CHAPTER 11

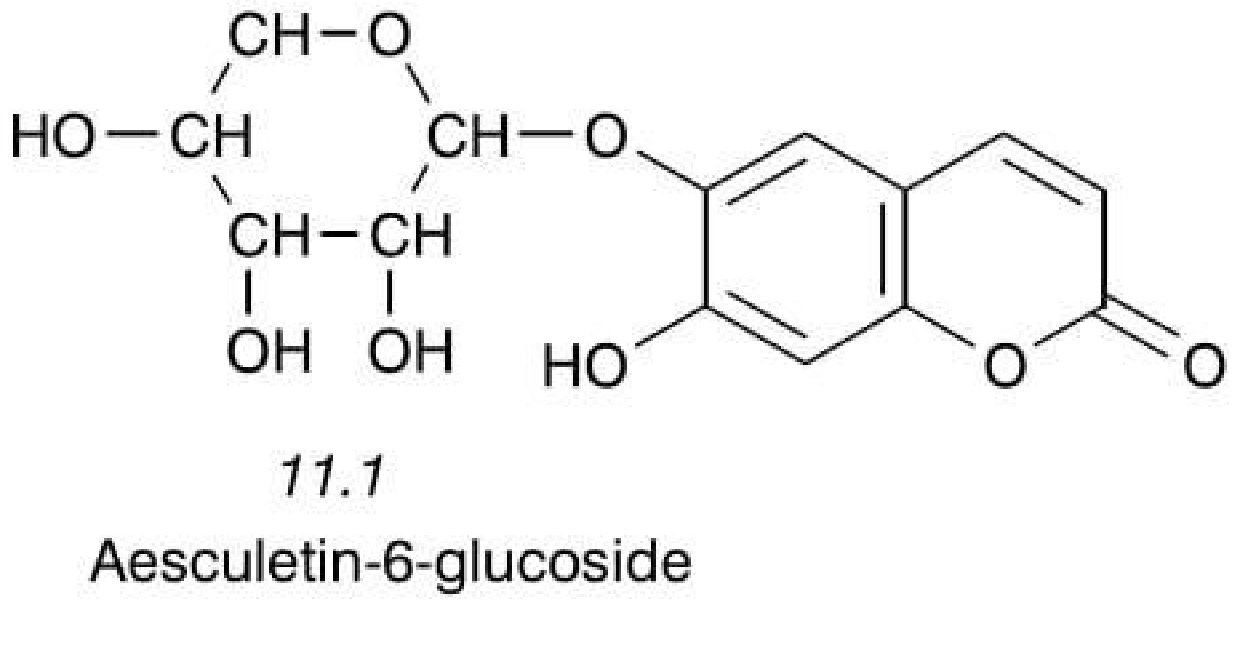
Fluorescent brightening agents

John Shore

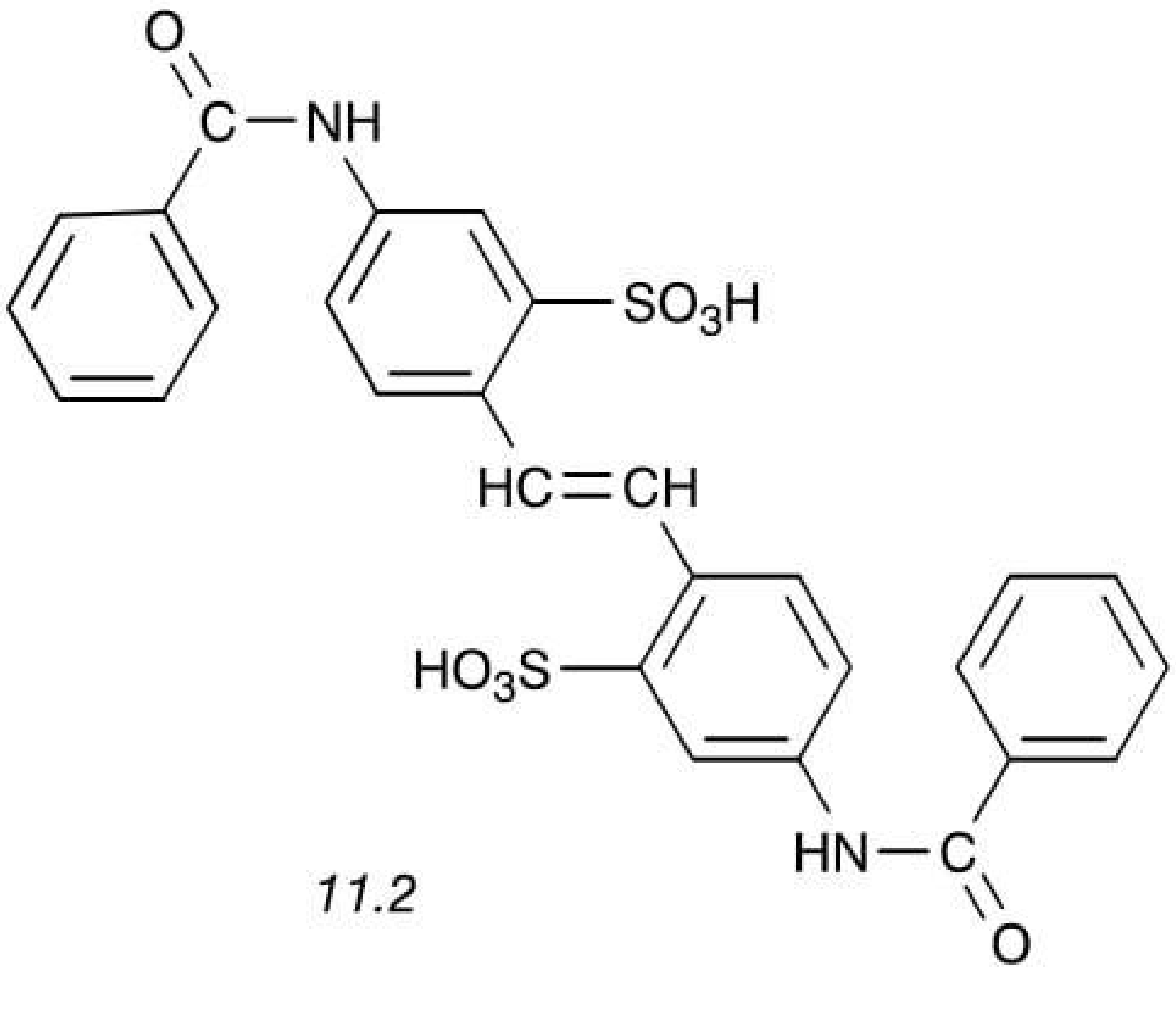
11.1 INTRODUCTION

Partly from an association of whiteness with cleanliness and partly for aesthetic reasons to achieve a more pleasing contrast with coloured goods, from the earliest times people have searched for methods of producing ever whiter textiles. The oxidative bleaching of vegetable fibres on exposure to air and sunlight, as well as the reductive bleaching of animal fibres by the action of fumes from burning sulphur, have been known for thousands of years. Natural blue minerals such as lapis lazuli (section 2.10.2), ground up and applied at very low concentrations, have been used for centuries to mask any residual yellowish colour remaining after bleaching, the overall greyish effect being perceived as 'white'. Today whiteness is achieved by a combination of chemical bleaching and the use of so-called fluorescent brightening agents (FBAs).

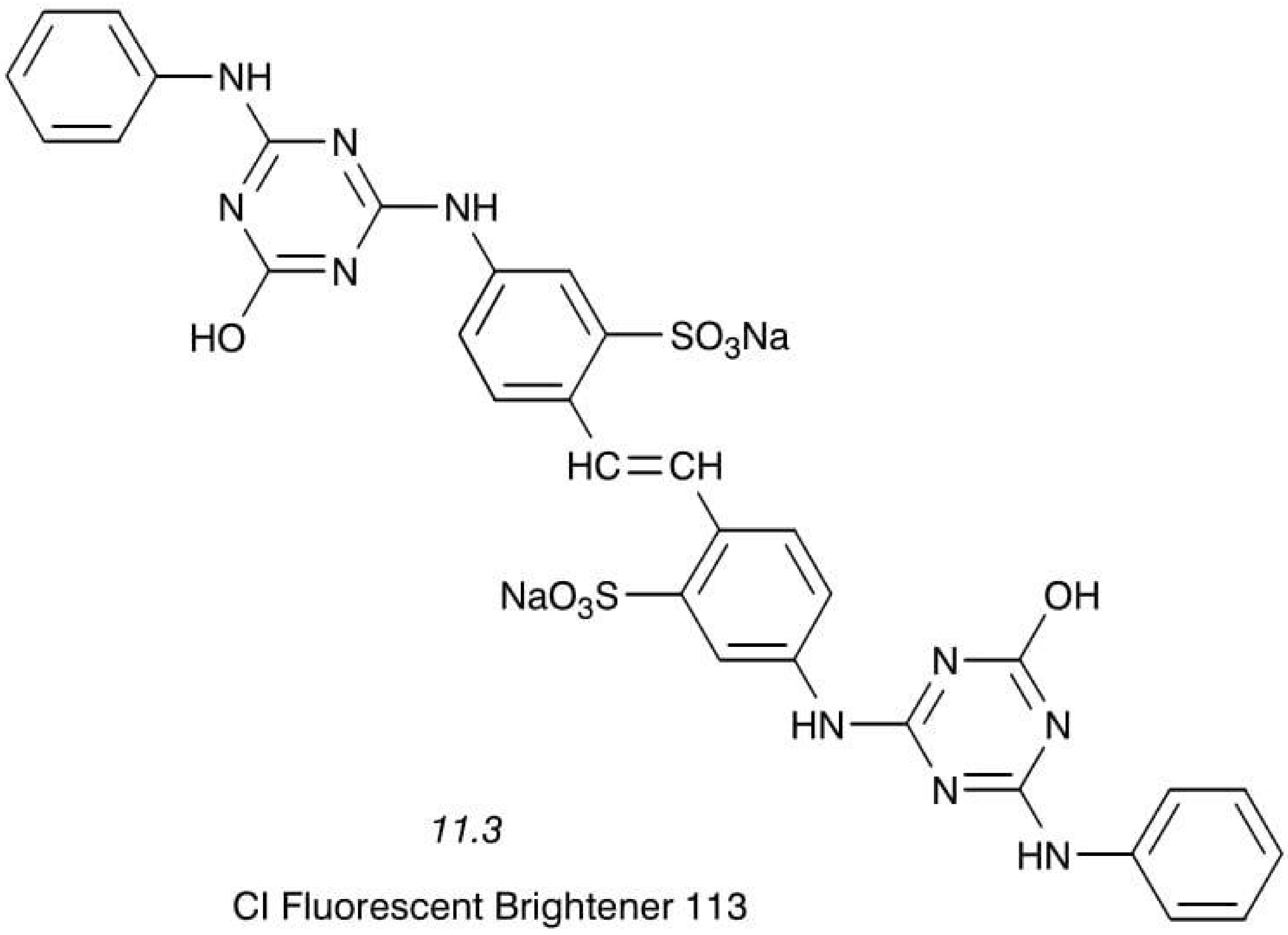
Fluorescent hydroxy-substituted derivatives of coumarin (benzo-α-pyrone) occur naturally, including aesculetin (6,7-dihydroxy) in horse chestnut, daphnetin (7,8-dihydroxy) in daphne and umbelliferone (7-hydroxy) in spurge laurel. Paul Krais in 1929, in the first recorded application of an FBA to textiles, carried out tests on half-bleached linen using an aqueous extract of aesculetin-6-glucoside (11.1) from horse chestnut bark [1]. The addition of blue-violet light to the total light reflected from the fabric produced a 'whiter than white' effect. Unfortunately, aesculetin showed poor fastness to light and washing. Nevertheless, Krais's work stimulated research in this area and in 1934 Paine and Radley patented the use of 4,4′-bis(benzoylamino)stilbene-2,2′-disulphonic acid (11.2) in banknotes [2]. The first commercial bis(triazinylamino)stilbene derivative (11.3) was introduced by I G Farben in 1940 as a brightener for cotton.



