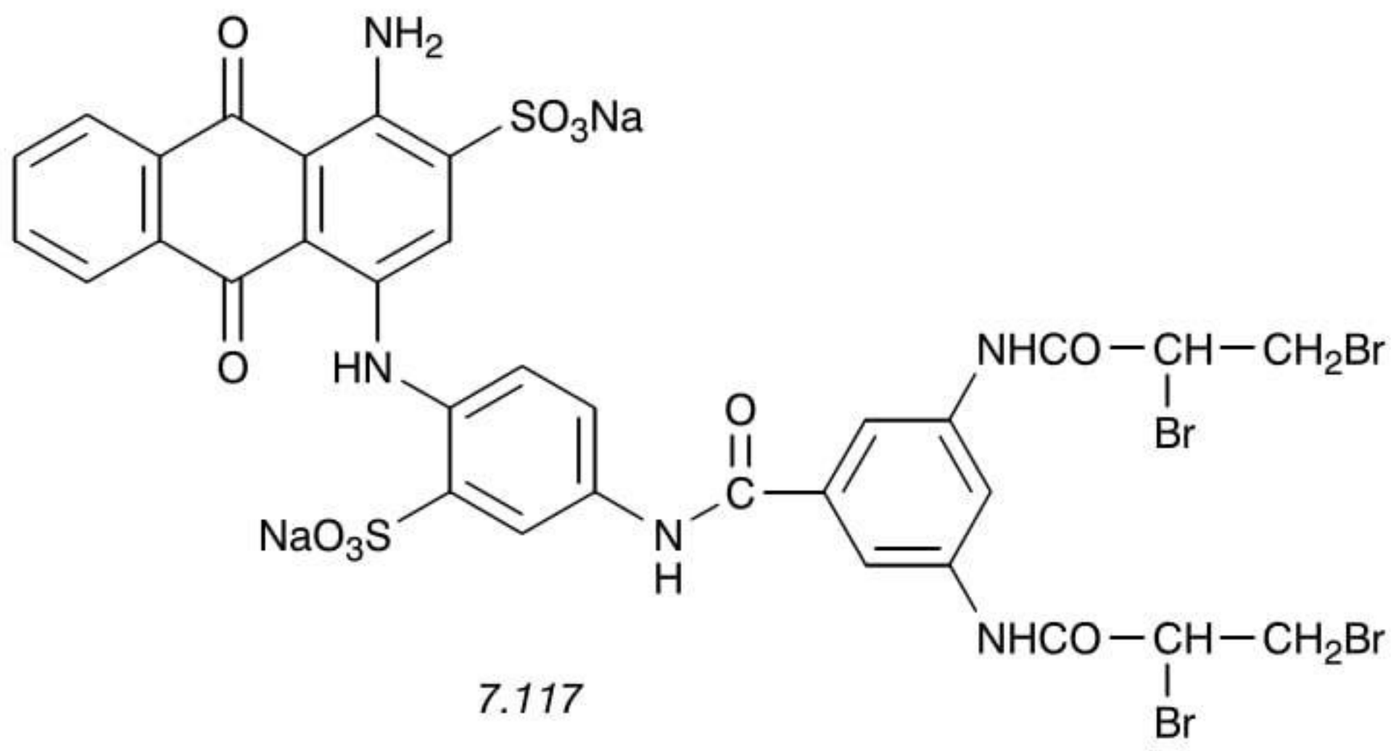


Scheme 7.55

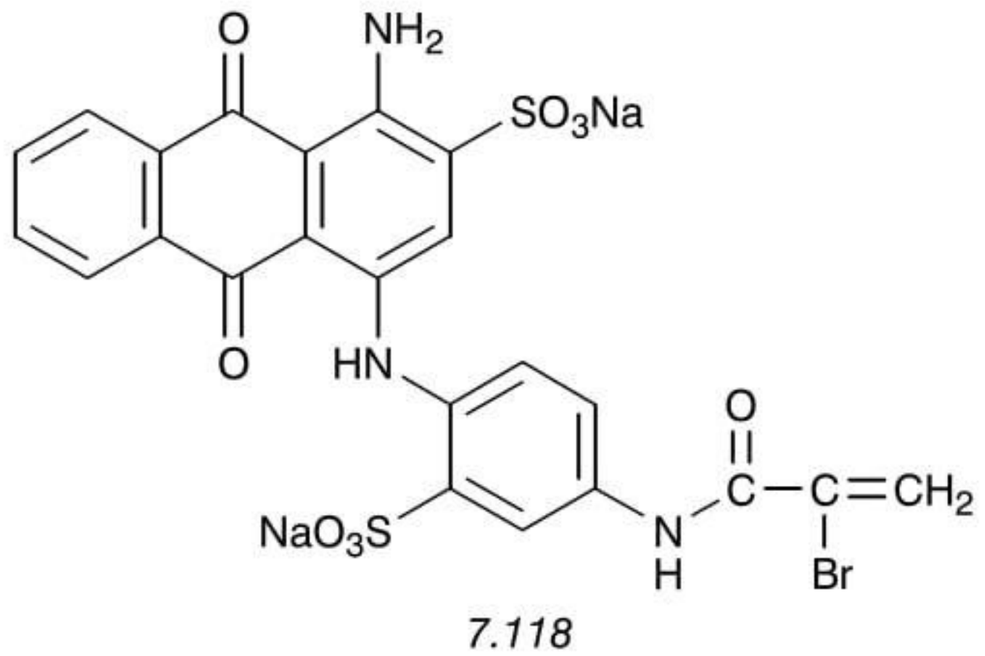
readily fixes to amino groups in silk by a nucleophilic addition mechanism (Scheme 7.55). The nonionised vinylsulphone groups ensure much higher exhaustion than the sulphatoethylsulphone precursor form, especially in the case of the bifunctional CI Reactive Black 5 (7.36). Avoidance of electrolyte additions is highly beneficial from the environmental viewpoint [122].

The Lanasol (Ciba) dyes marketed for the dyeing of wool, containing α-bromoacrylamide or α,β-dibromopropionamide groups, can also be used for dyeing silk to achieve high fixation in an alkaline medium [118,123]. The percentage fixation of the homobifunctional bis(dibromopropionamide) dye 7.117 is exceptionally high. This dye is almost completely fixed on the silk fibre, whereas the monofunctional analogue 7.118 shows much lower fixation [118]. At pH 9, the dibromopropionamide groups in dye 7.117 rapidly eliminate hydrogen bromide to yield the reactive α-bromoacrylamide form.

The high fixation levels achieved on silk by various homobifunctional reactive dyes containing two identical reactive systems per molecule, as well as the increasing success of



7.117



7.118

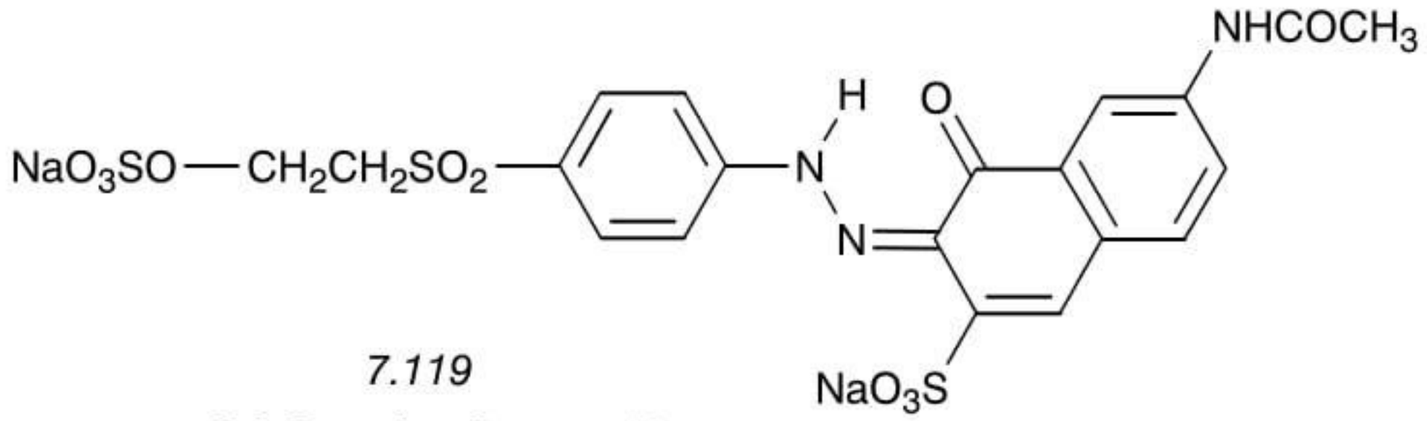
heterobifunctional dyes on cellulosic fibres, have prompted a detailed study of CI Reactive Red 194 (7.76) on silk. This monoazo dye contains a sulphatoethylsulphone precursor grouping linked to the H acid coupler through a chlorotriazine bridging group of lower reactivity.

Maximum exhaustion and fixation of this bifunctional red dye on silk was achieved by dyeing at 90 °C and a neutral pH in the presence of 60 g/l electrolyte. The isoelectric point of silk fibroin is found at pH 3–4 and the salt addition is necessary to suppress the negative charge on the surface of the fibre. For optimum fixation, however, the pH must be high enough for the nucleophilic amino groups in the fibre to be present almost entirely in their unprotonated form and for the sulphatoethylsulphone precursor groups to yield their vinylsulphone active form. Dyeing under alkaline conditions results in lower exhaustion and fixation, not only because of the high concentration of ionised carboxylate groups in the fibre but also because of increased alkaline hydrolysis of the reactive groups in the dye [124].

All reactive dyes inhibit the dissolution of silk fibroin in appropriate solvents but the effect is much more pronounced with bifunctional dyes because these are capable of forming crosslinks between the polymer chains. Solubility tests are particularly sensitive to the formation of crosslinks and can give an estimate of the degree of crosslinking [125–127]. The solvent selected should be effective in disrupting hydrogen bonding between polymer segments without bringing about scission of covalent bonds. The solubility of silk in a solution of calcium chloride in aqueous ethanol (molar ratio 1:2:8) was determined for dyeings of one monofunctional and three bifunctional reactive dyes at various applied depths. A few typical results are given in Table 7.7. Even at a concentration of 0.05 mol/kg

Table 7.7 Solubility of silk dyed with various reactive dyes [124]

CI Reactive	Structure	Applied depth (% o.w.f.)	Dye on fibre (mol/kg)	Solubility (%)
Orange 16	7.119	1	0.010	99
Black 5	7.36	2	0.012	60
Red 194	7.76	2	0.013	51
Red 120	7.48; X = Cl	6	0.010	41



7.119

C.I. Reactive Orange 16

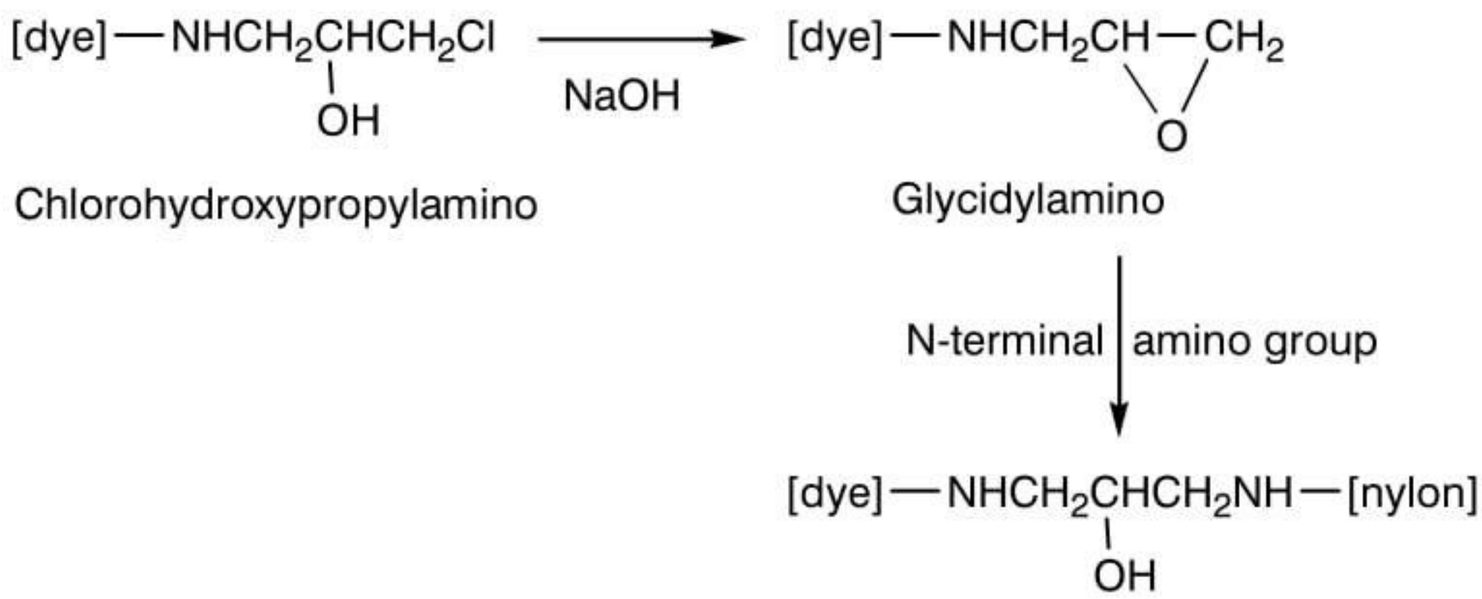
of CI Reactive Orange 16, the solubility of the dyed silk was still 83%, indicating how much greater is the effect of bifunctional crosslinking on this property.

The formation of crosslinks in silk fibroin increases the tenacity and resistance to deformation of the fibres, as reflected in the initial modulus and the yield point. This protective effect conferred by fixation of the bifunctional dye CI Reactive Red 194 was not shown by the monofunctional Orange 16, which is unable to form crosslinks. The loss in tenacity of undyed silk that is observed on treatment at 90 °C and pH 7 for 2 hours is attributable to lowering of the degree of polymerisation (DP) by hydrolysis of peptide bonds. The crosslinking action of bifunctional dyes tends to compensate for this loss in DP and provides an intermolecular network that helps to maintain the physical integrity of the fibre structure [124].

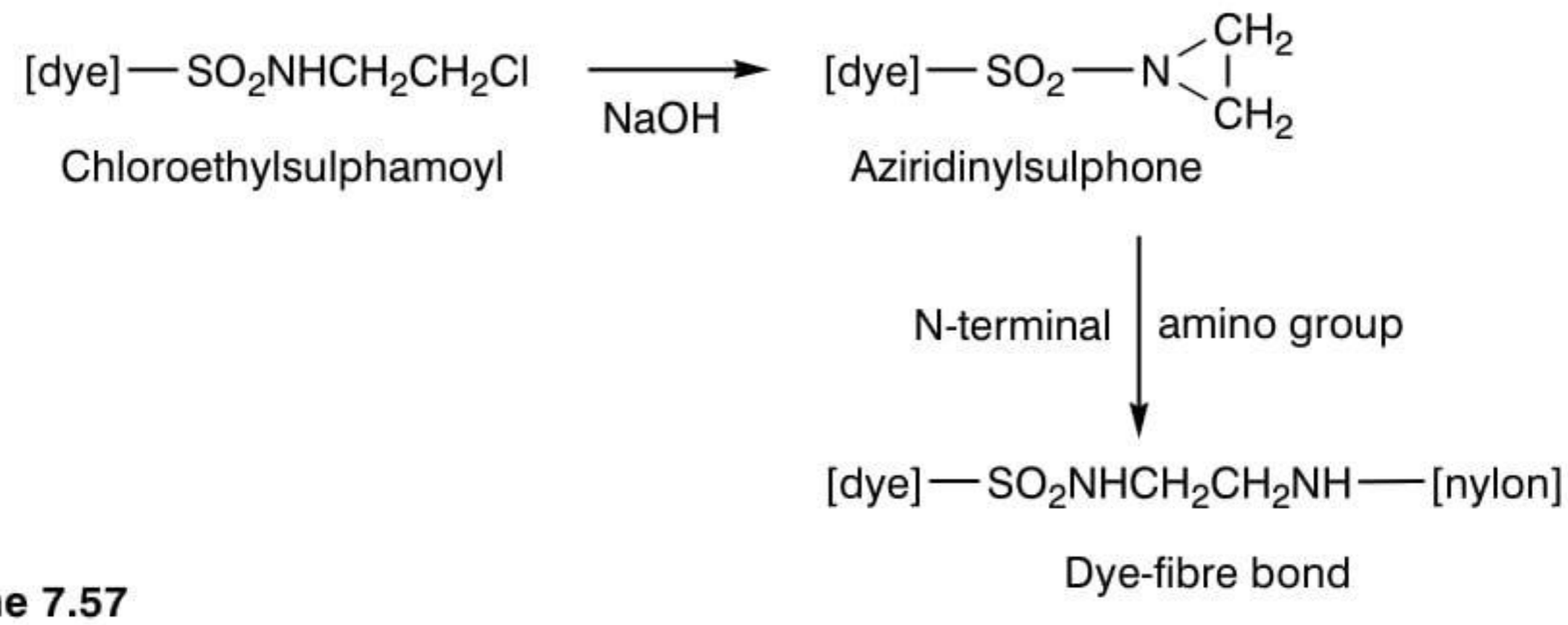
7.9 REACTIVE DYES ON NYLON

In spite of their unique status as the only commercial range of reactive dyes designed specifically for the dyeing of nylon, the Procinyl (ICI) disperse reactive dyes were developed and maintained on a shoestring budget compared with conventional reactive dyes that achieved greater success on other fibres. The range never contained more than six members, yet three different reactive systems were represented. The only blue was a 1,4-diaminoanthraquinone containing two 3-chloro-2-hydroxypropyl groups, precursors of the glycidyl reactive system that reacted only slowly and inefficiently with *N*-terminal amino groups in nylon (Scheme 7.56). The only yellow chromogen was a 4-aminoazobenzene derivative bearing an aminochlorotriazine grouping of only low to moderate reactivity. The remaining dyes of moderate light fastness covering the orange to rubine sector were each based on a simple monoazo chromogen with a 2-chloroethylsulphamoyl group, precursor of the relatively more active aziridinyl reactive system (Scheme 7.57).