11.1
Aesculetin-6-glucoside



11.2



11.3

CI Fluorescent Brightener 113

After the Second World War, development of synthetic FBAs was extremely rapid. Several hundred commercial products, representing a wide variety of chemical types, have since been marketed, with FBAs probably corresponding to approximately 10% of world demand for dyestuffs. Several excellent books and reviews of the chemistry, application and properties of FBAs have appeared [3–13].

FBAs are used to brighten not only textile materials but also paper, leather and plastics. They are important constituents of household detergent formulations. More specialised areas of application include lasers, liquid crystals and biological stains. By far the most important uses for FBAs, however, are in applications to textiles and paper. Much of what follows will be concerned with these two categories.

Descriptive terms such as ‘fluorescent whitening agents’, ‘optical brighteners’ and ‘optical bleaches’ have all been used for the products described in this chapter as FBAs. Many of these terms have validity and the term ‘fluorescent brightening agents’ is preferred here only because it has been adopted in the indexes of *Chemical Abstracts*.

An FBA is a strongly fluorescent substance that absorbs ultraviolet radiation, emits light in the blue-violet region of the visible spectrum and is substantive to the substrate for which it is intended. The product should be applicable without undesirable side-effects, such as staining or subsequent photosensitisation of degradation, on any other substrate that may be present. The treated material should retain its properties during its working life and under the conditions in which it will be found. For commercial success the product will also need to be priced attractively and supplied to the customer in a form that is convenient and practical to use. The marketed product and the active brightener that it contains must not exhibit toxicity problems nor create an environmental hazard.

11.2 MODE OF ACTION OF A FLUORESCENT BRIGHTENER

All dyes absorb light. Fluorescent dyes re-emit the absorbed energy as light of longer wavelengths. An FBA is a fluorescent chemical that absorbs in the ultraviolet region of the spectrum and emits blue-violet light. A typical FBA shows maximum absorption at a wavelength between 340 and 380 nm and emits visible light at a maximum emission between 425 and 450 nm. When describing a substrate treated with an FBA, the terms ‘remitted’, (reflected plus emitted) and ‘remission’ (reflectance plus emission), which take into account the fluorescence component of the total light emitted from the brightened substrate, are preferred to ‘reflected’ and ‘reflectance’.

When present on a substrate an effective FBA increases the apparent reflectance of the article in the blue-violet region of the spectrum. The treated material remits more light in the visible region than does an untreated white sample and thus appears ‘whiter than white’. These effects are indicated in Figure 11.1, which illustrates the importance of thorough preparation of the substrate to be brightened. Curve C represents the remission of an unbleached ‘dirty’ fabric. On treatment with an FBA this material is brightened but the treated sample (curve D) may be less bright than a clean but unbrightened fabric (curve A) and much less bright than the same fabric after brightening (curve B). The details of fabric preparation and bleaching processes are discussed fully elsewhere [14]. In some cases brightening and bleaching can be carried out simultaneously and these possibilities will be discussed later in this chapter.

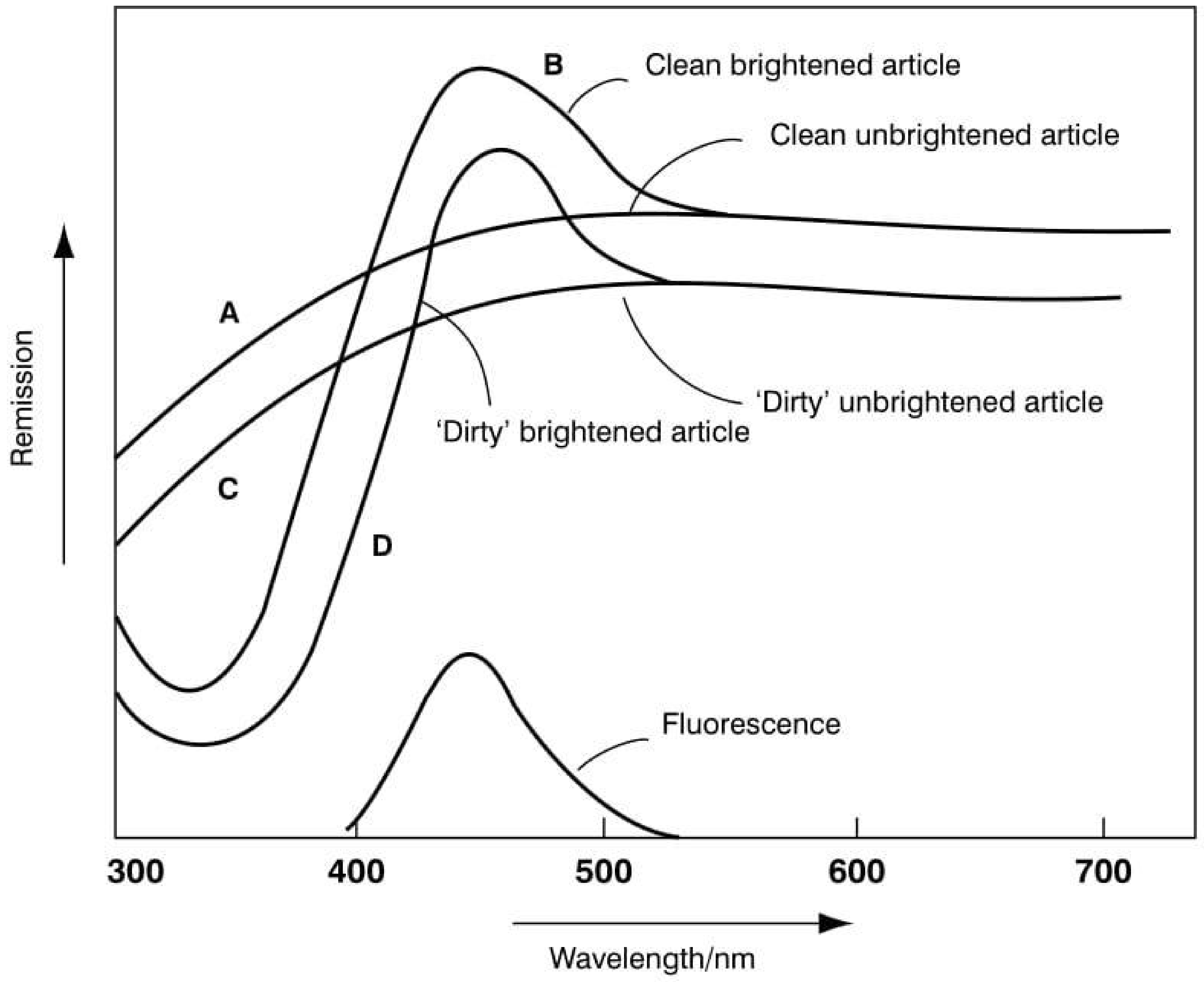


Figure 11.1 Remission of brightened and unbrightened fabric

An efficient FBA must absorb strongly in the ultraviolet region and must also re-emit a major proportion of the absorbed energy as visible light, that is, it must have a high fluorescence efficiency. Although fluorescence can occur from the α-bonds of many organic compounds, strong fluorescence is associated with π-bonded electrons. All FBAs therefore contain a considerable number of conjugated double bonds.

Processes occurring during absorption and fluorescence are shown in Figure 11.2, where

S_0, S_1, S_2, … represent so-called singlet states in which all the electrons have paired spins, and T_1, T_2, … represent triplet states in which two electrons have unpaired spins. The energy levels of both ground (S_0) and activated states (S_1, S_2, …) are subdivided into vibrational and rotational energy levels. The vibrational energy levels are shown in Figure 11.2. Differences in rotational levels are very small and can be ignored for the present discussion.

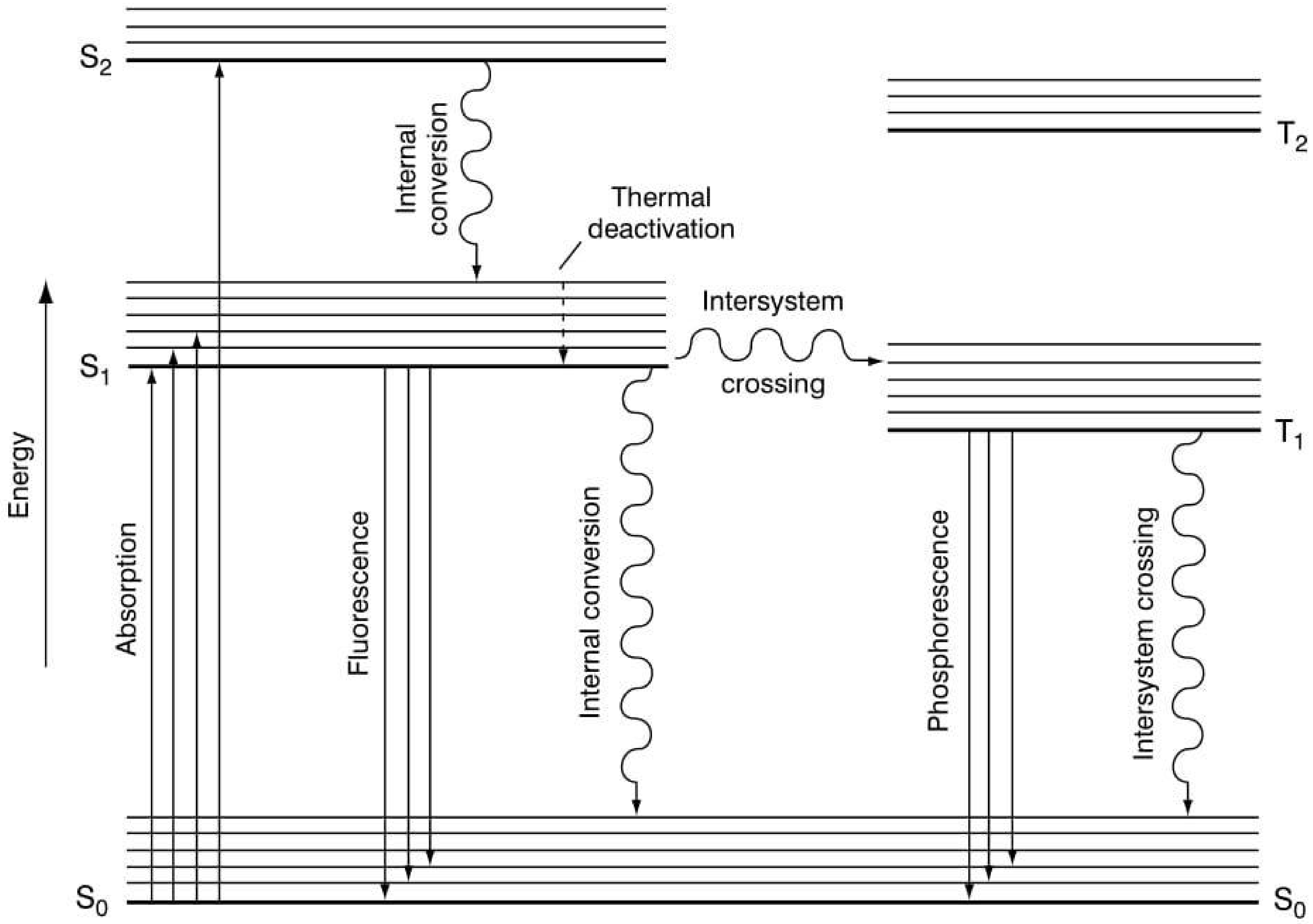


Figure 11.2 Absorption and fluorescence processes

When an FBA absorbs a photon of light an electron is raised from the ground state (S_0) of the molecule to one of its activated singlet states (S_1, S_2, …). Transitions from a singlet to a triplet state are quantum-mechanically 'forbidden'. Absorption occurs when the molecule is in its ground state, the vibrational level of the activated state reached by absorption being decided by the size of the quantum of energy (E) involved ($E = hc/\lambda$, where h is Planck's constant, c the velocity of light in a vacuum and λ the wavelength). Vibrational energy levels are extremely close to each other and vibrational energy is lost very rapidly (within about 10^{-12} s) before fluorescence occurs, when the molecule returns from the lowest vibrational level of the activated state (S_1) to one of the vibrational levels of the ground state (S_0) whilst simultaneously emitting a photon of light. Fluorescence lifetime is typically about 10^{-9} s. Energy can also be lost from the activated singlet state by non-radiative processes (internal conversion) or by 'forbidden' intersystem crossing to give the triplet state. The triplet state in turn can lose energy, returning to the ground state by phosphorescence or by a further radiationless intersystem crossing. Phosphorescence always occurs at a longer wavelength than fluorescence because the energy difference between T_1 and S_0 is less than that between S_1 and S_0. FBAs do not exhibit significant phosphorescence. For a more detailed discussion of the principles of fluorescence the reader is referred to books by Lumb [15] and Lakowicz [16].

Typical absorption and fluorescence spectra are shown in Figure 11.3. Since energy is lost in the activated state (S_1) before fluorescence, the emission maximum always occurs at a lower wavenumber than the absorption maximum. The difference, which is termed the Stokes shift, can be calculated approximately from the absorption spectrum using the Pestemer rule [17,18]. This rule states that the Stokes shift is 2.5 times the half-bandwidth at the absorption maximum.

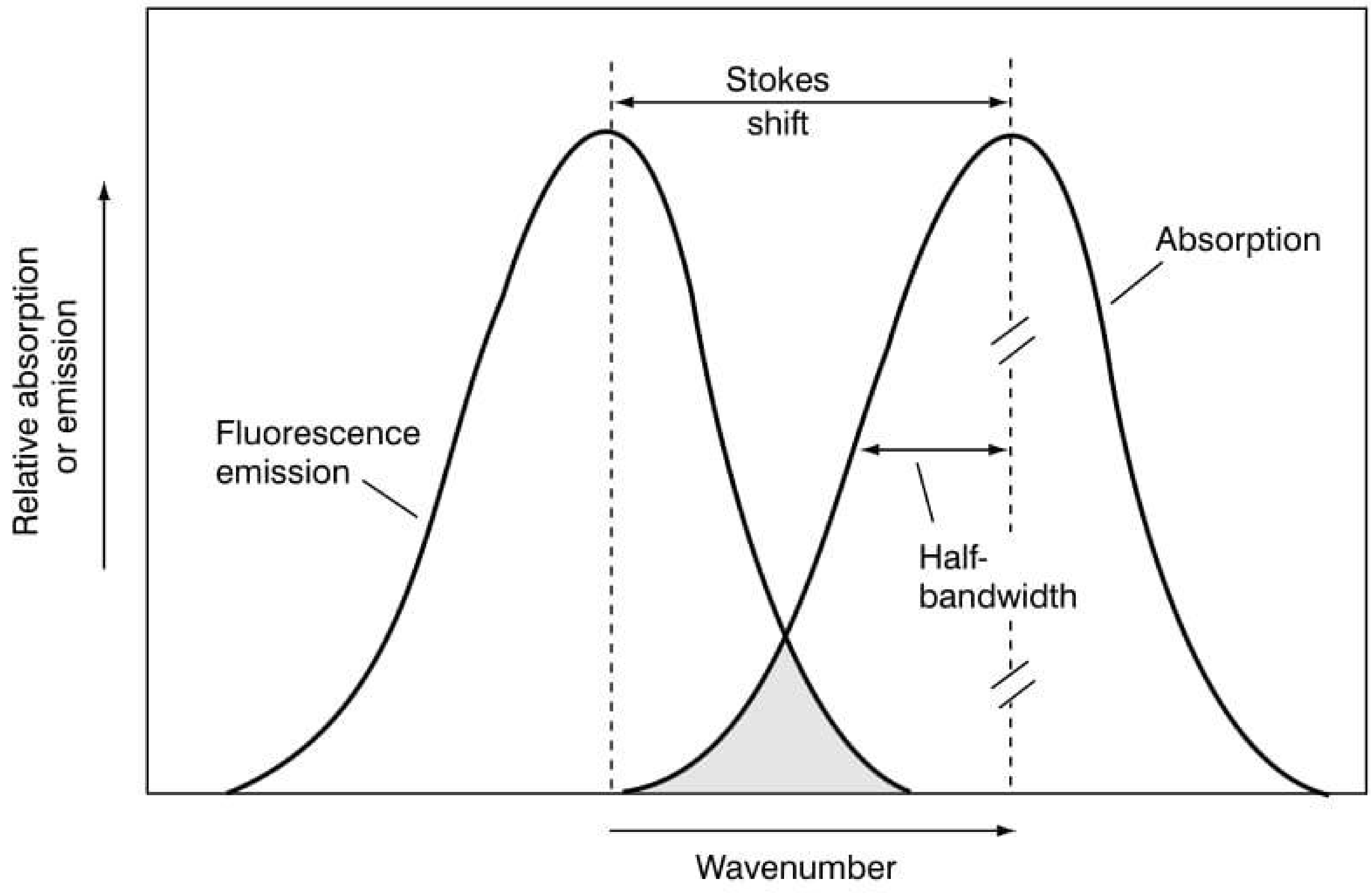


Figure 11.3 Typical absorption and emission curves for an FBA (polar solvent)

For the following reasons the Stokes shift of an FBA should not be too large:

(1) The closer the maximum wavelength of light absorption of an FBA approaches the visible region, the greater is the energy content of sunlight at the earth's surface that is available for fluorescence excitation and the greater the potential fluorescence. An FBA with a Stokes shift of 60 nm or less would have a maximum absorption at 370 nm or longer and it would still show maximum fluorescence in the blue region of the spectrum.

(2) Although absorption and fluorescence spectra are not always (or even normally) symmetrical, a smaller Stokes shift reduces the chance of significant fluorescence in the green or yellowish green regions of the spectrum. Green or yellowish green fluorescence reduces whiteness.

A possible method for predicting absorption bandwidths of chromogenic molecules or FBAs using PPP–MO theory (section 1.5) has been devised. It is based on the empirical linear relationship stated by the Pestemer rule. Thus theoretical Stokes shifts are computed by the PPP–MO method and related to bandwidths. The requisite MO parameters for various typical absorption bands have been developed for use in these calculations. Reasonable correlation between calculated and experimental half-bandwidth data was found, suggesting that this approach has practical potential in predicting colour tone and brightness intensity [19].