The degree of fixation of these dyes under conventional dyeing conditions at 80–90 °C was rather low. Migration and coverage of dye-affinity variations was good but the wet



Scheme 7.56



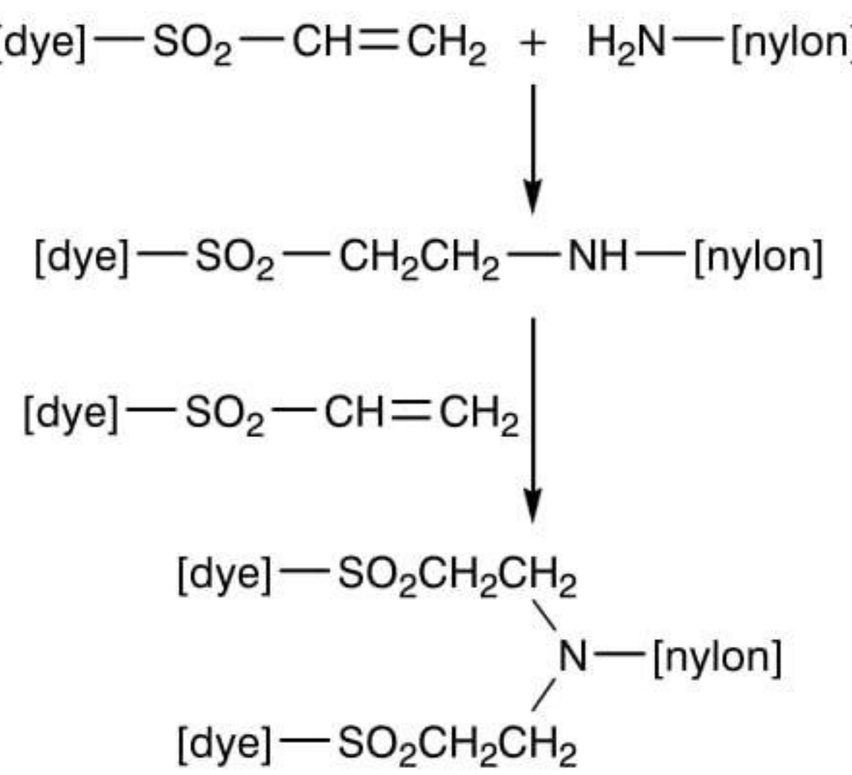
Scheme 7.57

fastness was not much better than that of high-energy disperse dyes. Only by alkaline aftertreatment or high-temperature dyeing at 120 °C could fixation be improved, but with some risk of unlevel dyeing if a high pH or temperature was reached too quickly. The dyeing of nylon/cellulosic blends with Procinyl dyes and anionic reactive dyes was more successful, because the alkaline fixation stage necessary for the latter on the cellulosic component also ensured good fixation of the Procinyl dyes on nylon. In general, however, the technical performance of this small range of dyes seldom justified their cost and they were eventually withdrawn.

Anionic reactive dyes designed for cellulosic fibres or wool are able to give bright shades of high wet fastness on nylon but their drawbacks are clearly evident. The degree of fixation is limited by the number and accessibility of primary amine end groups in nylon. Below this limit (roughly 1% o.w.f. on normal nylon, higher on deep-dye variants) such dyeings show excellent wet fastness but at greater depths the fastness deteriorates as the proportion of unfixed dye present increases. Most anionic reactive dyes contain two or more sulpho groups per molecule and this can result in blocking effects in mixture recipes containing dyes that vary markedly in affinity for nylon. When high-reactivity dyes are applied in depths up to the limit of available end groups, these dyes show very poor migration properties. Catalytic fading can be a problem in certain combination shades.

It has been pointed out [99] that, in theory at least, a monofunctional vinylsulphone dye is capable of reacting twice with a primary amino *N*-terminal group in nylon (Scheme 7.58). In practice, however, fixation limits for these dyes are not significantly higher than for high-reactivity dyes of the haloheterocyclic types. When one multisulphonated reactive dye molecule has reacted, steric hindrance and strong mutual electrostatic repulsion effects inhibit access of a second reactive molecule to the imino group in the dye-fibre linking unit.

This problem has been confirmed recently in a study of the mechanism of covalent reaction between nylon 6.6 and the sulphatoethylsulphone dye CI Reactive Blue 19 (7.37). Acid hydrolysis of the dyed fibre and HPLC analysis of the hydrolysate yielded the 6-aminohexylaminoethylsulphonyl derivative of Blue 19. Even when the dyeing procedure was optimised to achieve maximal exhaustion and fixation to the fibre [128], only about 30% of the *N*-terminal amino groups in the nylon 6.6 were accessible because of mutual blocking effects between these bulky anionic dye molecules.



Scheme 7.58

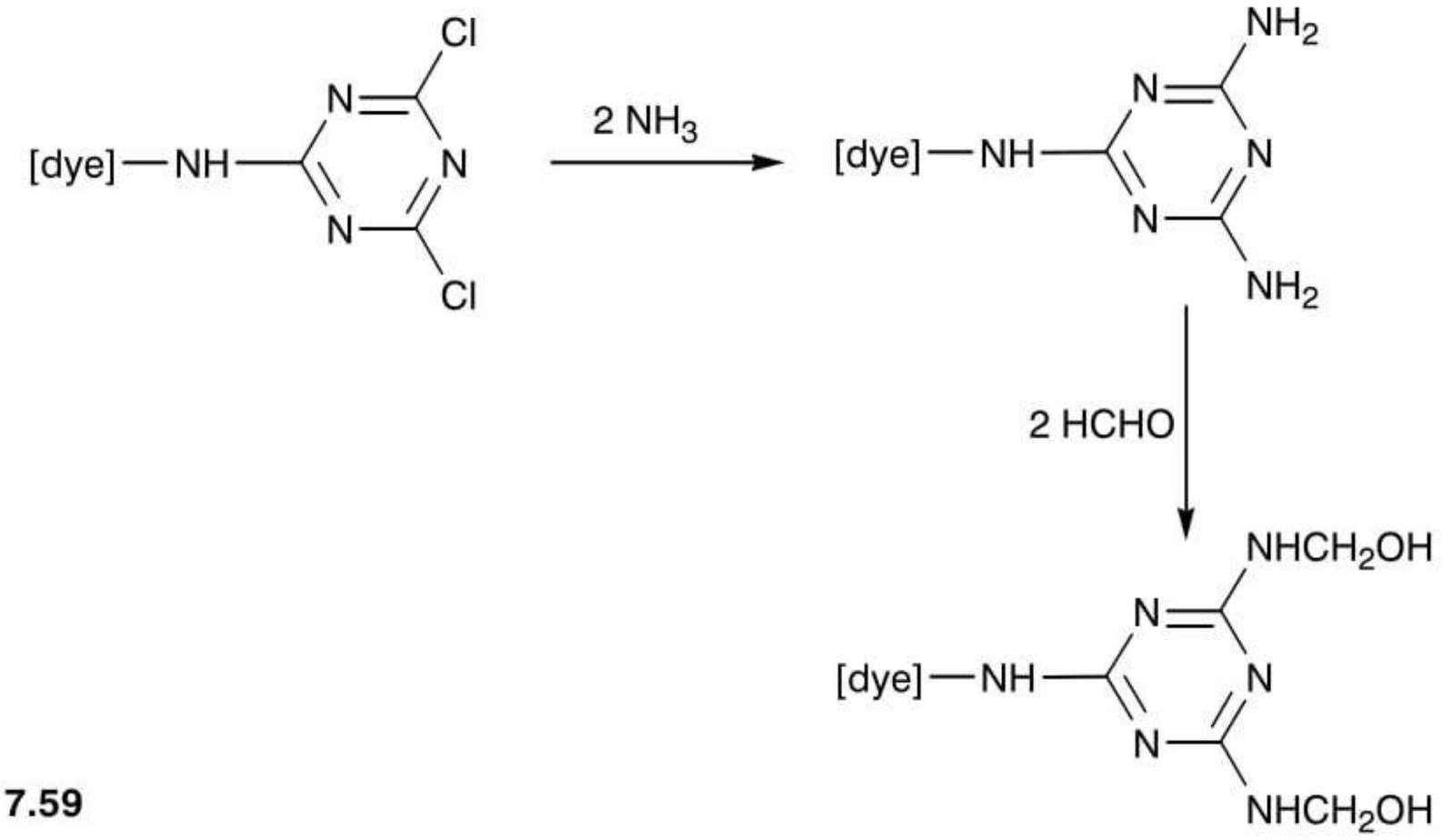
7.10 NOVEL REACTIVE DYEING PROCESSES

Precedents show that attempts to forecast the probability of attainment of truly original techniques of coloration are fraught with difficulty. No dyeing expert of the early 1950s could have predicted the impact that reactive dyes would make within that decade. With a new millennium offering continuing challenges, however, the acknowledged world experts in this field are not deterred by this from speculating how this game will go next [129,130]. What is beyond doubt is that there are still important research targets remaining unfulfilled and that reactive systems still offer sufficient versatility to play a major part in these developments.

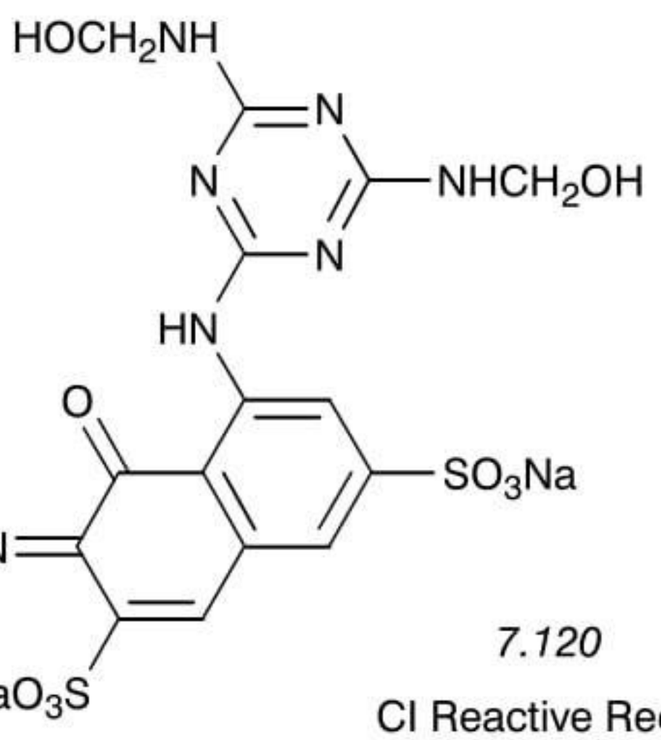
There has been a noteworthy revival of interest recently in adapting the concept of crosslinking reactants, so overwhelmingly successful in chemical finishing processes, to the more demanding task of attaching coloured molecules to cellulose or other fibres containing nucleophilic groups. Early attempts to achieve this technology transfer failed because they relied too closely on the chemistry of the existing finishing processes. Thus in the Procion Resin process of the early 1960s, a reactive dye of the chlorotriazine type was condensed with an amino sugar, such as *N*-methy1glucosamine. The carbohydrate residue on the resulting dye molecule participated in crosslinking of the cellulosic fibre using a suitable *N*-methylol reactant [131].

The introduction of Calcobond dyes a few years later by American Cyanamid exploited a similar principle but incorporated the *N*-methylol groups into the dye molecule itself [132]. The labile chloro substituents in dichlorotriazine dyes were converted to amino groups by substitution with ammonia and the resulting melamine residue made cellulose-reactive again by reaction with formaldehyde (Scheme 7.59). A typical member of this range was CI Reactive Red 92 (7.120). A characteristic problem of the Procion Resin process and of the

Calcobond dyes was that the colour fastness to light was adversely affected. The fastness to acid treatment was no better than that of the resin finish, i.e. the dyeings could be stripped by boiling at a pH below 5.



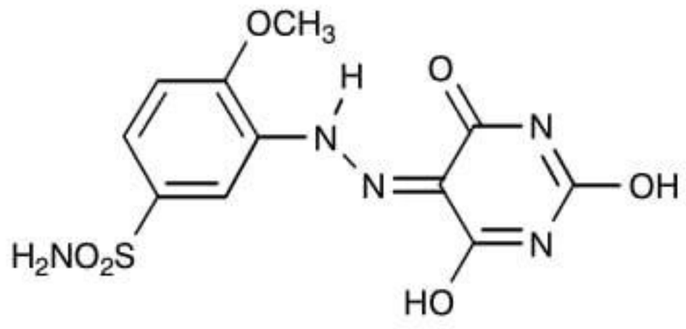
Scheme 7.59



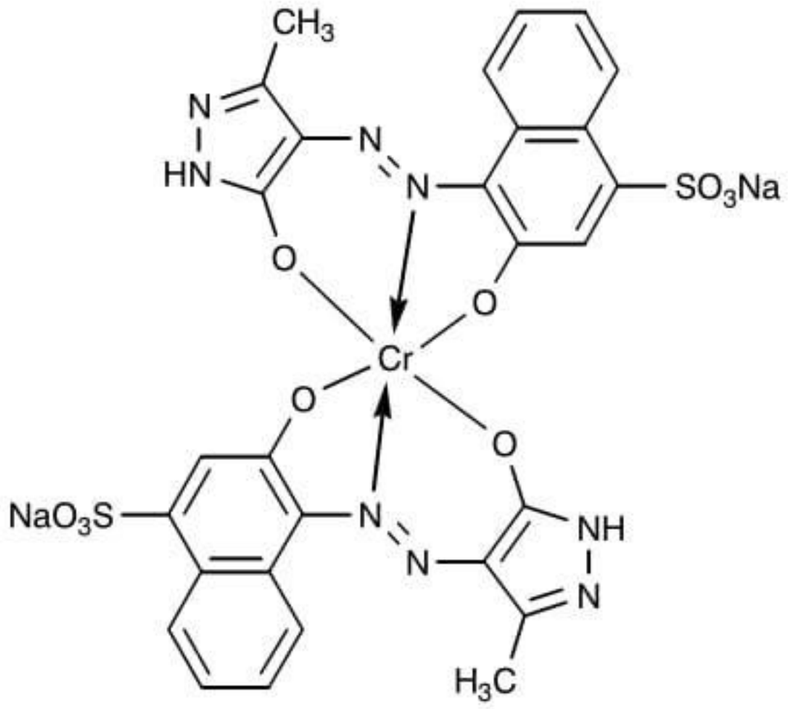
7.120

CI Reactive Red 92

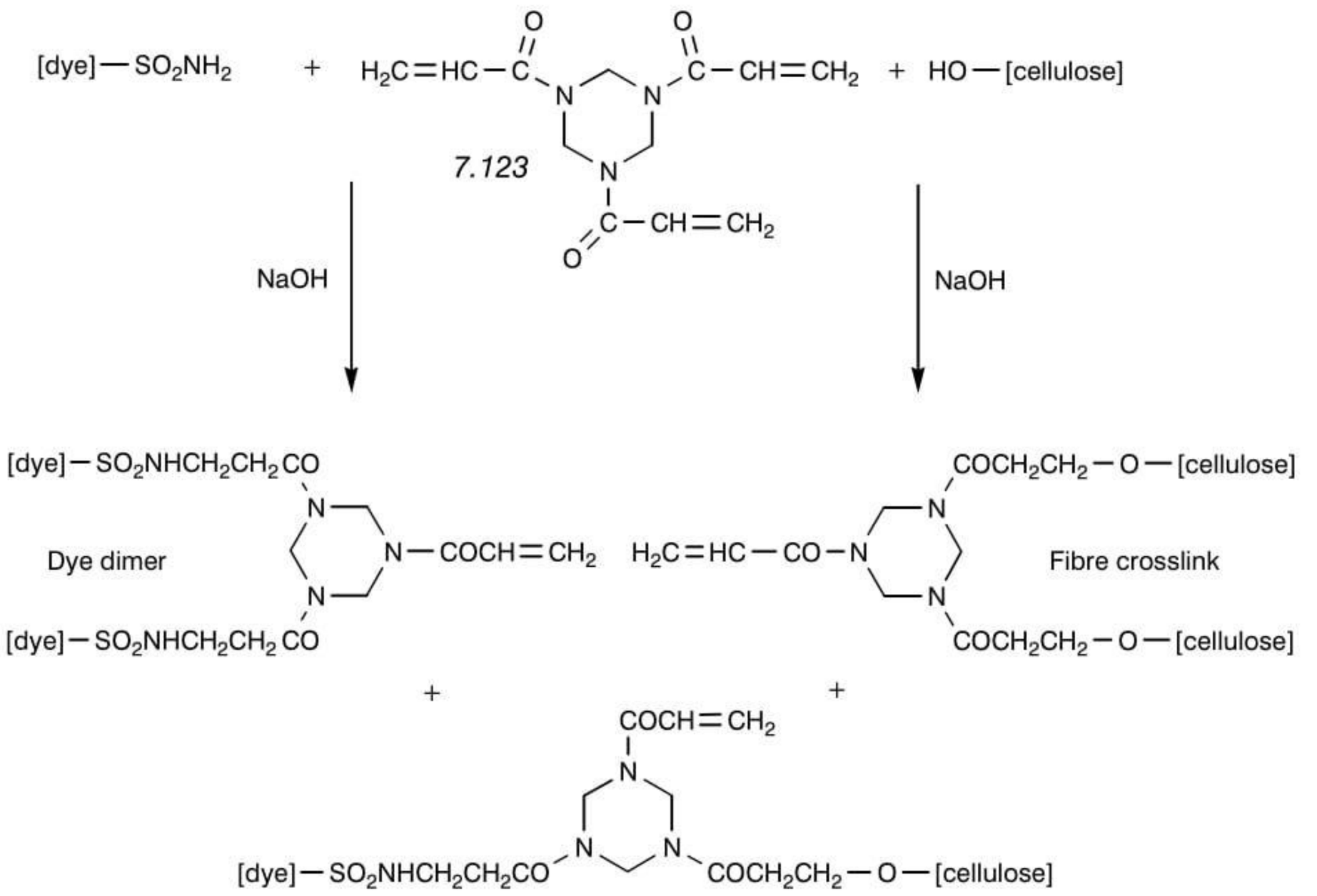
The most interesting departure from conventional reactive dyeing methods of the 1960s was the Basazol (BASF) approach [133]. Selected unmetallised chromogens and 1:2 chromium complexes containing nucleophilic groups such as primary or secondary amino, arylsulphonamide or unsubstituted pyrazolone residues were used (7.121 and 7.122 are typical examples). These were applied to cellulosic fabrics by padding or printing, together with the non-substantive crosslinking agent 1,3,5-tris(acryloyl)hexahydro-s-triazine (7.123). Above pH 10.5 the sulphonamide group is sufficiently nucleophilic to undergo Michael addition with the acryloyl groups of Fixing Agent P. This trifunctional product is sufficiently reactive and versatile to form dye–fibre links, as well as dye dimers or trimers and crosslinks between cellulose molecules [134]. Although Basazol dyes were not hydrolysable, dimerisation and cellulose crosslinking do represent competitive side reactions (Scheme 7.60). Some acryloyl groups will be hydrolysed (Scheme 7.61). The system was not adaptable to exhaust dyeing and the Basazol products were later withdrawn from the market.



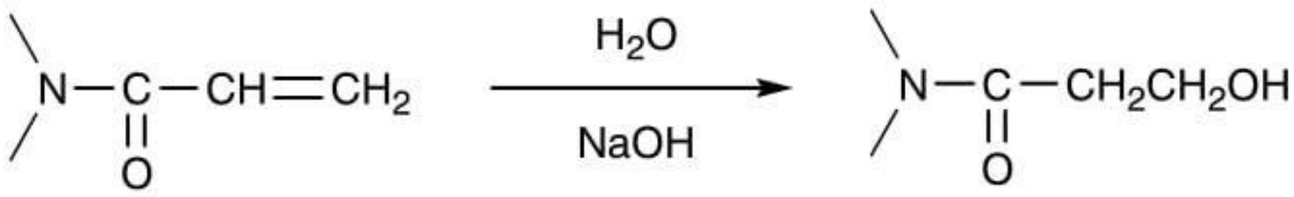
7.121



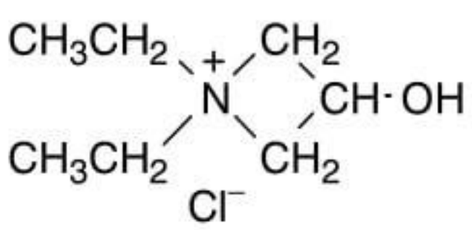
7.122



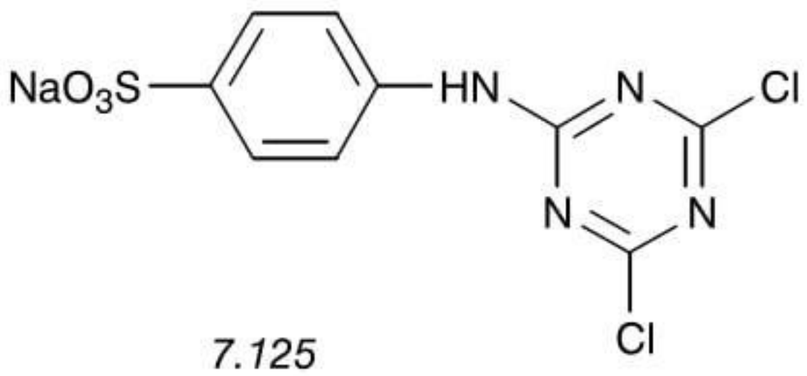
Scheme 7.60



Scheme 7.61



7.124



7.125

A relatively uncontrolled attempt to enhance the colour yield and fastness to washing of selected direct dyes involved addition to the dyebath of a colourless reactant that was intended to form covalent attachments between these dyes and hydroxy groups in cellulose [135]. Most of the dyes selected contained at least two primary amino groups in aminonaphthol residues. The reactants evaluated were cyanuric chloride (7.3), *N,N*-diethyl-3-hydroxyazetidinium chloride (7.124) and 2,4-dichloro-6-(4′-sulphoanilino)-s-triazine (7.125), all of which will indeed react readily with primary arylamines. Some of the dyes selected, however, contained only diphenylurea or salicylic acid residues and these are most unlikely to react efficiently under dyeing conditions.

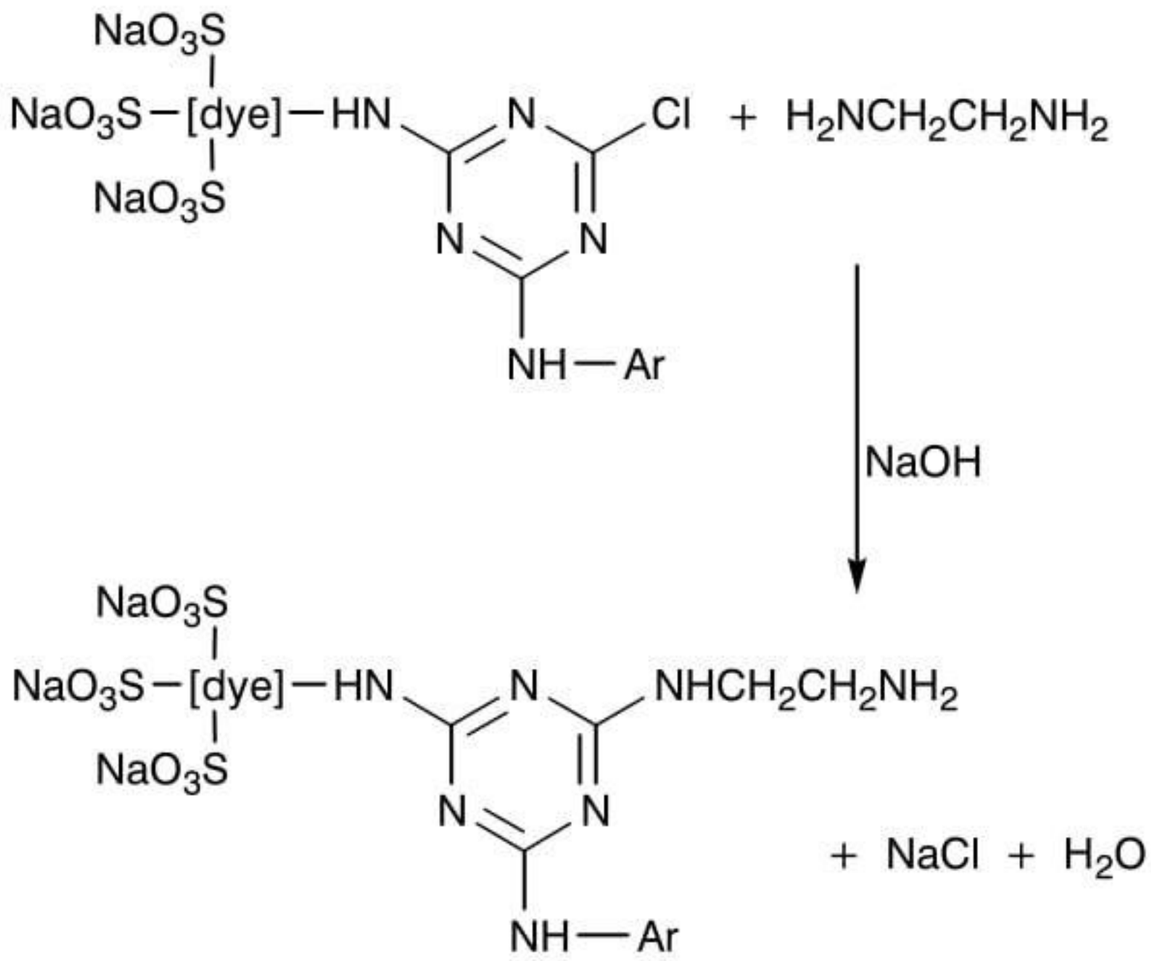
In a later development [136,137], cyanuric chloride was proposed as an aftertreatment for cotton already dyed with direct dyes containing amino groups. This approach appears even less likely to succeed than *in situ* addition to the dyebath. Serious hazards are associated with the handling of cyanuric chloride under these conditions. This highly reactive compound is a primary skin irritant and is known to cause severe allergic reactions in certain individuals. Dye–agent reaction will be inefficient because of hydrolytic deactivation. Uptake of cyanuric chloride (or its hydrolysis products) by the dyed cotton will be poor.

A much more controlled approach to the concept involves incorporating the reactive function into the substrate and carrying out the dyeing with a non-hydrolysable dye containing a nucleophilic group [138]. Various nucleophilic groups come into consideration, but the aliphatic amino group gives the best results in practice as it is more reactive than arylamino, phenolic or aliphatic hydroxy groups. In terms of nucleophilicity, the aliphatic thiol group is even more reactive, but thiol compounds are often malodorous and tend to oxidise to their disulphide derivatives [52]. An aminoalkyl derivative of the monoazo H acid dye CI Reactive Red 58 was prepared by reaction with ethylenediamine (Scheme 7.62).

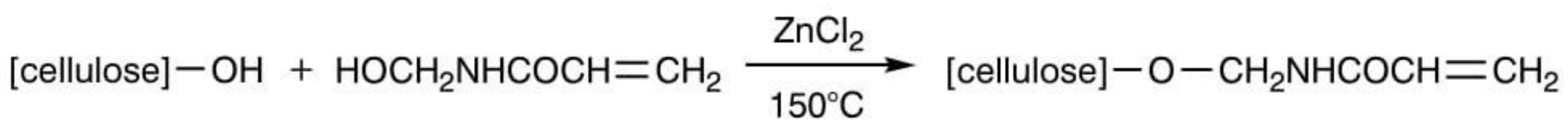
Acrylamidomethylated cellulose prepared by the pad–bake condensation of *N*-methylolacrylamide with cotton (Scheme 7.63) reacts readily with nucleophilic dyes of this kind. High fixation is achieved either by exhaustion at pH 10.5 in 80 g/l salt solution or by pad–batch treatment at the same pH for 24 hours (Scheme 7.64). These aminoalkyl dyes show zwitterionic characteristics below pH 8 and this lowers the nucleophilicity of the primary amino group (Scheme 7.65). Practically no dye is removed on alkaline soaping of these dyeings at the boil, compared with ca. 30% desorption of unfixed dye after application of the dichlorotriazine analogue CI Reactive Red 58 to untreated cotton. The dyeing of activated cotton with the aminoalkylated derivative thus offers significant savings, since only a minimal rinse would be adequate and soaping at the boil could be omitted [52].

A simple yet rather drastic method of introducing reactive sites into the cellulose macromolecule is to use periodate as a relatively specific oxidant. This ring-opening reaction converts the vic-diol grouping in the 2,3-positions of some of the glycoside rings into a dialdehyde (Scheme 7.66). The aldehyde groups can provide sites for fixation of dye molecules containing nucleophilic aminoalkyl groups, such as a symmetrical bis(aminoalkyl) derivative of a bis(aminochlorotriazine) triphenodioxazine blue reactive dye [139]. The azomethine groups formed are sensitive to hydrolysis unless reduced to the secondary amine.