The quantum efficiency of fluorescence of a molecule is decided by the relative rates of fluorescence, internal conversion and intersystem crossing to the triplet state. Up to the present time it has proved impossible to predict these relative rates. Thus, whilst it is now possible to calculate theoretically the wavelengths of maximum absorption and of maximum fluorescence of an organic molecule, it remains impossible to predict which molecular structures will be strong fluorescers. Design of new FBAs still relies on semi-empirical knowledge plus the instinct of the research chemist.

11.3 EVALUATION OF FBAs: MEASUREMENT OF WHITENESS

Almost all man-made fibres destined for sale as white goods are producer-brightened by the manufacturer and white textiles are almost always laundered using detergents containing cellulose-substantive FBAs [20]. To evaluate an FBA it is necessary both to apply the product to the desired substrate and to measure the whiteness of the treated material. Measurement of the fluorescence intensity of the FBA-treated substrate provides useful additional, although different, information.

Visual judgement of whiteness is highly subjective. Many factors, such as the observer's age, sex and colour perception, and even the hue of 'white' materials normally encountered in the observer's country, help to decide on individual preference for either a red-violet or a blue-green shade of white.

Instrumental measurement of whiteness has been the subject of much research. The parameters needed for unambiguous characterisation in the assessment of whiteness and tint of fluorescent substrates have been reviewed [21]. The importance of seeking good correlation between different instruments is stressed [20]. Various trials have demonstrated that it is possible to adjust modern instruments used to measure the optical characteristics of FBA-treated samples of paper so that the results agree with a standard deviation of the order of one CIE whiteness unit [22].

Many whiteness (W) formulae have been proposed. All are based on CIE colour space and the X,Y,Z tristimulus values. Three of these equations are those of Berger [23] (Equation 11.1), Stensby [24] (Equation 11.2) and the CIE 1982 formula (Equation 11.3).

$$W = 3B + G - 3R \tag{11.1}$$

$$W = L + 3a - 3b \tag{11.2}$$

$$W = Y + 800(x_n - x) + 1700(y_n - y) \tag{11.3}$$

The R,G,B values of the Berger formula measured by tristimulus colorimeters are linearly related to the X,Y,Z tristimulus values of the CIE system. The Stensby formula incorporates the L,a,b tristimulus values of the Hunter system. In the CIE 1982 formula, x_n and y_n are the chromaticity coordinates of the D_{65} (2° or 10° observer) light source.

Information on the hue of whiteness is provided by dividing CIE colour space, in the neighbourhood of the D_{65} achromatic point, into a series of parallel strips corresponding to variations in hue of whiteness. The principle is illustrated in Figure 11.4. According to this system, a neutral white has a nuance (NU) value of zero. Greener shades have values between 0 and +5, whereas violet shades have values between 0 and –5. The NU value can be calculated from chromaticity data. Typical values giving a result corresponding to the judgement of a standard observer are shown in Equation 11.4.

$$NU = -1132x + 725y + 115.45 \tag{11.4}$$

The brightened specimen under test must be carefully prepared and meticulous attention to the instrumentation and state of equipment is necessary if reliable data are to be obtained. The subject is complex and has been well reviewed by Griesser and co-workers [25,26].

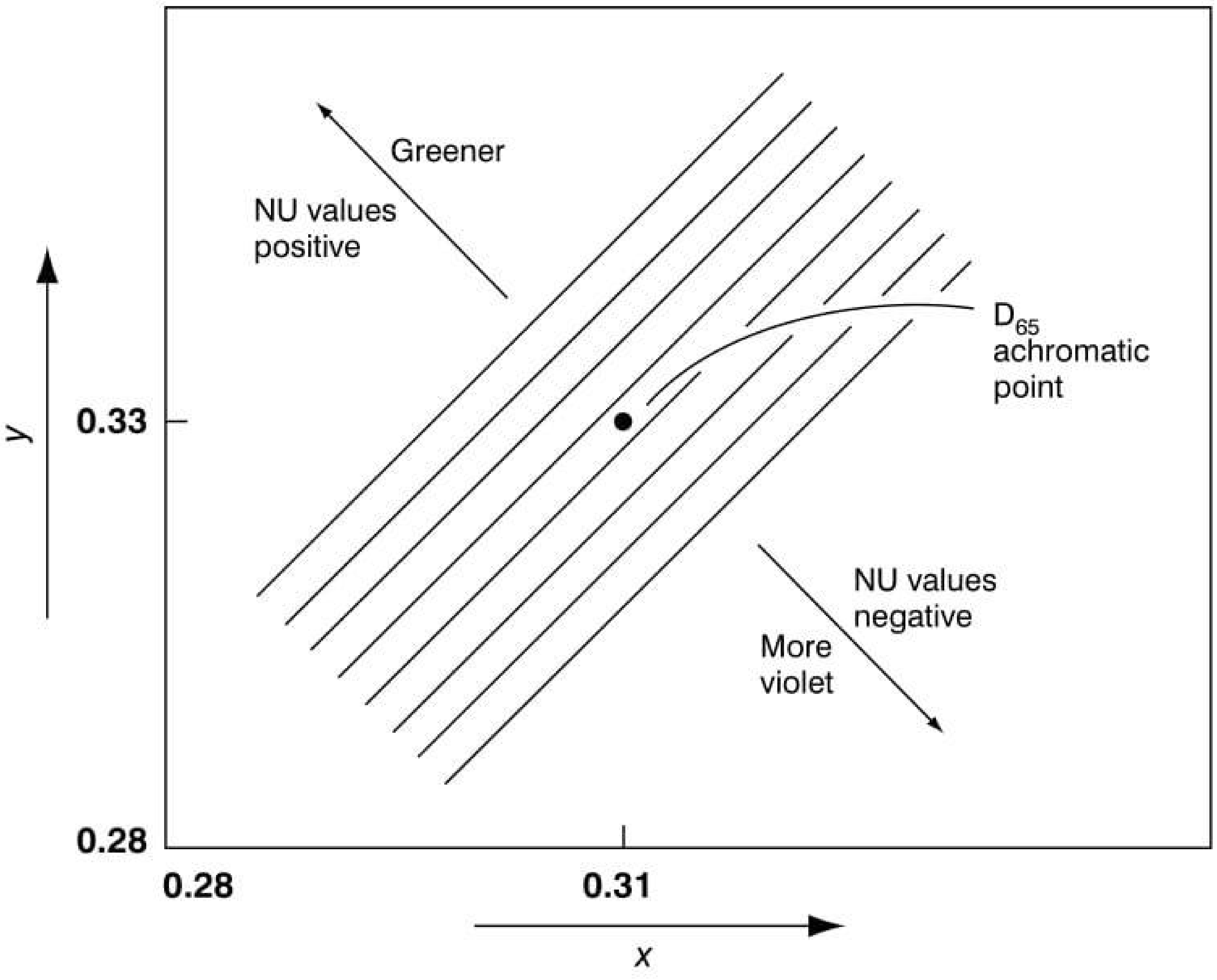


Figure 11.4 Colour space and hue of whiteness

To an average observer a sample of white material brightened with a low concentration of an FBA will exhibit a bluish tone corresponding to a dominant wavelength in the vicinity of 467 nm. As the amount of FBA present in the substrate is increased this hue changes. At first the sample may become slightly more violet but as the maximum possible whiteness is approached there is a distinct change in hue towards green until the sample becomes overloaded with FBA, whiteness falls and the material is perceived as coloured rather than white. Typical effects are illustrated in Figure 11.5.

In industry a direct comparison for strength between two FBAs is frequently required. Where both brighteners contain the same active component, or where they give a closely similar shade of white, such a comparison presents little difficulty. Where the two products yield quite different shades of white, however, comparisons between them are usually meaningless. A typical situation is illustrated in Figure 11.6.

At concentrations below that yielding the maximum whiteness achievable there is an approximately linear relationship between whiteness and the logarithm of the concentration

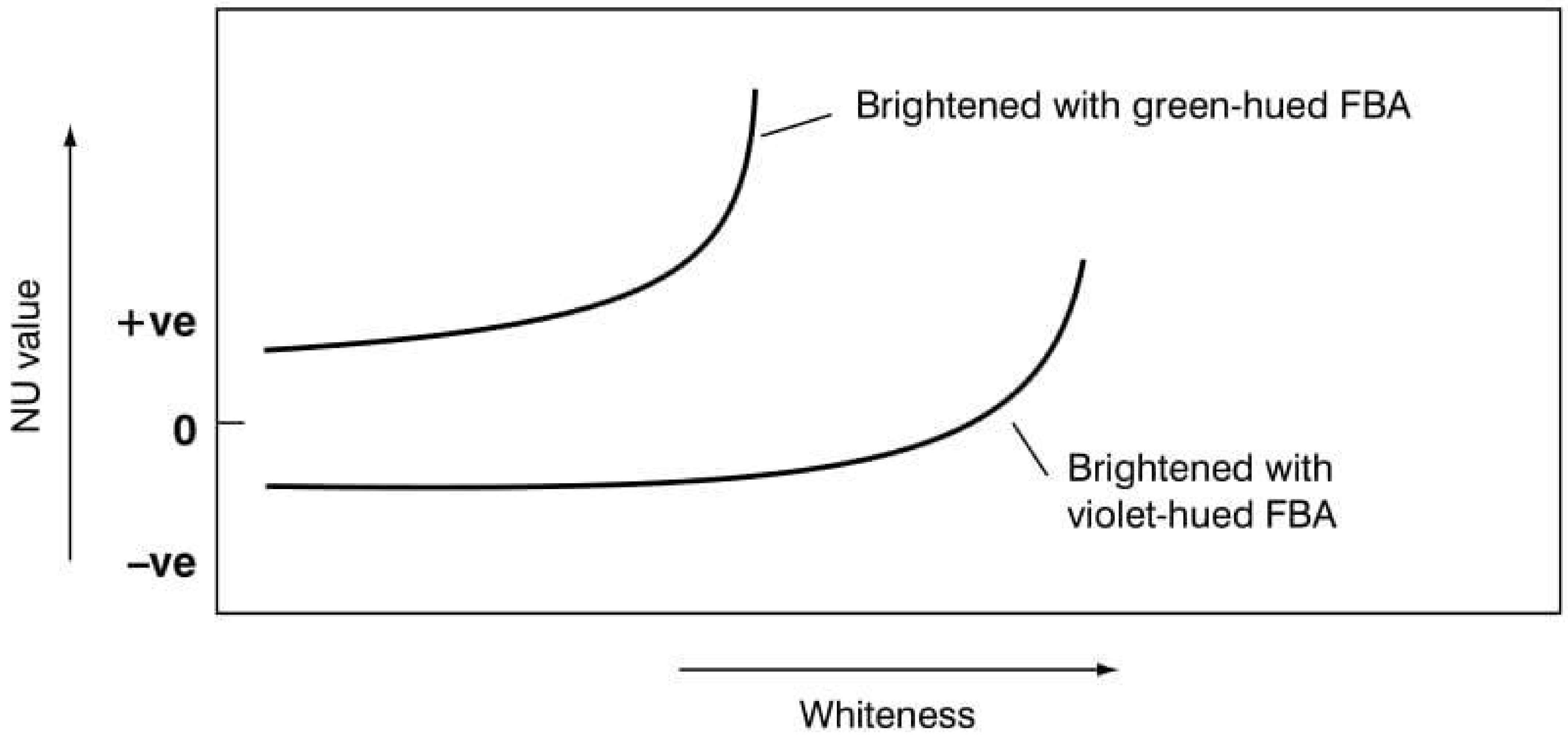


Figure 11.5 Variation of hue with whiteness

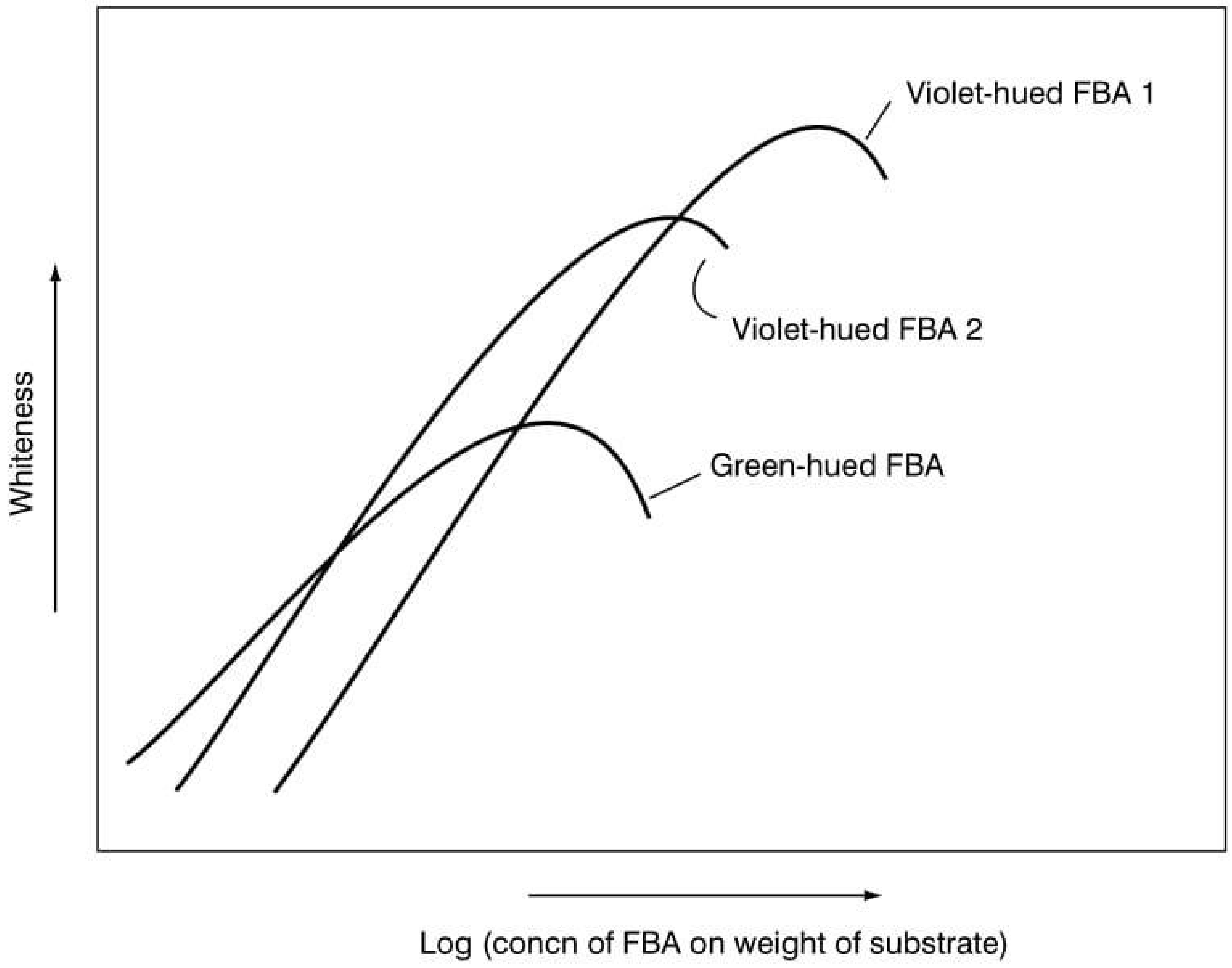


Figure 11.6 Dependence of whiteness on concentration

of FBA present on the substrate. If two FBAs are similar in hue the straight line portions of the graph are almost parallel and a single-strength relationship can readily be calculated. If two FBAs differ in hue, however, their relative effectiveness changes with the degree of whiteness, products that give greener hues generally being more effective at low concentrations.

Methods for the instrumental measurement of whiteness are well established but visual comparison remains important, even in well-equipped laboratories. Some degree of quantification is achieved by the method of paired comparisons, in which a panel of observers is presented with pairs of FBA-treated samples and asked to decide, without undue delay, which is the brighter. The total of positive scores can be used as a measure of whiteness and the results presented graphically as shown in Figure 11.7. Although time-consuming to carry out, a paired comparison series produces results that can be regarded with considerable confidence and that usually correlate well with a comparison based on the CIE whiteness formula.

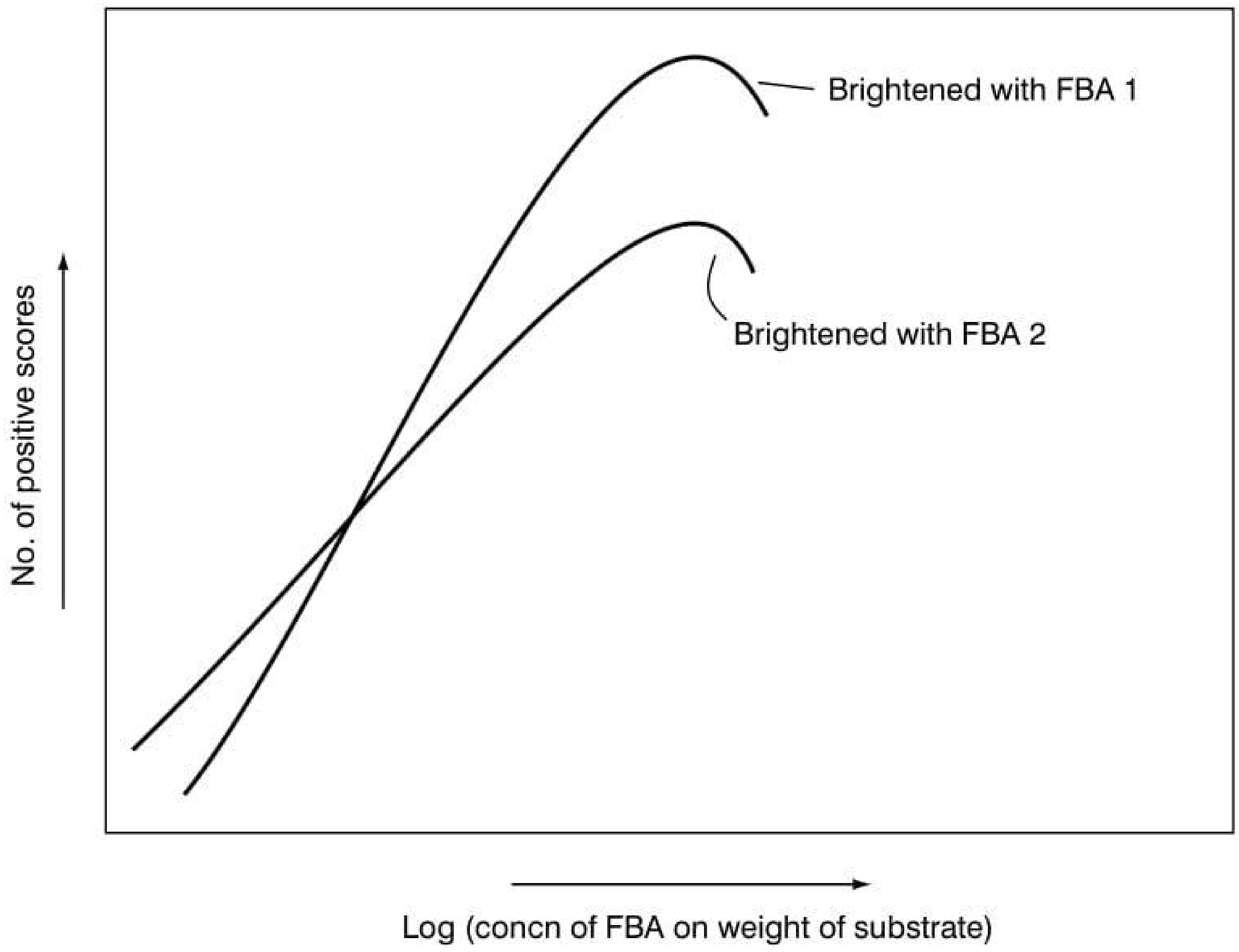


Figure 11.7 Presentation of results of a paired comparison

11.4 GENERAL FACTORS INFLUENCING FBA PERFORMANCE

Apart from needing to be cost-effective, a good FBA must be capable of producing a high level of whiteness. As the amount of FBA on a substrate is increased, whiteness increases until a maximum value is reached (Figure 11.6). Further application of FBA results in lower whiteness. On polyester the fall in whiteness with increasing concentration of FBA is apparently not accompanied by a fall in total fluorescence [27]. On cotton both whiteness and total fluorescence fall, the decrease in whiteness occurring before that in fluorescence [28]. In general the main cause of the fall in whiteness with increasing concentration of FBA is an increase in aggregation of the FBA on the substrate, resulting in a shift in fluorescence hue. The effect is shown in Figure 11.8. Not surprisingly, FBAs that give a greenish hue at concentrations below the maximum whiteness tend to produce a lower maximum white than those exhibiting a violet hue. Other factors such as substantivity are of considerable importance, of course. A computer-based expert system has been devised as an aid to selection of the most suitable FBAs for specific applications to various fibres using the processing equipment available in any given finishing works [29].