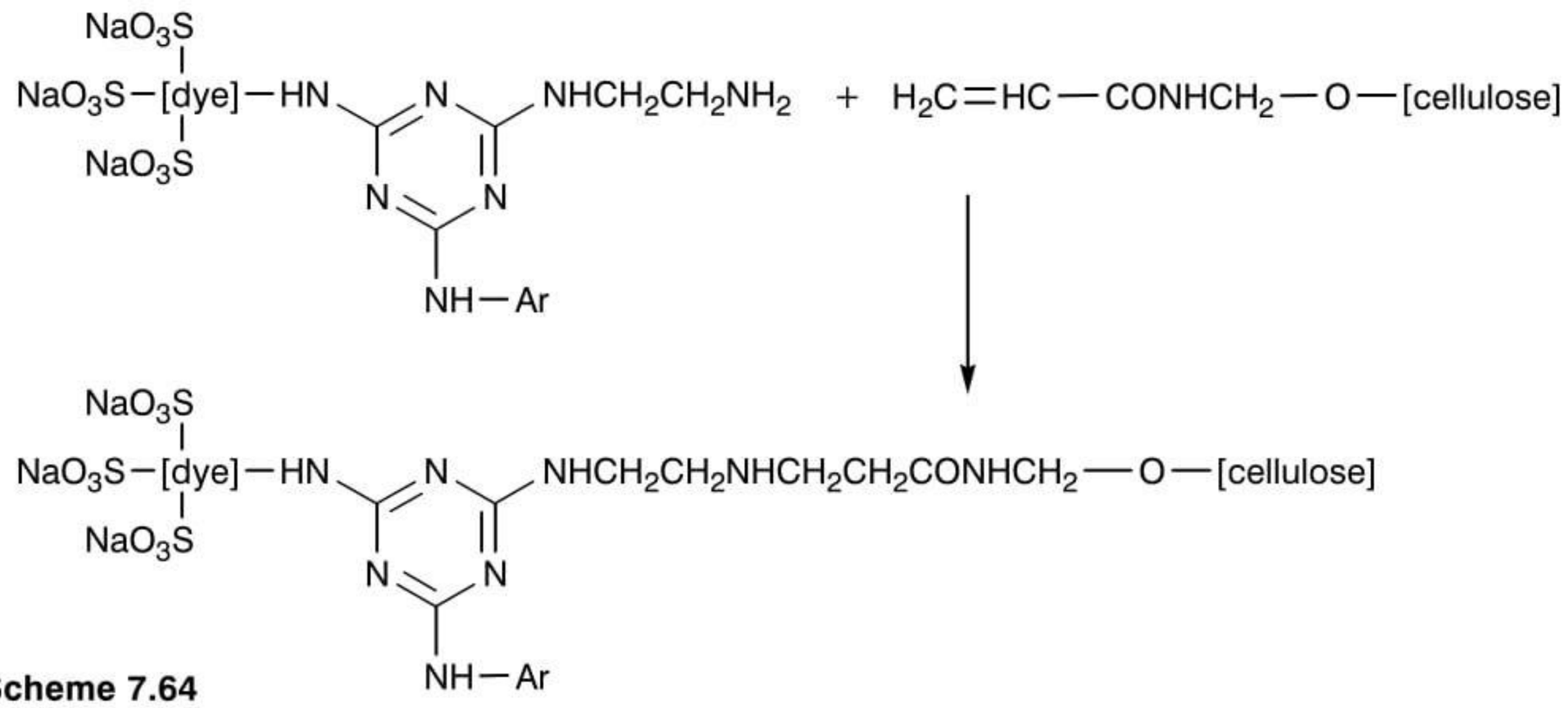
The highly reactive compound disodium 4,4′-bis(dichlorotriazinylamino) stilbene-2,2′-disulphonate (7.126; known as DAST or T-DAS), an important intermediate in the manufacture of stilbene-type fluorescent brightening agents (section 11.6.1), has been evaluated recently as a crosslinking agent for the fixation of dyes with nucleophilic groups. Compound 7.126 was applied to cotton simultaneously with the hydrolysed form of CI



Scheme 7.62



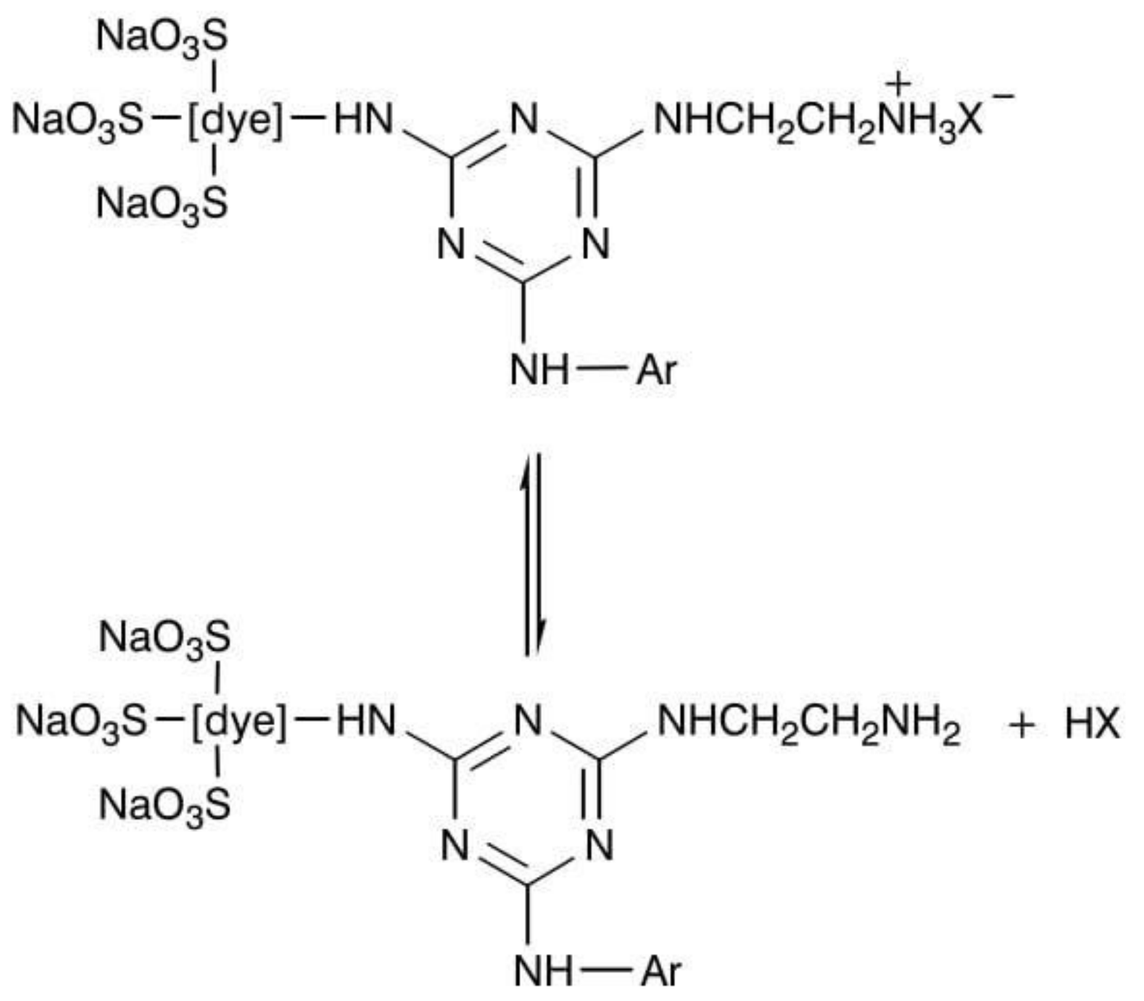
Scheme 7.63



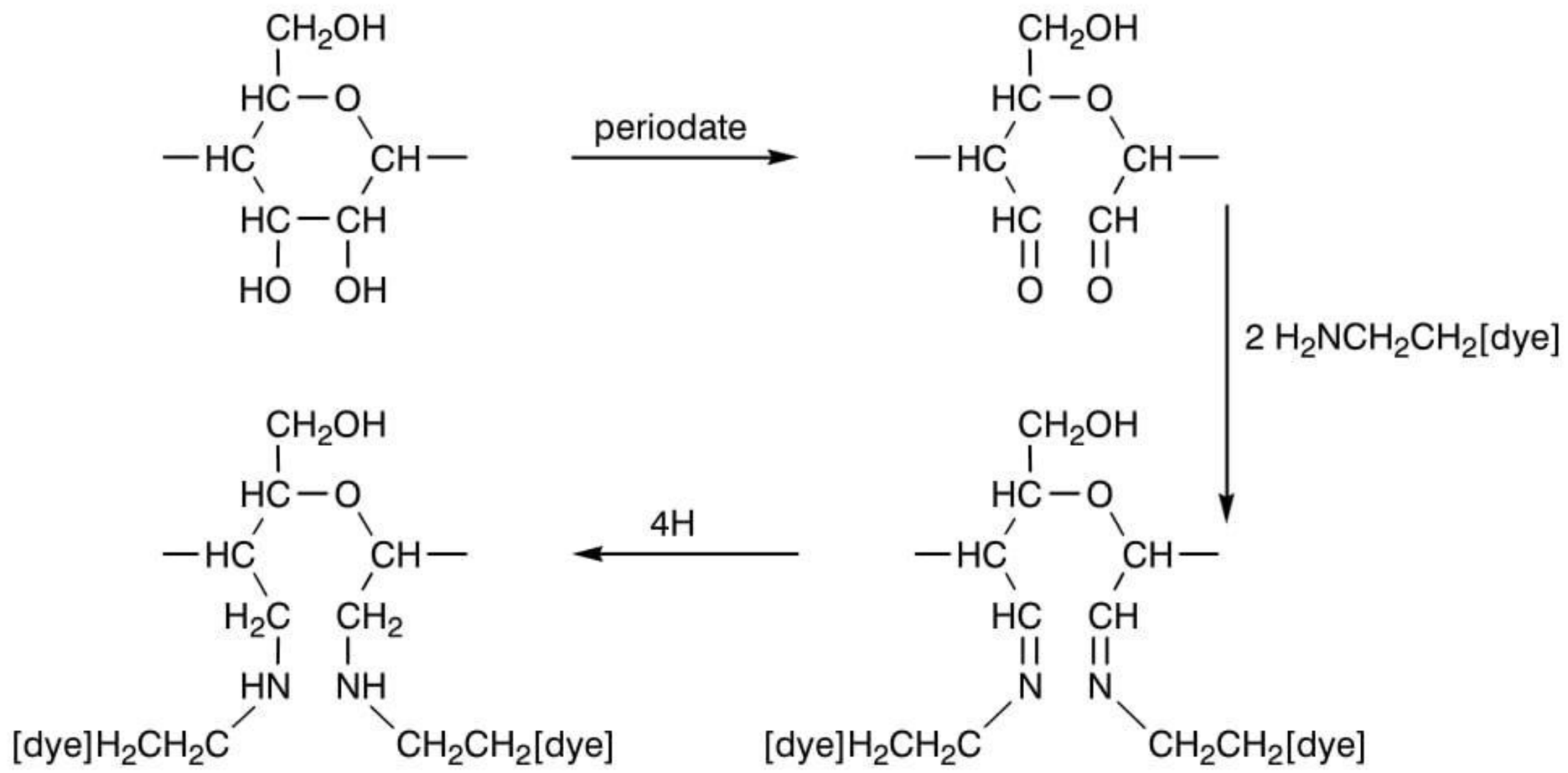
Scheme 7.64

Reactive Black 5 (7.127) by an exhaust process and optimal conditions for fixation were determined [140]. The substantivity of this agent for cellulose is not ideal, as it requires a high salt concentration to ensure a fixation level of 80%. To achieve 85% fixation of dye 7.127 by this method, an addition of 50 g/l sodium sulphate was necessary [29].

The novel cationic reactant 2,4-dichloro-6-(2′-pyridinoethylamino)-s-triazine (7.128) was evaluated as a means of activating cellulose by pad–batch application at pH 8.5 for 24 hours. This agent contains two reactive chlorine atoms but under these mild conditions only



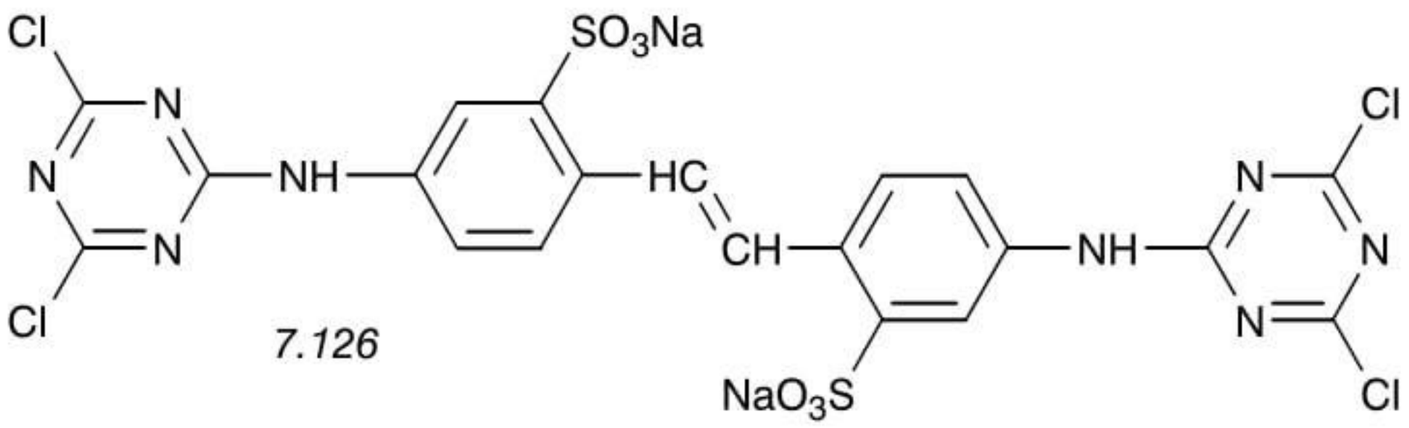
Scheme 7.65



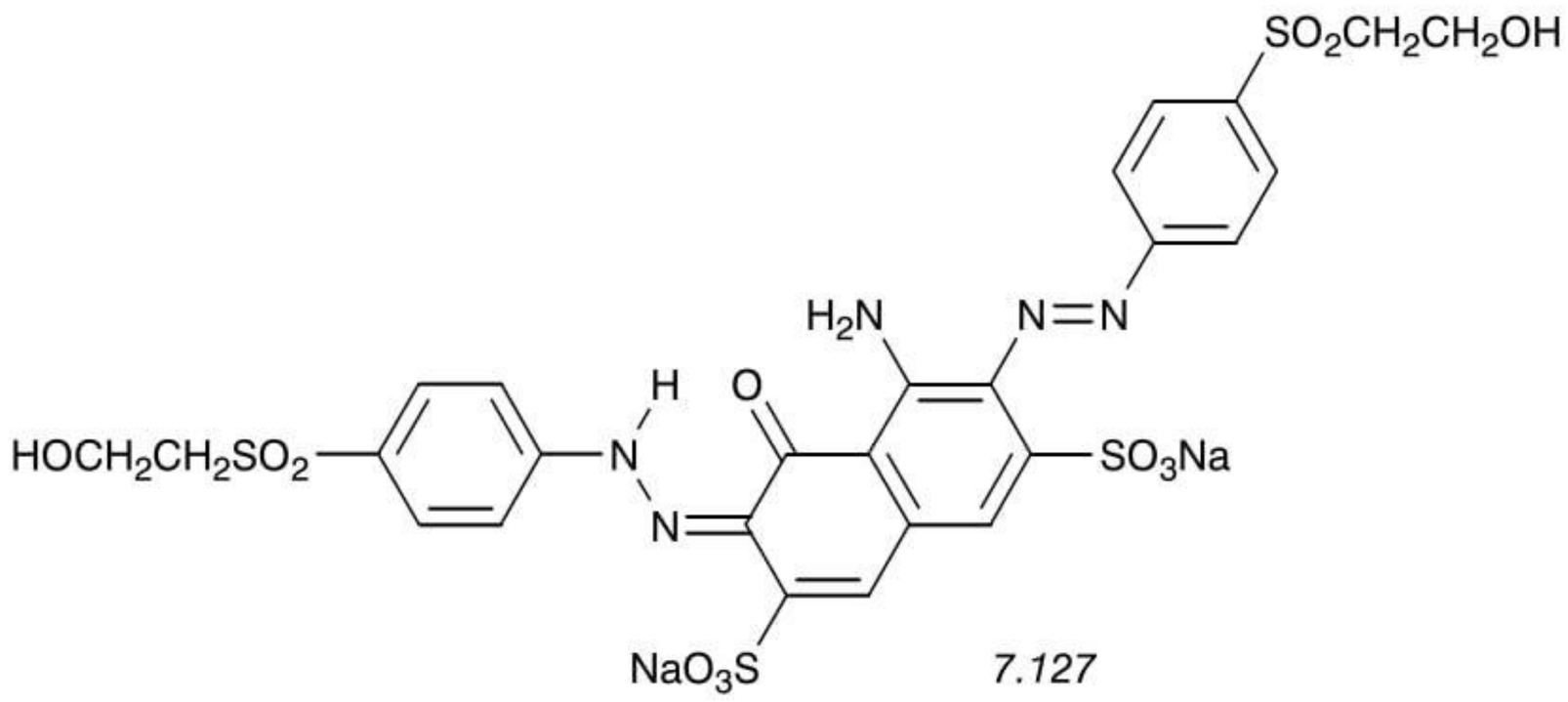
Scheme 7.66

one of them reacts with a hydroxy group in cellulose (Scheme 7.67). The electron-donating cellulosyl substituent deactivates the triazine ring, ensuring that the second chlorine atom remains unreacted. Aliphatic amino groups are more powerful nucleophiles than cellulose hydroxy groups, so that an efficient substitution reaction is still possible during subsequent dyeing with an aminoalkylated dye (Scheme 7.68). After a cold water wash, dyeings were carried out on the modified cotton fabric without salt at pH 9, using the monofunctional aminoalkylated derivative of CI Reactive Red 58 and a bifunctional analogue (7.129) synthesised by reacting one mole of CI Reactive Red 120 (7.48; X = Cl) with two moles of ethylenediamine. Good substantivity and fixation were achieved on cotton treated with 5.4% o.w.f. of the cationic reactant, particularly using the bifunctional nucleophilic dye [141].