The presence of salts and additives can have an important influence on the performance of an FBA. Traces of transition-metal ions such as iron and copper have an adverse effect on fluorescence [30], but this can be controlled using conventional polyphosphate or EDTA-type sequestering agents [31]. Other salts, even sodium sulphate or sodium chloride, have been claimed to enhance the fluorescence of FBAs in solution [32]. Apart from the normal

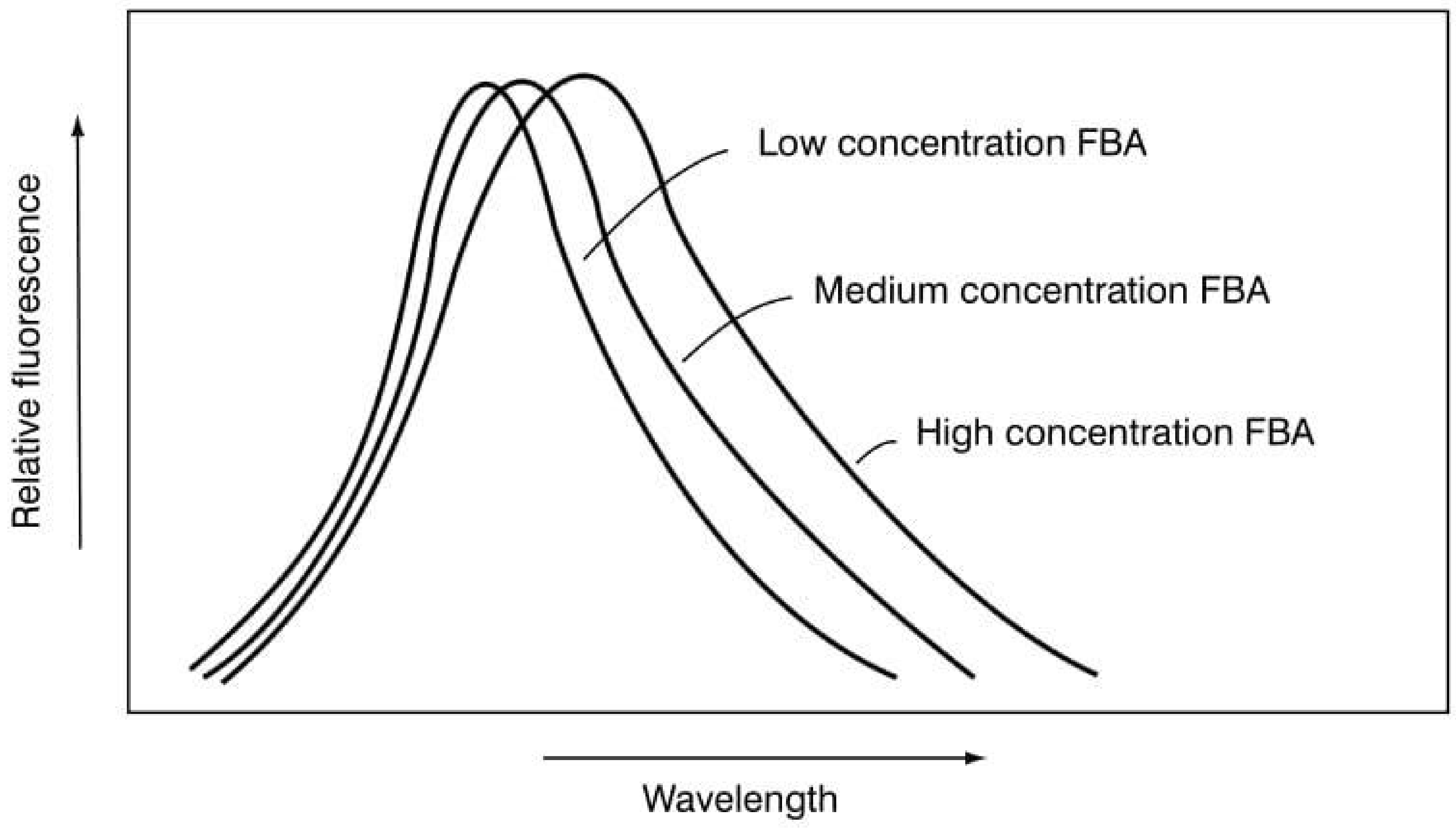


Figure 11.8 Effect of FBA concentration on fluorescence hue

effect of such electrolytes in minimising electrostatic repulsion between anionic FBAs and the negatively charged surface of cellulose, their influence on the whiteness of a brightened substrate is doubtful.

Surfactants, not surprisingly, exert a highly significant influence on the fluorescence of FBAs in solution. This effect is associated with the critical micelle concentration of the surfactant and may be regarded as a special type of solvent effect. Anionic surfactants have almost no influence on the performance of anionic FBAs on cotton, but nonionic surfactants may exert either positive or negative effects on the whiteness of the treated substrate [33]. Cationic surfactants would be expected to have a negative influence, but this is not always so [34]. No general rule can be formulated and each case has to be considered separately.

The influence of additives needs to be kept under constant consideration when formulating commercial brands of FBAs. Liquid formulations are of considerable commercial importance and it is often necessary to use solvents such as diethylene glycol, poly(ethylene glycol) and alkoxylated alkylphenols in order to achieve stable solutions. Surfactants can help to stabilise FBA-resin bath combinations but in other circumstances they can adversely affect the performance of the formulation, not only in its capacity to brighten the substrate but also in the desired end-use of the brightened fabric. For example, nylon brightened by the pad–thermosol method using a liquid formulation containing a large amount of an alkoxylated polymer cannot be used as a substrate for colour printing unless previously washed. Without a wash-off, diffuse prints are obtained.

Violet or bluish violet dyes can be used in combination with FBAs for shading purposes. These shading dyes are used sparingly at no more than 2% of the weight of FBA applied. They are of particular importance when the material to be brightened is slightly yellow. The shading dye converts the pale yellow hue of the substrate to a perceived grey, enhancing the effectiveness of the FBA. These effects can be considerable. Many types of violet or bluish violet dye may be used. Typical examples include crystal violet (CI Basic Violet 3) used in the brightening of paper stock or cotton, CI Disperse Violet 28 and CI Acid Violet 43 applied with cotton brighteners. Disperse dyes are also selected for shading with disperse FBAs on polyester and with basic FBAs on acrylic fibres.

On slightly yellow cotton the addition of a shading dye is particularly convenient, since the substrate becomes bleached during the wash-wear cycle. Detergent formulations contain FBAs that are substantive to cotton and loss of shading dye during washing is unlikely to have a noticeable effect on the perceived whiteness of the article. Shading dyes are of limited use with thoroughly prepared and well-bleached cotton. The importance of the inherent degree of whiteness of cotton in determining its response to finishing processes has been emphasised. The effects of dry heat on peroxide-bleached cotton fabrics treated with brighteners that varied in substantivity were investigated. Remission spectroscopy was used to analyse the origins of thermal yellowing [35].

FBAs applied in combination may show a synergistic effect. Synergism is, at present, only of commercial interest with polyester brighteners. This phenomenon is discussed further in section 11.10. Conversely, the presence of a trace impurity in an FBA formulation may greatly reduce its effectiveness. In industrial laboratories much time and effort is expended in developing processes to minimise the content of such impurities or even to eliminate them completely.

11.5 CHEMISTRY AND APPLICATIONS OF FBAs

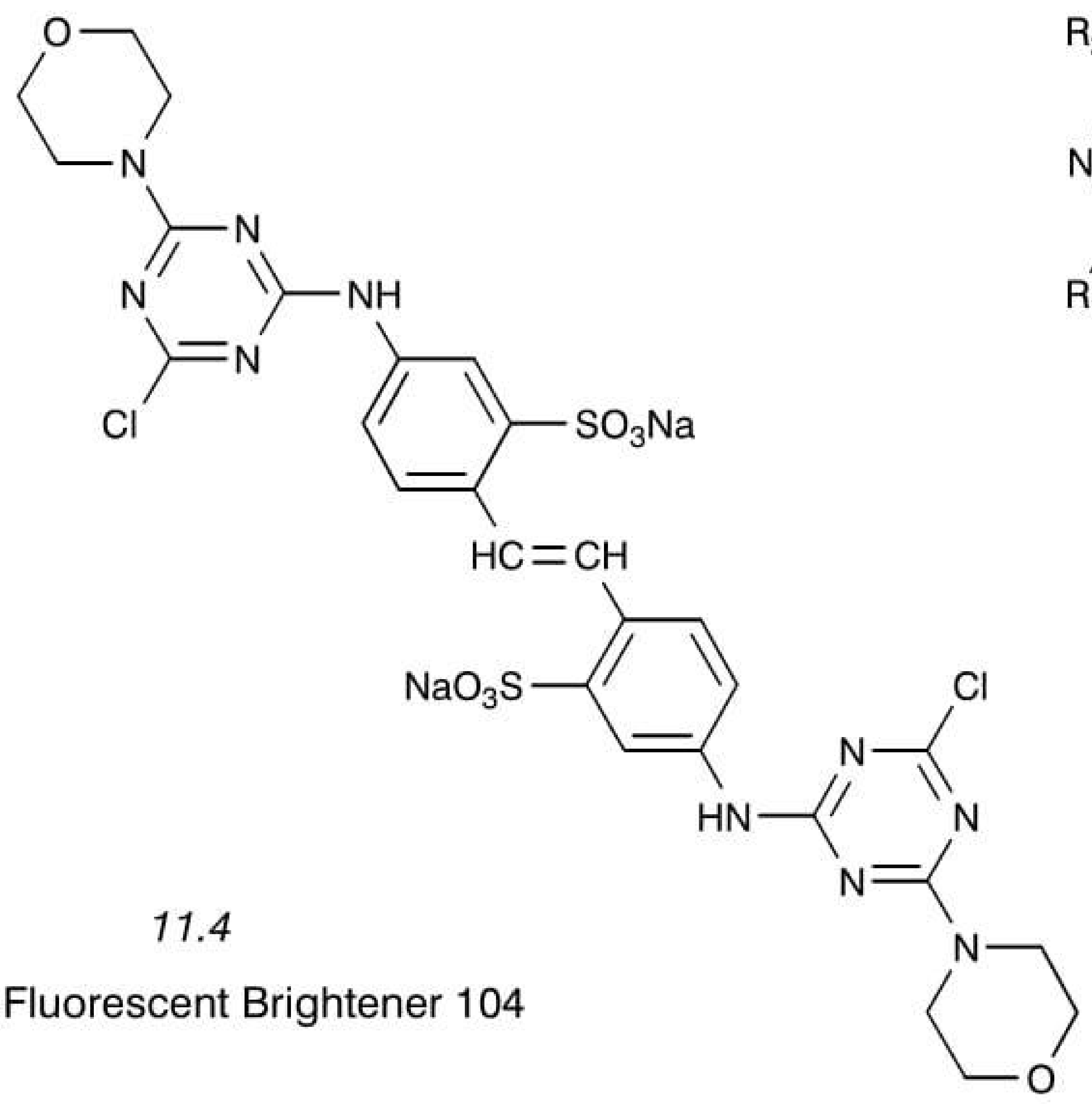
FBAs are available for application to all types of substrate. Thus there are anionic FBAs for application to cellulosic materials in the presence of added salts, anionic types for application to nylon or wool in the presence of acid, cationic types for acrylic fibres, disperse types for polyester, and so on. Brighteners such as CI Fluorescent Brightener 104 (11.4), capable in principle of being fixed to wool or cellulosic fibres by reaction with nucleophilic groups in the substrate have been reported but have never achieved commercial importance. Such FBAs in their reactive forms show diminished fluorescence because the presence of labile halogen atoms leads to quenching. Hydrolysis or reaction with the fibre is accompanied by development of fluorescence but an aftertreatment step is essential to ensure that all the active chloro substituents present have been removed from the FBA absorbed by the substrate [36]. The chemical structures of FBAs are many and varied although, of course, they all contain some sort of extended π-electron system. In the following discussion all the main chemical types are mentioned, but mainly in terms of application rather than chemistry of preparation.

11.6 BRIGHTENERS FOR CELLULOSIC SUBSTRATES

The earliest FBAs were developed for application to paper. Even today larger tonnages of brightener are marketed for application to cellulosics than to any other substrate.

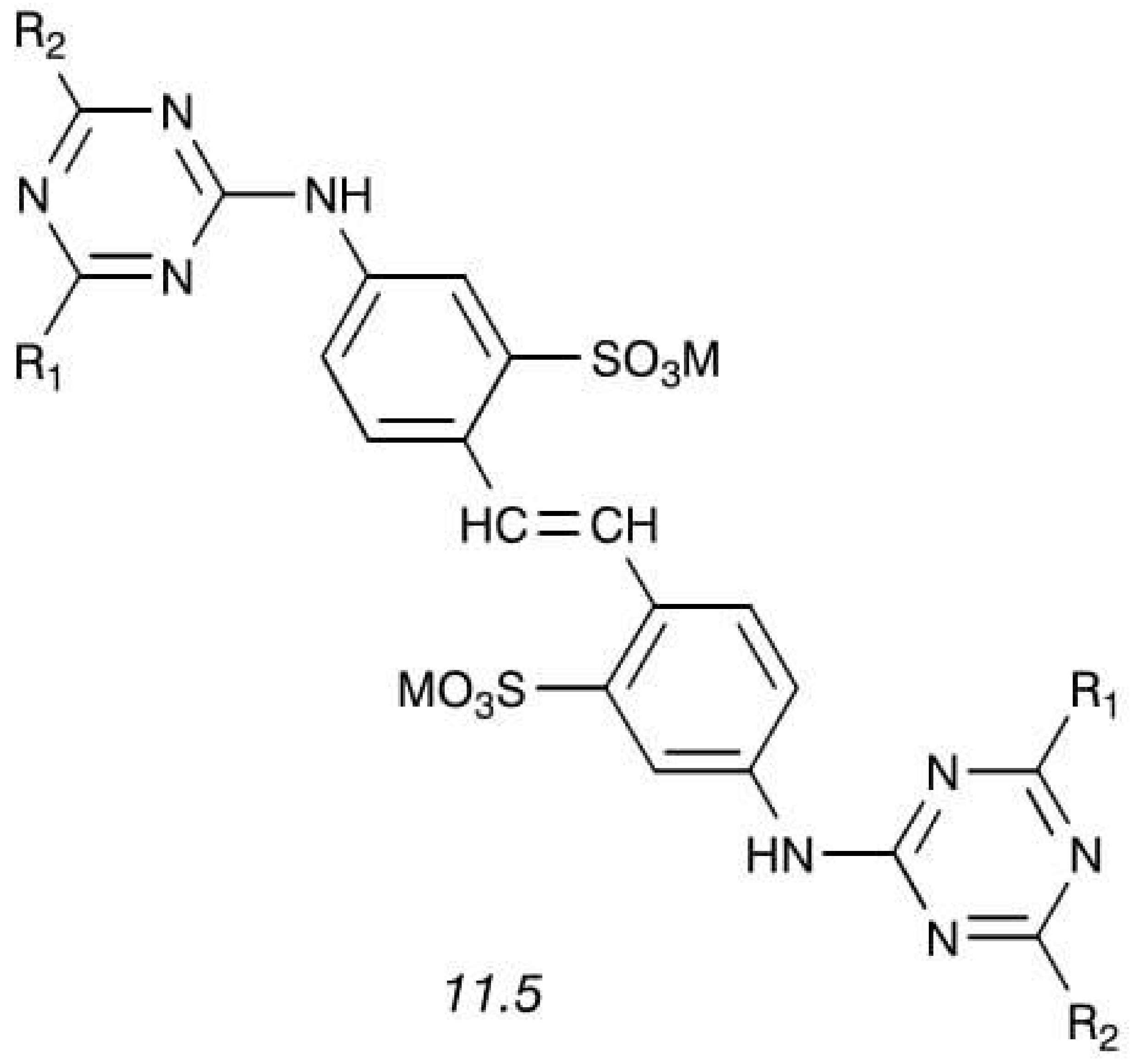
11.6.1 FBAs for cotton

Brighteners are applied to cotton by methods similar to direct dyes. By far the most common are triazinyl derivatives of diaminostilbenedisulphonic acid (DAS) of general formula 11.5, where M is an alkali metal, ammonium or alkylammonium cation. Examples of groups R_1 and R_2 are shown in Table 11.1. Most suppliers of FBAs market such compounds, often called DAST brighteners. Products in this class have sometimes been marketed because the supplier needed to offer something different for commercial reasons, or to avoid infringing a competitor's patent, rather than for any real technological necessity.



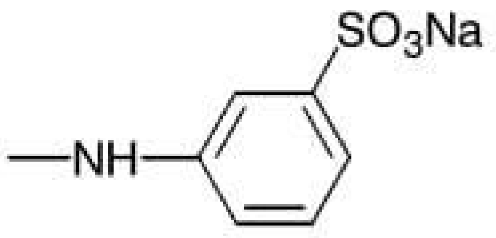
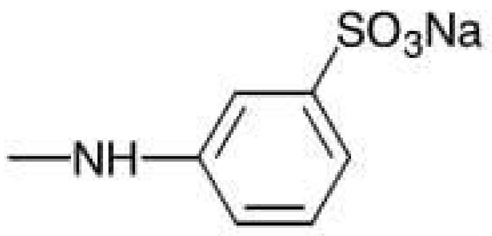
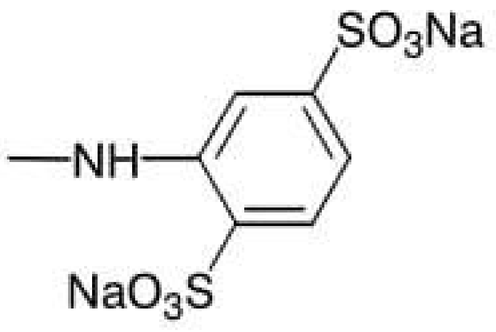
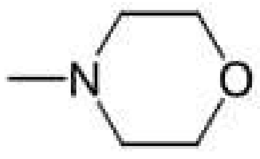
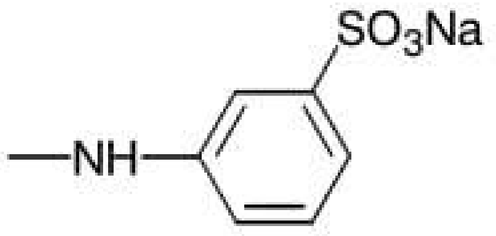
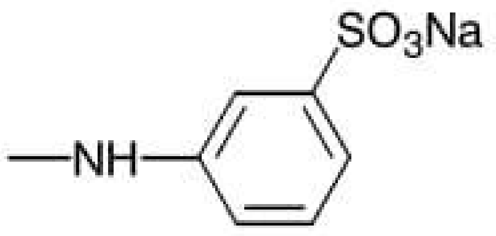
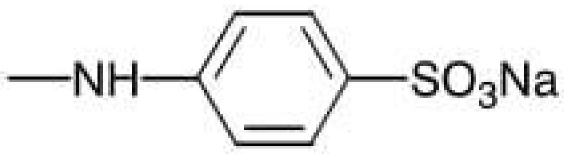
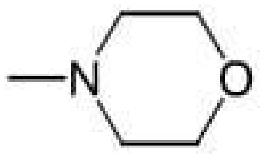
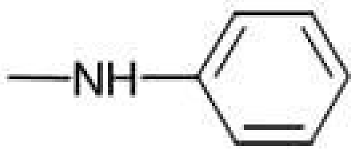
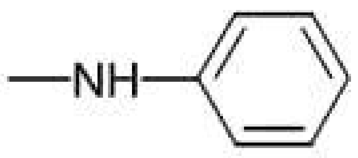
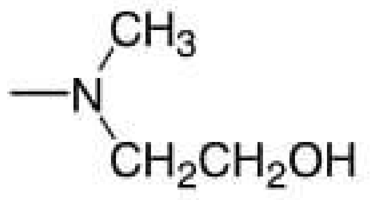
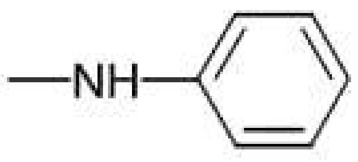
11.4