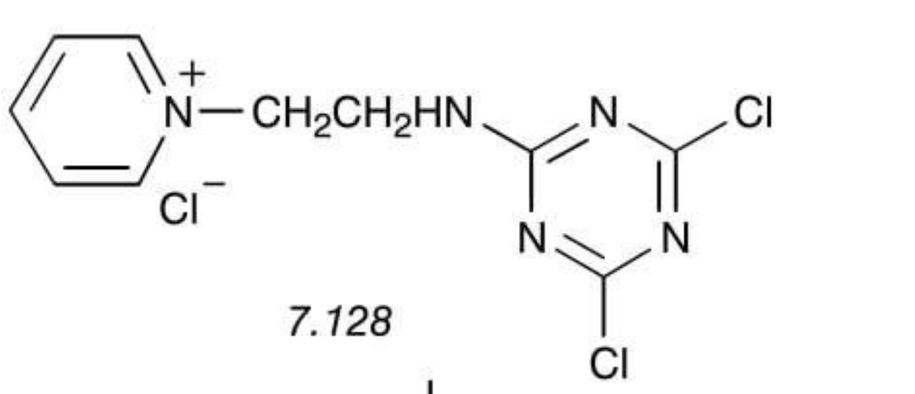
Nucleophilic aminoalkyl dyes of the types described above can be fixed on cotton that has



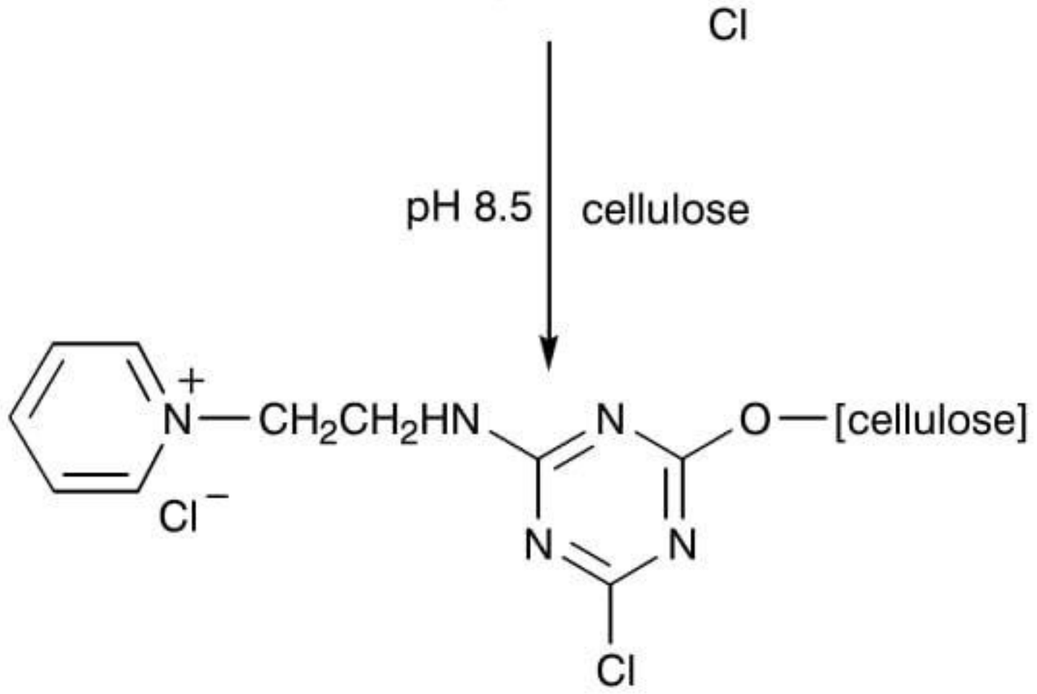
7.126



7.127

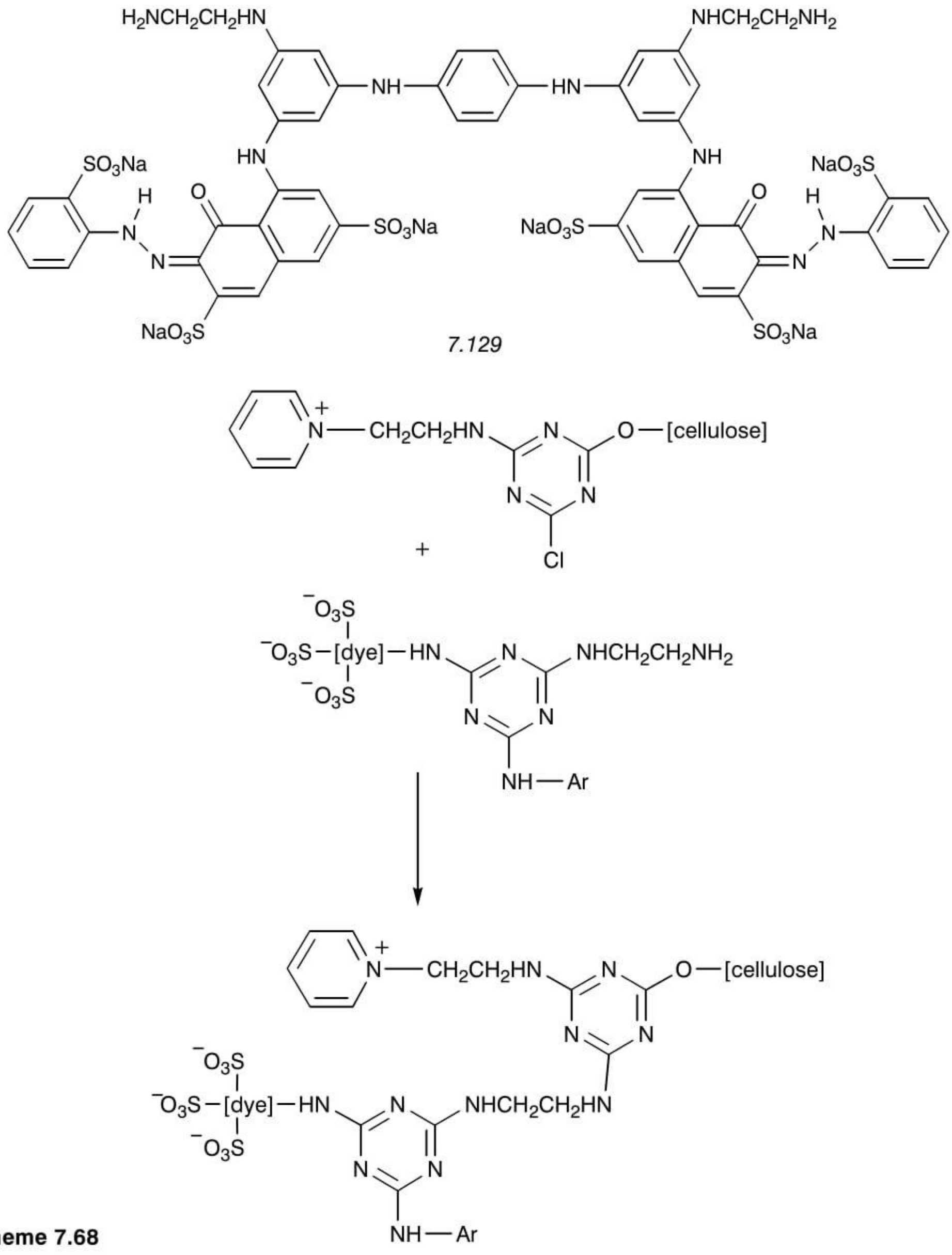


7.128



Scheme 7.67

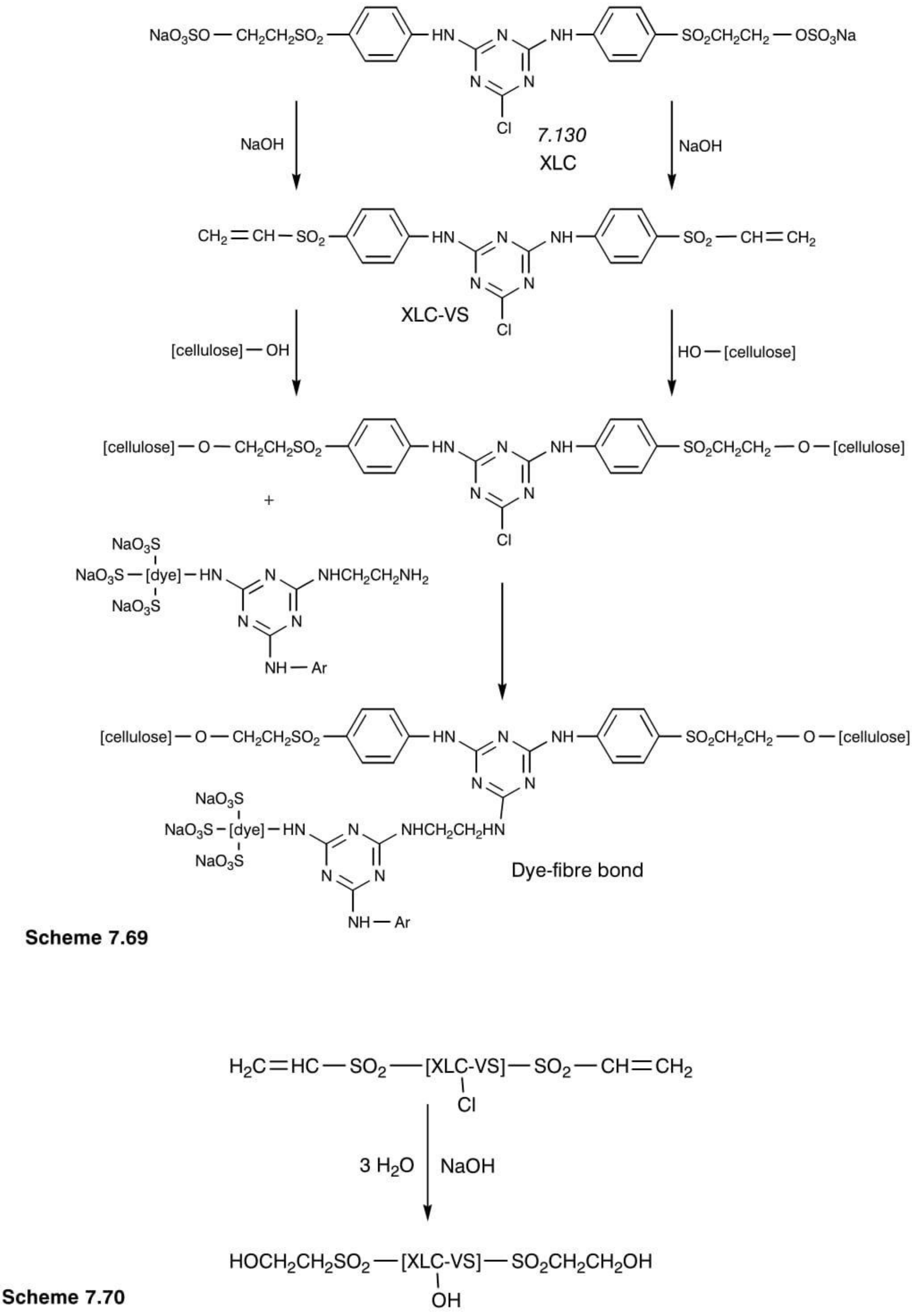
been pretreated with the trifunctional anionic reactant 2-chloro-4,6-bis(4′-sulphato-ethylsulphonylanilino)-s-triazine (7.130), which has been given the codename XLC [142]. After conversion to the active bis-vinylsulphone form (XLC–VS), crosslinking of the cellulose is possible under conditions that do not excessively hydrolyse the chlorotriazine function. As in the case of the cationic pretreating agent 7.128, this provides a suitable site for attachment of the aminoalkyl dye (Scheme 7.69).



Scheme 7.68

If the size of this extended bridge grouping containing five ring systems (including Ar) is compared with that needed by the original vinylsulphone dyes ($SO_2CH_2CH_2O$ in Scheme 7.25) to link the dye chromogen to cellulose, one must ask whether the gain in fixation is justifiable. Some of the active vinylsulphone and chloro substituents in reactant XLC–VS will be lost by hydrolysis (as in Scheme 7.70).

This versatile water-soluble reactant has been evaluated in wool and nylon dyeing. The nucleophilic aminoalkyl derivatives of orthodox aminochlorotriazine dyes behave like traditional acid dyes on wool owing to their zwitterionic character under neutral-dyeing conditions (Scheme 7.65). Improved wet fastness can be achieved using the reactant XLC



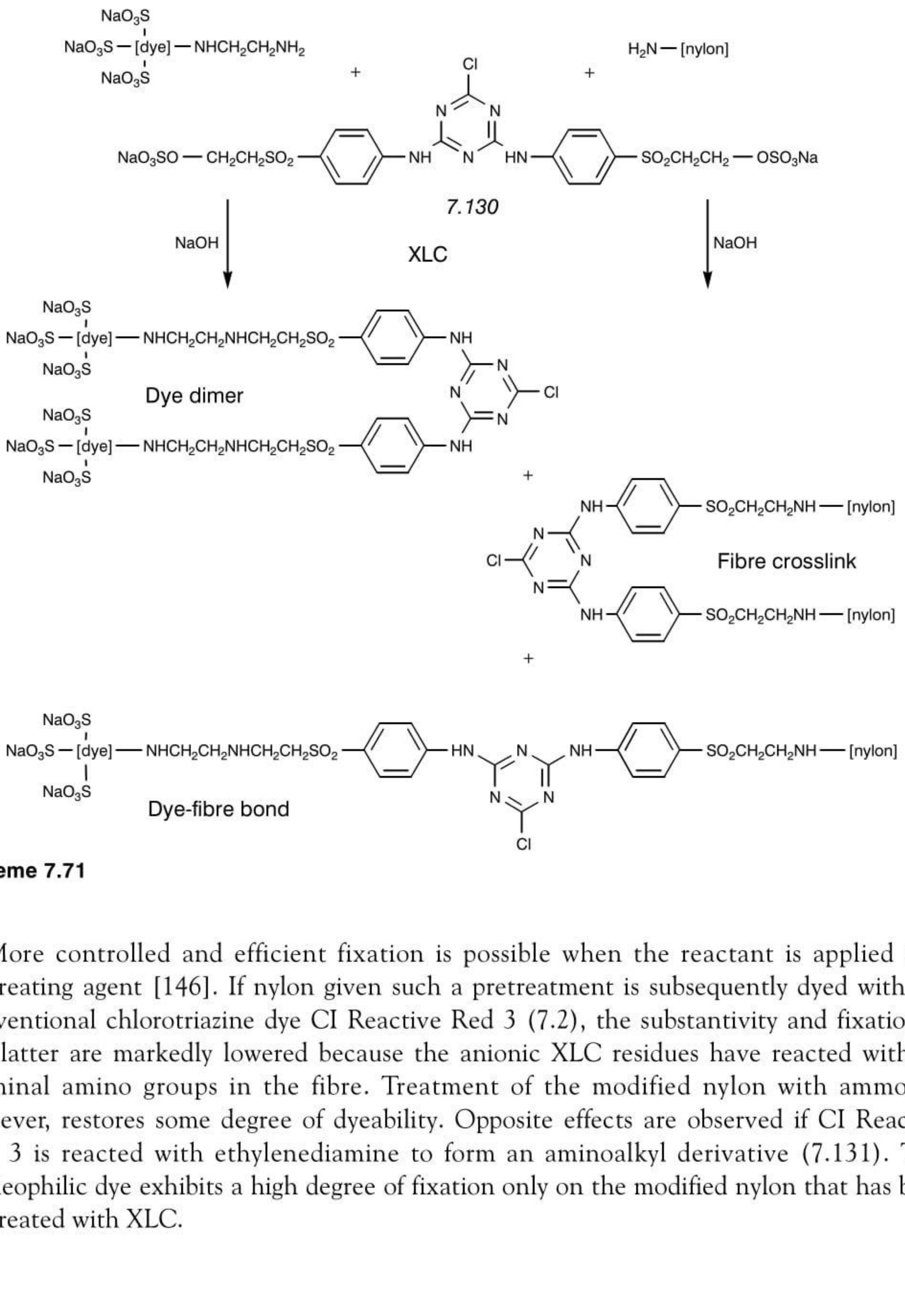
Scheme 7.69

Scheme 7.70

[143]. The effect of this additive on the conventional dyeing of wool with the anthraquinone sulphatoethylsulphone dye CI Reactive Blue 19 (7.37) was investigated.

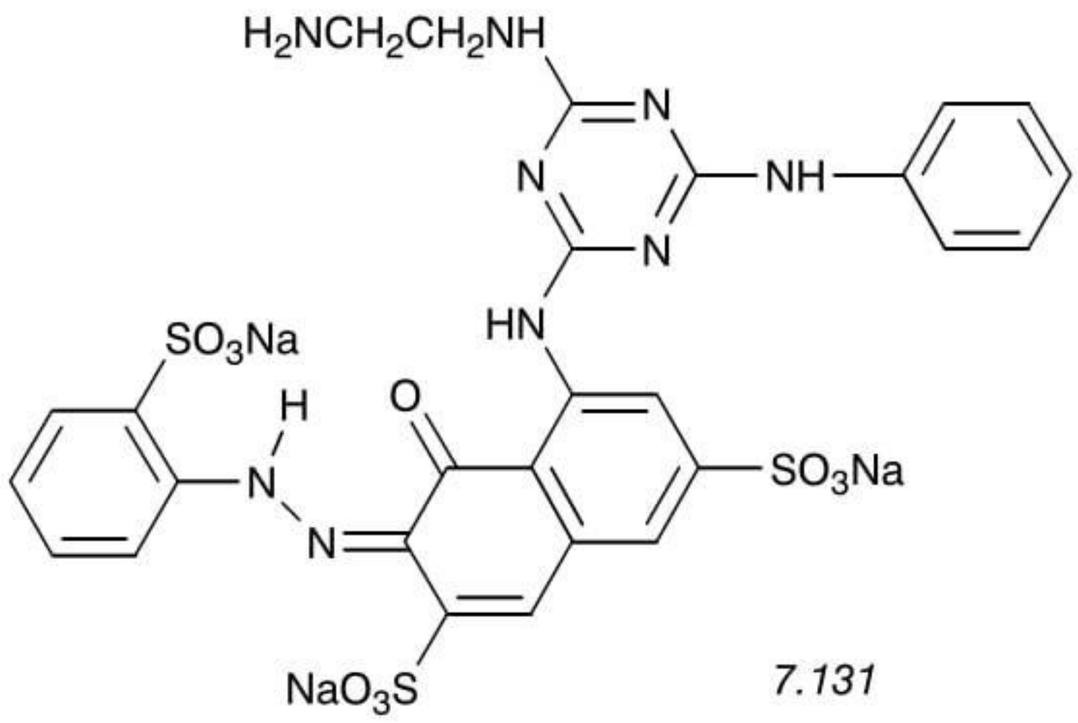
Aminoacid analysis and solubility tests for crosslinking revealed that XLC participated in various reactions leading to crosslinked wool [144].

In further work on nylon [145], this trifunctional reactant was applied simultaneously with various nucleophilic dyes of the aminoalkyl type (Scheme 7.71). As in the case of the Basazol system on cellulose (Scheme 7.60), the intended formation of covalent dye–fibre linkages has to compete with side reactions, such as partial hydrolysis (Scheme 7.70), di- or trimerisation that may lead to less than optimum fastness, or substrate crosslinking that may adversely influence desirable fibre characteristics.

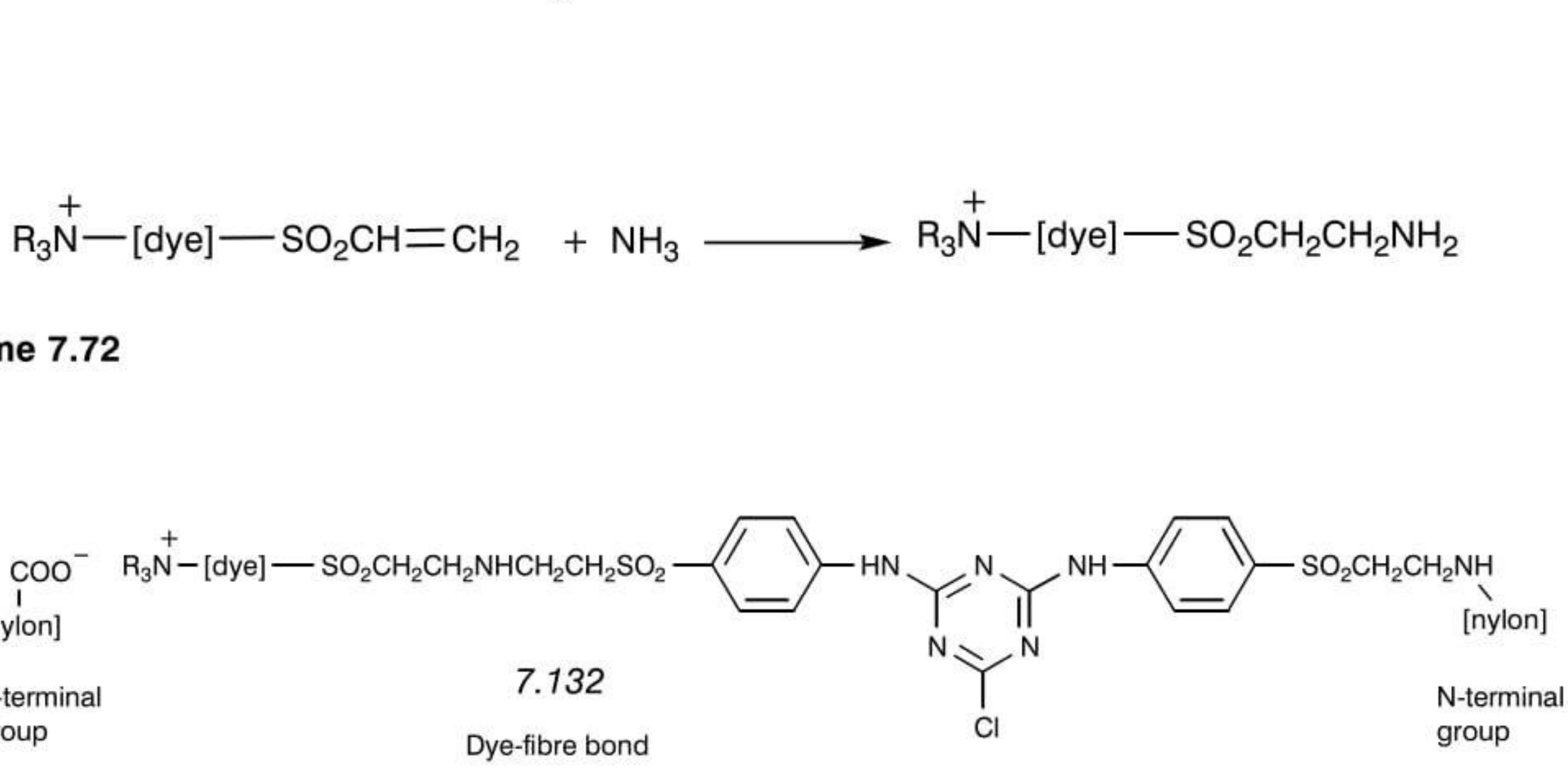


Scheme 7.71

More controlled and efficient fixation is possible when the reactant is applied as a pretreating agent [146]. If nylon given such a pretreatment is subsequently dyed with the conventional chlorotriazine dye CI Reactive Red 3 (7.2), the substantivity and fixation of the latter are markedly lowered because the anionic XLC residues have reacted with *N*-terminal amino groups in the fibre. Treatment of the modified nylon with ammonia, however, restores some degree of dyeability. Opposite effects are observed if CI Reactive Red 3 is reacted with ethylenediamine to form an aminoalkyl derivative (7.131). This nucleophilic dye exhibits a high degree of fixation only on the modified nylon that has been pretreated with XLC.



7.131

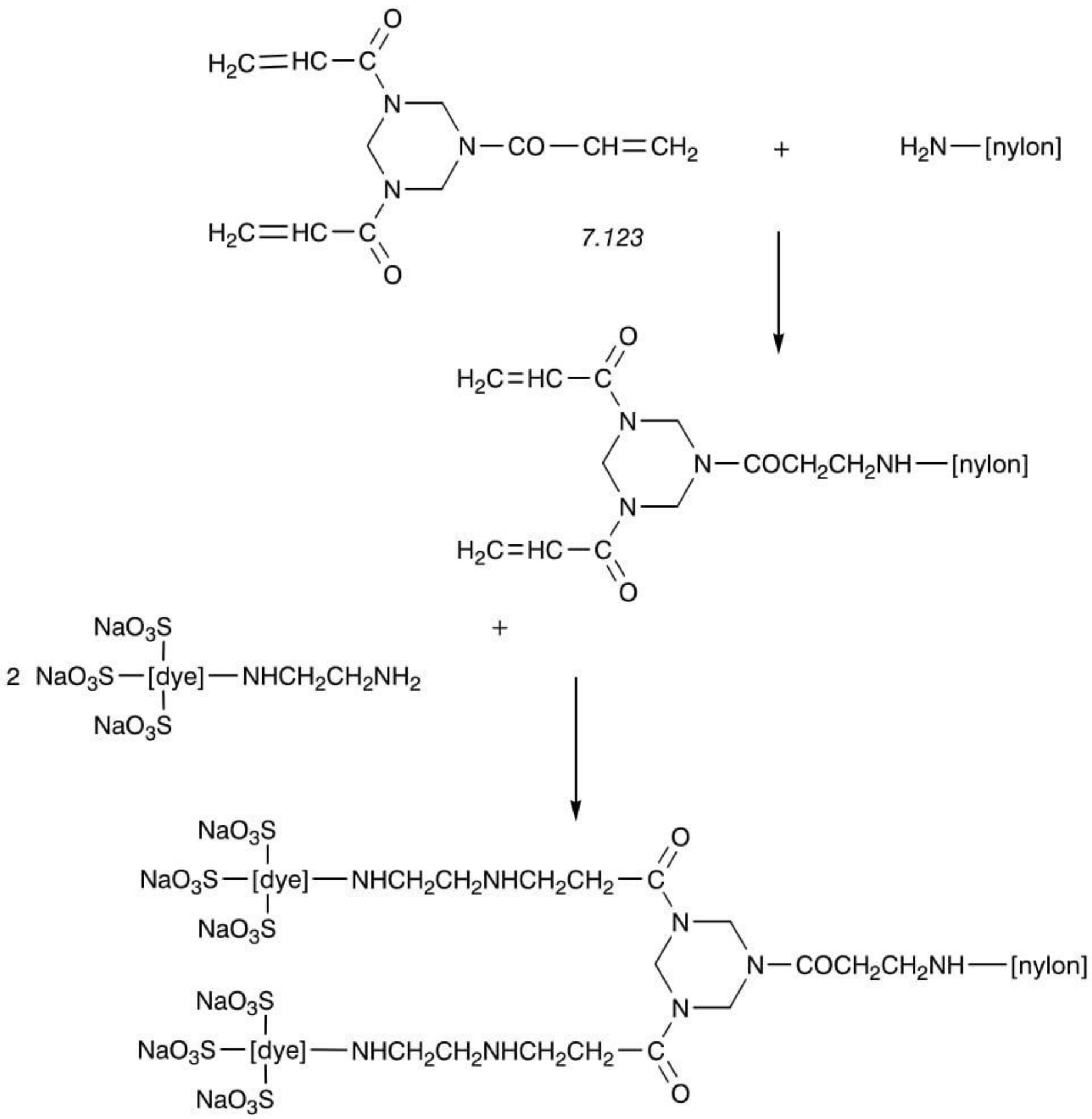


Scheme 7.72

7.132

In more recent work by the same authors [147], a monofunctional aminoalkyl dye showed high exhaustion on nylon under mildly acidic conditions. Aftertreatment of this dyeing with XLC–VS, the active bis-vinylsulphone form of the precursor 7.130, resulted in a significant degree of covalent bonding of the dye to nylon. This approach of using a crosslinking reactant to fix a nucleophilic dye showing orthodox dyeing behaviour on nylon was also applied to a specially prepared cationic dye. This contained a vinylsulphonyl group and was converted to a nucleophilic aminoethylsulphonyl derivative by reaction with ammonia (Scheme 7.72). This was readily absorbed on nylon C-terminal sites at pH values above 10. The anionic crosslinking agent XLC was subsequently applied to provide bridging links between these dye molecules and *N*-terminal amino groups in nylon. The weak link in this system (7.132) is the electrostatic bond between the cationic dye and the C-terminal carboxylate group. Any dye di- or trimers formed with the same trifunctional XLC molecule will be held to the nylon only by virtue of this electrostatic attraction and will be deficient in wet fastness. Partial premature hydrolysis (Scheme 7.70) of the crosslinking agent that reacts with single dye molecules may detract from the colour yield or wet fastness properties.

Interest in Fixing Agent P (7.123) has been revived in the context of nucleophilic aminoalkyl dyes of the 7.129 and 7.131 types. Nylon pretreated with this symmetrical trifunctional reactant contains residual acryloyl sites that will undergo an addition reaction with nucleophilic dye molecules [145]. Although in theory each *N*-terminal amino group in the fibre can give rise to two acryloyl sites (Scheme 7.73), crosslinking between two *N*-

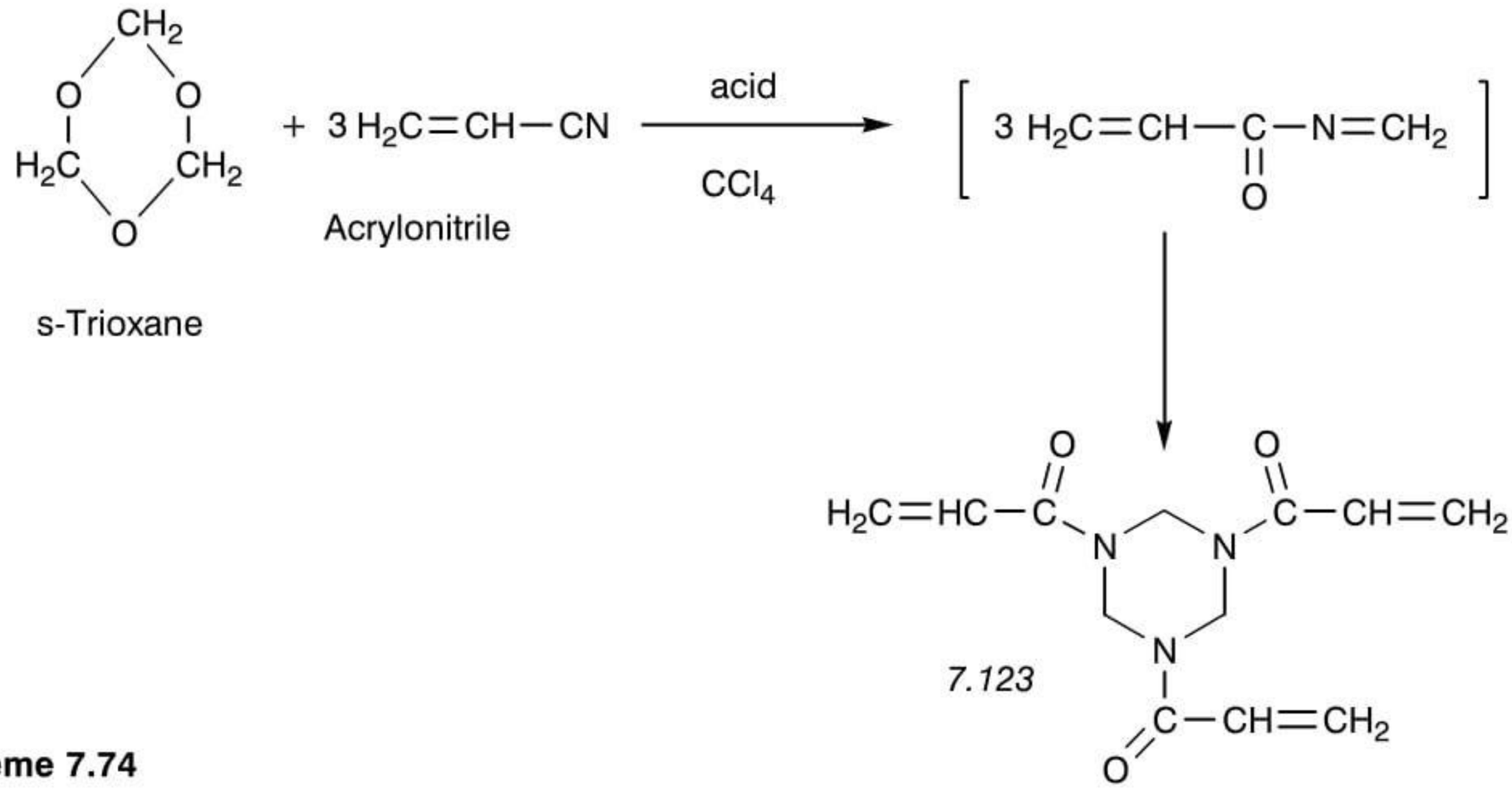


Scheme 7.73

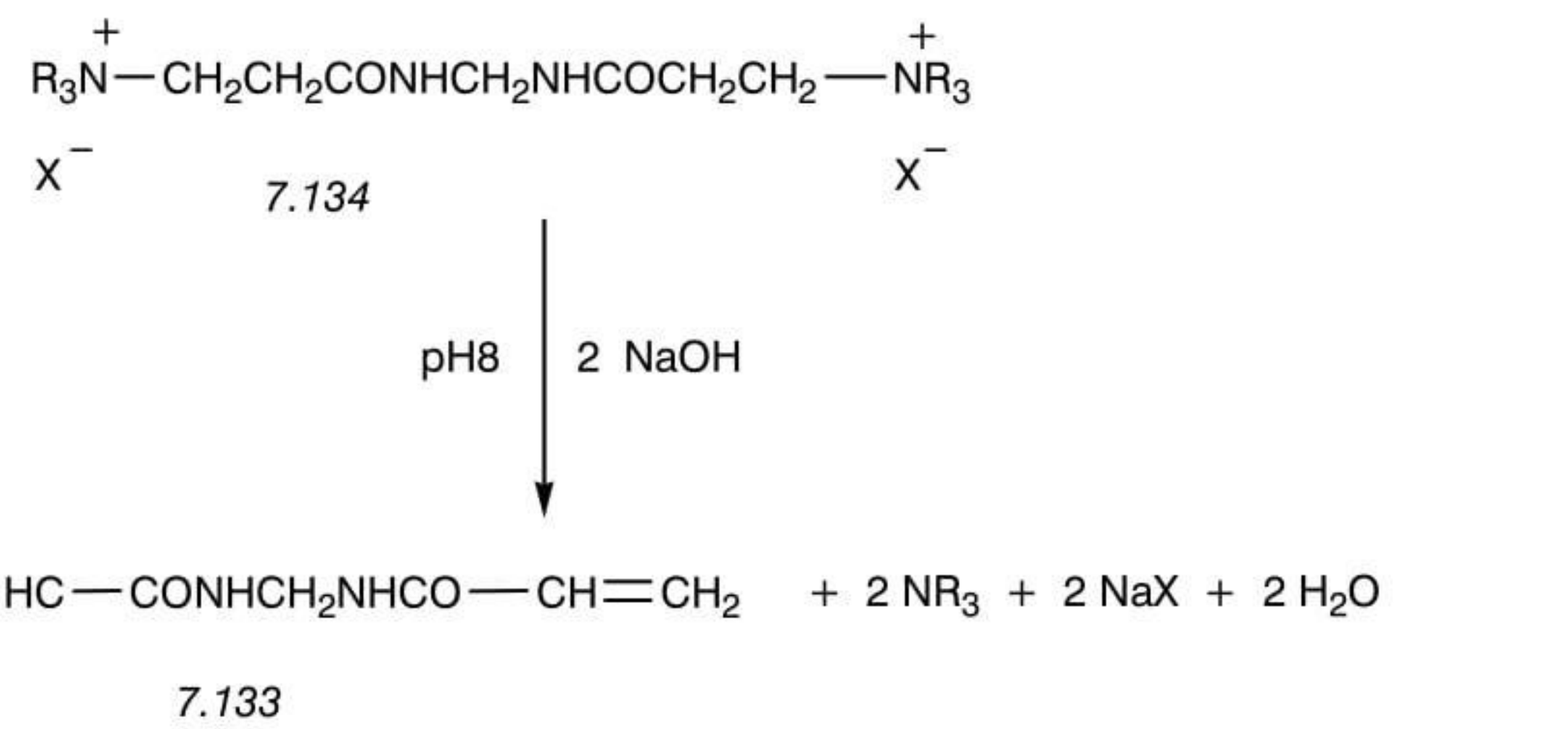
terminal groups, with or without subsequent dye fixation, will increase the proportion of trifunctional reactant required. Partial premature hydrolysis (Scheme 7.61) will have a similar effect on consumption of the agent.

On wool, dyeings of the bis(aminoethyliminotriazine) dye 7.129 and of the corresponding aminoalkyl derivative of CI Reactive Red 58 were carried out at the boil and pH 5 for 60 minutes. A dispersion of the symmetrical reactant 7.123 was then added and dyeing continued for 30 minutes before adjusting to pH 7 to complete the fixation stage in a further 30 minutes. Compared with a control dyeing of the bis(aminochlorotriazine) analogue CI Reactive Red 120 (7.48; X = Cl) for the same total time at the boil and pH 5, the new approach offers deferred fixation and hence improved levelness. The wet fastness performance was significantly enhanced but light fastness was adversely affected [148].

Reactant 7.123 can be prepared by reacting acrylonitrile with s-trioxane (Scheme 7.74) using an acid catalyst in carbon tetrachloride as solvent [147]. Two commercially available bifunctional reactants, *N,N′*-bis(acryloyl)methylenediamine (7.133) and its water-soluble bis-quaternary precursor (7.134), have been evaluated to achieve dyeings of similar quality at lower cost. The precursor is readily converted to the active reactant at about pH 8 during



Scheme 7.74

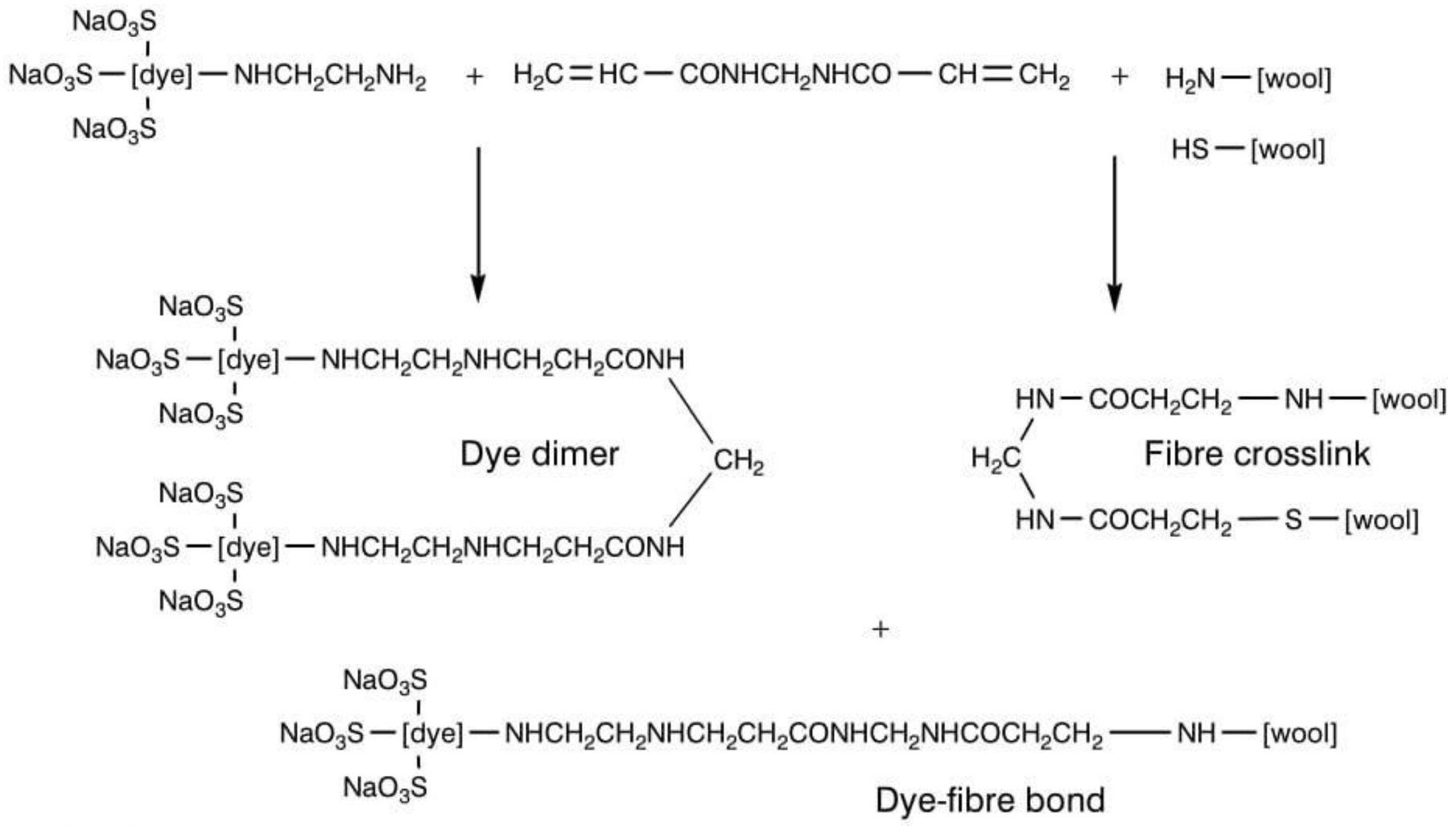


Scheme 7.75

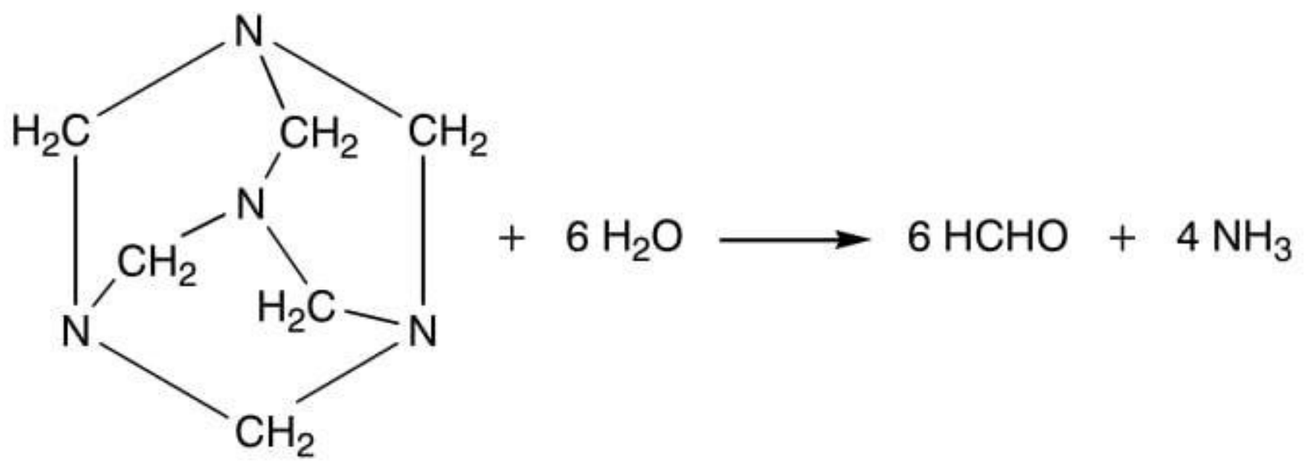
the dyeing process (Scheme 7.75). Monofunctional (7.131) and bifunctional (7.129) nucleophilic dyes were applied to wool by variants of the process already established using reactant 7.123. The reactivity of agent 7.133 was lower (Scheme 7.76), however, so that fixation was higher when it was applied at the start of the process. The bis-quaternary precursor cannot be used in this way because of its cationic character. Partial hydrolysis of the active reactant (Scheme 7.61) is unavoidable. The light fastness of dyeings using the bis-quaternary precursor was marginally lower and the aminoalkyl derivatives of cellulose-substantive chlorotriazine dyes tended to stain adjacent cotton in tests of fastness to washing and perspiration [149].

The alicyclic tertiary base hexamethylenetetramine (7.135) hydrolyses at the boil to release the simple crosslinking agent formaldehyde (Scheme 7.77). This has been evaluated in wool dyeing by applying the aminoethyl analogue of CI Reactive Red 3 (7.131) and hexamethylenetetramine simultaneously at the boil and pH 5. Covalent dye–fibre fixation did not commence until sufficient formaldehyde had been released at the boil, so the dye was able to migrate during the heating-up phase and good level dyeing was achieved [150].

Recent trends in unorthodox reactive dyeing systems, including Schemes 7.63–7.76 generally employing nucleophilic aminoethyliminotriazine dyes prepared as outlined in



Scheme 7.76



7.135

Scheme 7.77

Scheme 7.62 together with a variety of reactive intermediates or crosslinking agents intended to link together the dye and the substrate, raise some important questions. This research has encompassed variants of such systems on cotton, wool and nylon, mainly by exhaust application. Conventional reactive dyes have so far accounted for only about 20% of all dyes used worldwide on cellulosic fibres. Reactive dyes amount to only about 5% of all dyes used on wool and their current usage on nylon is negligible.

The special nucleophilic dyes designed for these novel systems are derived from cellulose-substantive chromogens and below pH 8 their aminoalkyl groups impart a zwitterionic character (Scheme 7.65), especially to the bifunctional type (7.129). Like direct dyes with both amino and sulpho substituents (section 3.1.2), aggregation problems can be foreseen. Although these novel dyes are free from problems of hydrolytic deactivation, the risk of premature hydrolysis leading to impaired fixation has been transferred to the activated fibre (Scheme 7.67) or the crosslinking reactant (7.130) essential for their application. Pretreatment of the fibre with a colourless reactant must be exceptionally reproducible, to ensure that the subsequent exhaustion, levelling and fixation of the dyes remains acceptably consistent. If penetration of the pretreating agent or crosslinking reactant into the fibre is poor, ring dyeing will occur and the colour yield and fastness performance will be adversely affected.

The high substantivity for cellulose of these nucleophilic dyes inevitably ensures that staining of adjacent cotton is unacceptable in wet fastness tests when the novel systems are evaluated on wool or nylon [149]. For the control dyeing representing target behaviour on wool a conventional α-bromoacrylamide dye of similar hue, such as CI Reactive Red 66, should be used. The monochlorotriazine dye from which the aminoethyliminotriazine derivative is prepared is not a valid control [148,149], because such dyes have never given satisfactory results on wool. Recent developments with conventional reactive dyes for wool have highlighted the design of low-cost, dull chromogens to compete more effectively with chrome dyes (section 7.7). It is not easy to see how such targets can be reconciled with these relatively elaborate novel systems.

The problems of dyeing nylon with reactive dyes are rather different (section 7.9), although the demand to compete with low-cost, non-reactive alternatives is even greater. Normal nylon contains only a limited number (ca. 40 milliequiv./kg) of accessible primary amine end groups available for covalent fixation of reactive dyes or crosslinking reactants. It is not normally difficult to ensure that virtually all of these react with a conventional monofunctional reactive dye. What is much more challenging is to design a compatible range of dyes to cover the entire colour gamut without unacceptable blocking effects in mixture recipes. In full depths the demand for accessible sites of reaction in normal nylon greatly exceeds their supply. The search for a viable reactive dyeing system in this area will probably have to involve an ultra-deep dyeing variant (>80 milliequiv./kg) as the preferred substrate, although this would be more costly than normal nylon and would exhibit less than ideal physical properties.

It will be interesting to see whether such novel reactive dyeing systems will become competitive alongside the long-established orthodox monofunctional ranges (section 7.3) and still-proliferating bifunctional structures (section 7.4) that have made gradual if not spectacular inroads into the textile sectors traditionally dyed with various ranges of non-reactive dyes. Safe handling of any necessary crosslinking reactants in substance or as an active component of the textile substrate will have to be given careful consideration. Each unusual intermediate required in the synthesis of a novel colorant or co-reactant molecule, as well as every possible side reaction or degradation pathway leading from the dyed textile and its associated waste waters, can no longer be introduced without posing searching questions of health and safety (section 1.7).

REFERENCES

1. C F Cross and E J Bevan, *Researches on cellulose* (1895–1900) 34.
2. I D Rattee, *Rev. Prog. Coloration*, **14** (1984) 50.
3. E Brunnschweiler and G Siegrist, *Textilveredlung*, **19** (1984) 305.
4. W E Stephen, *Chimia*, **19** (1965) 261.
5. W E Stephen and I D Rattee, *J.S.D.C.*, **76** (1960) 6.
6. J Wegmann, *J.S.D.C.*, **76** (1960) 205.
7. J Shore, Ed., *Cellulosics Dyeing* (Bradford: SDC, 1995) 189.
8. A H M Renfrew and J A Taylor, *Rev. Prog. Coloration*, **20** (1990) 1.
9. P Rys and H Zollinger, *Text. Chem. Colorist*, **6** (1974) 62.
10. I D Rattee, *J.S.D.C.*, **85** (1969) 23.
11. C V Stead, *Dyes and Pigments*, **3** (1982) 161.
12. M A Avsac, *Teintex*, **30** (1965) 163.
13. H R Hensel and G Lützel, *Angew. Chem. Internat.*, **4** (1965) 408.
14. G Meyer and H Wirth, *Melliand Textilber.*, **43** (1962) 850.

15. K G Kleb, K Sasse and E Siegel, *Angew. Chem. Internat.*, **3** (1964) 312.
16. O A Stamm, *J.S.D.C.*, **80** (1964) 416.
17. T E Peacock, *Electronic properties of aromatic and heterocyclic molecules* (London: Academic Press, 1965) 103.
18. J Wolff and H Henk, *Textilveredlung*, **25** (1990) 213; IFATCC Cong., Lucerne (June 1990) lecture.
19. F Lehr, M Greve and A R Katrizky, *Dyes and Pigments*, **7**, No 6 (1986) 419.
20. A H M Renfrew, *Adv. Col. Sci.Tech.*, **1** (1998) 12.
21. T L Dawson and A S Fern, *J.S.D.C.*, **76** (1960) 210.
22. C Preston and A S Fern, *Chimia*, **15** (1961) 177.
23. Z Zheng-Hua and J Cheng-Zhong, *Dyes and Pigments*, **19**, No 4 (1992) 265.
24. J A Taylor, A H M Renfrew and J N Lovis, *J.S.D.C.*, **107** (1991) 455.
25. W Zuwang, L Peng, W Shirong and L Li, *Dyes and Pigments*, **38** (1998) 1.
26. W Möck, *Melliand Textilber.*, **45** (1964) 652.
27. S Abeta and K Imada, *Rev. Prog. Coloration*, **20** (1990) 19.
28. H Ackermann and P Dussy, *Helv. Chim. Acta*, **45** (1962) 1683.
29. H S Freeman and J Sokolowska-Gajda, *Rev. Prog. Coloration*, **29** (1999) 8.
30. K H Schündehutte and K Trautner, *Chimia Suppl.*, **22** (1968) 155.
31. E Bohnert, *J.S.D.C.*, **75** (1959) 581.
32. O A Stamm, *Helv. Chim. Acta*, **46** (1963) 3019.
33. P Rys and O A Stamm, *Helv. Chim. Acta*, **49** (1966) 2287.
34. L N Guo *et al.*, *J.S.D.C.*, **109** (1993) 213.
35. C B Smith and K A Thakore, *Text. Chem. Colorist*, **23** (Oct 1991) 23.
36. A H M Renfrew, *Reactive dyes for textile fibres: The chemistry of activated π–bonds as reactive groups* (Bradford: SDC, 1999).
37. S Abeta, K Imada and T Washimi, *Colour Science* '98, Vol 2, Ed S M Burkinshaw (Leeds: Leeds Univ., 1998) 60.
38. Z Zheng-Hua, X Jian-Mei and C Kong-Chang, *Dyes and Pigments*, **17**, No 3 (1991) 171, 217.
39. Z Zhu and Y Zhang, *Dyes and Pigments*, **21**, No 3 (1993) 173; **21**, No 4 (1993) 243.
40. Z Zheng-Hua and Z Wei-Ping, *Dyes and Pigments*, **24** (1994) 281; **25** (1994) 87.
41. O Thumm and J Benz, *J.S.D.C.*, **77** (1961) 734.
42. B L McConnell, L A Graham and R A Swidler, *Text. Research J.*, **49** (1979) 478.
43. A Burger and J J Anderson, *J. Amer. Chem. Soc.*, **79** (1957) 3575.
44. F Kurzer and K Douraghi-Zadeh, *Chem. Rev.*, **67** (1967) 107.
45. P O Nkeonye, *J.S.D.C.*, **102** (1986) 384.
46. M E Amato, S Fisichella and I D Rattee, *J.S.D.C.*, **103** (1987) 434.
47. E E Gillingham, D M Lewis and K Srikulkit, *Colour Science* '98, Vol 2, Ed. S M Burkinshaw (Leeds: Leeds Univ., 1998) 30.
48. D M Lewis and B Voncina, *Colour Science* '98, Vol. 2 Ed. S M Burkinshaw (Leeds: Leeds Univ., 1998) 231.
49. D M Lewis and E E Gillingham, AATCC Internat. Conf. & Exhib. (Oct 1995) 536.
50. J I N R Gomes *et al.*, *J.S.D.C.*, **112** (1996) 19.
51. A Frost and V Duveen, *J.S.D.C.*, **84** (1968) 304.
52. D M Lewis, *J.S.D.C.*, **109** (1993) 357.
53. S Fujioka and S Abeta, *Dyes and Pigments*, **3** (1982) 281.
54. S M Betrabet, V B Bagwe and E H Daruwalla, *J.S.D.C.*, **103** (1987) 338.
55. A H M Renfrew and P Cowell, *J.S.D.C.*, **114** (1998) 174.
56. R J English and D M Lewis, *Colour Science* '98, Vol 2, Ed. S M Burkinshaw (Leeds: Leeds Univ., 1998)1.
57. D M Lewis, *Rev Prog. Coloration*, **29** (1999) 23.
58. T L Dawson, *J.S.D.C.*, **80** (1964) 134.
59. J A Taylor and A H M Renfrew, *J.S.D.C.*, **106** (1990) 230.
60. L Dongzhi, G Kunyu and C Lubai, *J.S.D.C.*, **107** (1991) 319.
61. T Sugimoto, *J.S.D.C.*, **108** (1992) 497.
62. N Morimura and M Ojima, *Am. Dyestuff Rep.*, **74** (Feb 1985) 28.
63. S N Croft *et al.*, *J.S.D.C.*, **108** (1992) 195.
64. Z Zheng-Hua and J Limin, *Dyes and Pigments*, **36** (1998) 355.
65. Y Sheng and Z Zheng-Hua, *Dyes and Pigments*, **38** (1998) 137.
66. S Abeta *et al.*, *J.S.D.C.*, **107** (1991) 12.
67. Z Morita *et al.*, *Dyes and Pigments*, **30** (1996) 151; IFATCC Cong., Vienna (June 1996) 318.
68. A Uygur and M Hall, *Melliand Textilber.*, **77** (1996) 148; *J.S.D.C.*, **112** (1996) 167.
69. S Abeta, T Yoshida and K Imada, *Am. Dyestuff Rep.*, **73** (July 1984) 26.
70. K Imada, M Sasakura and T Yoshida, *Text. Chem. Colorist*, **22** (Nov 1990) 18.
71. U Meyer and S Muller, *Text. Chem. Colorist*, **22** (Dec 1990) 26.
72. P Dilger, U Meyer and P Rys, *Textilveredlung*, **23** (Jan/Feb 1998) 14.

73. N Harada *et al.*, *J.S.D.C.*, **107** (1991) 363.
74. M Matsui, U Meyer and H Zollinger, *J.S.D.C.*, **104** (1988) 425.
75. J P Luttringer and A Tzikas, *Textilveredlung*, **25** (1990) 311.
76. J P Luttringer, AATCC Internat. Conf. & Exhib. (Oct 1992) 318; *Text. Chem. Colorist*, **25** (May 1993) 25.
77. J M Sire and P Browne, *Melliand Textilber.*, **72** (1991) 465.
78. P Scheibli and S Koller, Proc. Conf. Reactive Dyes, Leeds Univ. (Sep 1989).
79. E Miosga, *Melliand Textilber.*, **79** (1998) 532.
80. C Schumacher, K Bredereck and F Reidl, IFATCC Cong., Vienna (June 1996) 65.
81. V Dlask and R Hulcova, *Dyes and Pigments*, **26** (1994) 83.
82. K Fritzsche, *J.S.D.C.*, **108** (1992) 225.
83. V Dlask, J Timar and R Hulcova, *Dyes and Pigments*, **25** (1994) 295.
84. M Gorensek, *Dyes and Pigments*, **40** (1998) 225.
85. F Lehr, *Dyes and Pigments*, **14**, No 4 (1990) 239.
86. M Durr and M Gisler, Proc. Conf. Reactive Dyes, Leeds Univ. (Sep 1989).
87. Z Morita, I H Kim and H Motomura, *Dyes and Pigments*, **18**, No 1 (1992) 11.
88. Y Yang and J E Hughes, AATCC Internat. Conf. & Exhib. (Oct 1997) 365; *Text. Chem. Colourist*, **29** (Nov 1997) 23.
89. I D Rattee and J I N R Gomes, *J.S.D.C.*, **101** (1985) 319.
90. J I N R Gomes and C J E Lima, IFATCC Cong., Vienna (Jun 1996) 392.
91. W Shik-Ha and C Joo-Lee, *Melliand Textilber.*, **67** (1986) 724.
92. C M Ladisch, R R Brown and K B Showell, *Text. Chem. Colorist*, **15** (1983) 209.
93. J Manay, J Price and J G Welborne, *Text. Chem. Colorist*, **17** (1985) 239.
94. J Shore, *J.S.D.C.*, **84** (1968) 408.
95. D M Lewis, *Rev. Prog. Coloration*, **8** (1977) 10; *J.S.D.C.*, **98** (1982) 165.
96. J S Church *et al.*, *Rev. Prog. Coloration*, **29** (1999) 85.
97. D M Lewis and S M Smith, Proc. 8th Internat. Wool Text. Res. Conf., Christchurch, Vol. 4 (1990) 177; *J.S.D.C.*, **107** (1991) 357.
98. K Hannemann, *J.S.D.C.*, **108** (1992) 202.
99. D M Lewis, *Rev. Prog. Coloration*, **28** (1998) 12.
100. W Mosimann, *Text. Chem. Colorist*, **1** (1969) 27.
101. D Mäusezahl, *Textilveredlung*, **5** (1970) 835; *Textil Praxis*, **26** (1971) 241.
102. A Buhler *et al.*, Proc. Internat. Wool Text. Res. Conf., Aachen, 5 (1975) 263.
103. G Leeson and R E Hester, *J.S.D.C.*, **106** (1990) 59.
104. J S Church *et al.*, *Dyes and Pigments*, **39** (1998) 291, 313.
105. K Hannemann and H Flensberg, *Melliand Textilber.*, **78** (1997) 160.
106. D Hildebrand and G Meier, *Textil Praxis*, **26** (1971) 499.
107. U Altenhofen, H Baumann and H Zahn, Proc. Internat. Wool Text. Res. Conf., Aachen, **5** (1975) 529.
108. K H Staubach, *Australian Text.*, **19** (1998) 28.
109. F Osterloh, *Textil Praxis*, **26** (1971) 164.
110. I Steenken *et al.*, *Textil Praxis*, **39** (1984) 1146.
111. P F Rouette, *Textil Praxis*, **27** (1972) 722.
112. D M Lewis, *J.S.D.C.*, **106** (1990) 270.
113. J L Burtness and B M Gatewood, AATCC Internat. Conf. & Exhib. (Oct 1995) 324.
114. W Zuwang, *Rev. Prog. Coloration*, **28** (1998) 32.
115. M L Gulrajani, *Rev. Prog. Coloration*, **23** (1993) 51.
116. P G H Bakker and A Johnson, *J.S.D.C.*, **89** (1973) 203.
117. B Vogt, U Altenhofen and H Zahn, *Textilveredlung*, **20** (1985) 90.
118. U Meyer *et al.*, *J.S.D.C.*, **102** (1986) 6.
119. S Zhang, J Li and J Yang, *J.S.D.C.*, **111** (1995) 195.
120. H U von der Eltz, *Melliand Textilber.*, **52** (1971) 687.
121. B R Venugopal, *Colourage*, **38**, No 6 (1991) 38.
122. D M Lewis and J Z Shao, *J.S.D.C.*, **111** (1995) 146.
123. A Liddiard, *J.S.D.C.*, **98** (1982) 359.
124. D Agarwal, K Sen and M L Gulrajani, *J.S.D.C.*, **112** (1996) 10, 321.
125. J B Caldwell, S J Leach and B Milligan, *Text. Res. J.*, **36** (1966) 1091.
126. W Mosimann and H Flensberg, Proc. Internat. Wool Text. Res. Conf., Tokyo, **5** (1985) 39.
127. P Ball, U Meyer and H Zollinger, *Text. Research J.*, **56** (1986) 447.
128. D M Lewis and W C MacDougall, *Text. Chem. Colorist*, **30** (May 1998) 31.
129. H Zollinger, *J.S.D.C.*, **110** (1994) 209.
130. D M Lewis, *J.S.D.C.*, **113** (1997) 193.

131. I D Rattee, *J.S.D.C.*, **78** (1962) 69.
132. H R McCleary *et al.*, *Amer. Dyestuff Rep.*, **56** (Jan 1967) 46.
133. G Lützel, *J.S.D.C.*, **82** (1966) 293.
134. U Baumgarte, *Melliand Textilber.*, **49** (1968) 1432.
135. M Kamel, B M Youssef and M M Kamel, *Dyes and Pigments*, **16** (1991) 57; *Textil Praxis*, **46** (1991) 1324.
136. B M Youssef, M M Kamel and M Kamel, *Dyes and Pigments*, **19** (1992) 223.
137. M M Kamel and M Kamel, *J.S.D.C.*, **108** (1992) 450.
138. D M Lewis and X P Lei, IFATCC Cong., Lucerne (June 1990) lecture; *J.S.D.C.*, **107** (1991) 102.
139. D M Lewis and K N Tapley, AATCC Internat. Conf. & Exhib. (Oct 1997) 77.
140. D M Lewis and J Yao, AATCC Internat. Conf. & Exhib. (Oct 1998) 375; *Adv. Col. Sci. Tech.*, **1** (1999) 93.
141. D M Lewis and X P Lei, AATCC Internat. Conf. & Exhib. (Oct 1992) 259.
142. D M Lewis, B Parton and K N Tapley, Internat. Conf. on Chem. and Applic. of Reactive Dyes, Harrogate (1992) poster.
143. X P Lei *et al.*, *Dyes and Pigments*, **30** (1996) 271.
144. B M Smith *et al.*, *Dyes and Pigments*, **28** (1995) 101.
145. D M Lewis and Y C Ho, AATCC Internat. Conf. & Exhib. (Oct 1994) 419; *Dyes Pigments*, **28** (1995) 171.
146. D M Lewis and Y C Ho, *Dyes and Pigments*, **28** (1995) 237.
147. D M Lewis and Y C Ho, *Dyes and Pigments*, **30** (1996) 301; **31** (1996) 111.
148. D M Lewis, Y N Wang and X P Lei, *J.S.D.C.*, **111** (1995) 12.
149. X P Lei, D M Lewis and Y N Wang, *J.S.D.C.*, **111** (1995) 385.
150. D M Lewis, X P Lei and Y N Wang, *J.S.D.C.*, **108** (1992) 383.