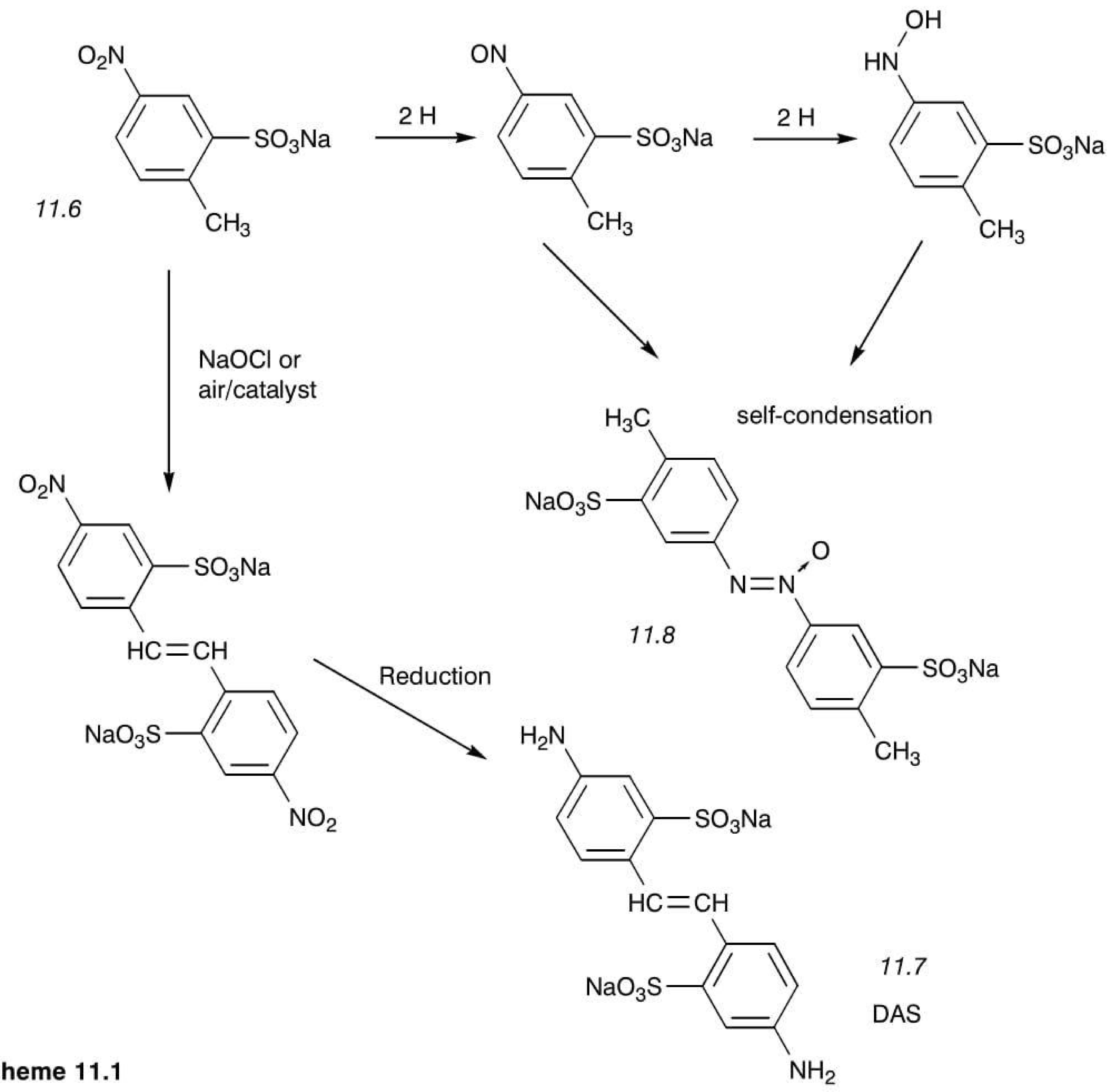
CI Fluorescent Brightener 104



11.5

Table 11.1 Important FBAs of type 11.5 used to brighten cotton

Substituents R_1 and R_2		Substantivity	Application
		Lower	Padding
			
	$-N(CH_2CH_2OH)_2$		
	$-NHCH_2CH_2OH$		
			
	$-N(CH_2CH_2OH)_2$		
	 $-N(CH_3)CH_2CH_2OH$		
	$-OCH_3$	Higher	Exhaust



Scheme 11.1

DAS (11.7) is synthesised from 4-nitrotoluene-2-sulphonic acid (11.6) by the route outlined in Scheme 11.1. An important factor in the preparation of DAST brighteners in the purity necessary for good performance is the purity of the DAS used as starting material. At one time DAS made in this way contained significant amounts of yellow azoxy compounds similar to 11.8, which formed the main components of the obsolescent dye Sun Yellow (CI Direct Yellow 11) made by the partial reduction and self-condensation of intermediate 11.6. Today the major manufacturers supply DAS essentially free from these undesirable impurities [37].

It is almost impossible to give a comprehensive list of all the FBAs of type 11.5 that have appeared on the market since the first (11.3) of them was patented in 1940, but several important commercial products are shown in Table 11.1. The less water-soluble products have been widely used in the past as brighteners for detergent formulations and are generally used to brighten cotton by exhaustion. The more soluble, less substantive types are usually applied by padding in continuous bleaching, as a white ground for printing or in resin finishing of woven goods for white garments or household textiles. Application methods have been well described by Williamson [9].

Where the groups R_1 and R_2 as defined in Table 11.1 are both derived from amines, variation of the amine has little influence on the hue of the white obtained. In general these products give slightly violet shades of white and the main technical justification for the existence of so many different structures in this class is the need for different levels of substantivity. The compound in Table 11.1 where R_2 is methoxy gives a distinctly violet tone. All these products have light fastness values in the range 3–4 on cotton. In principle, all the more substantive types may be applied in conjunction with a hydrogen peroxide bleach. Their stability towards chlorine bleaches such as sodium hypochlorite varies, but they are all essentially unstable towards these reagents [4].

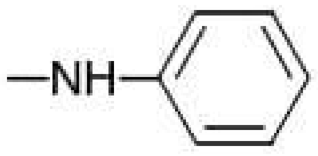
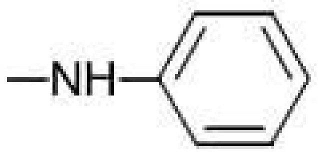
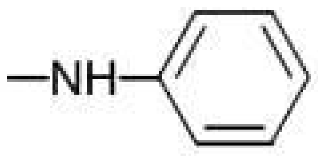
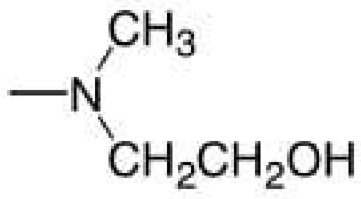
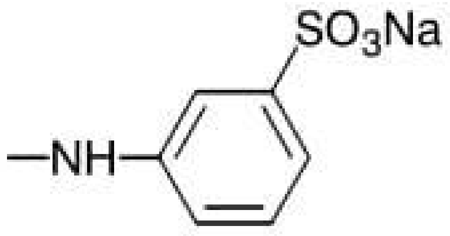
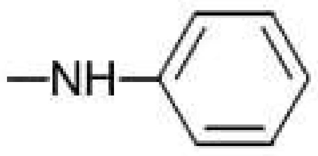
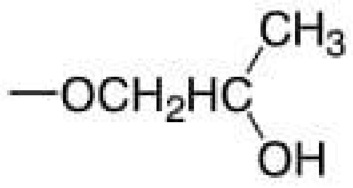
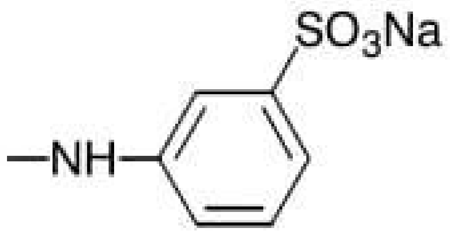
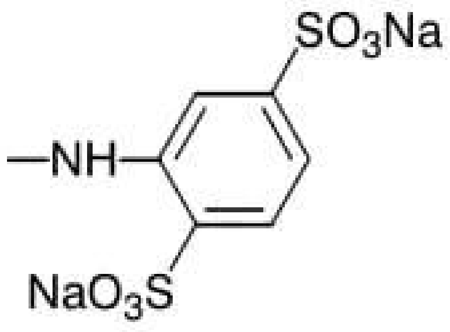
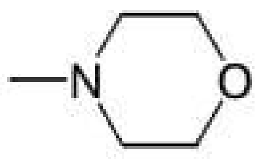
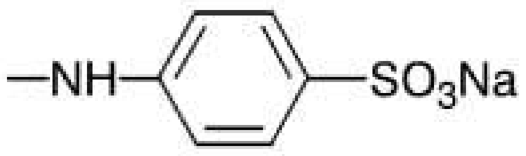
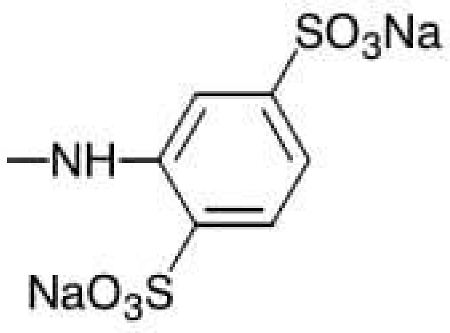
Nine DAST-type FBAs, including six of those listed in Table 11.1, were exhausted onto cotton fabric at two applied concentrations (0.05% and 0.5% on weight of fibre). Values of exhaustion, fluorescence intensity and whiteness index were determined, as presented for 0.05% o.w.f. in Table 11.2. Results at the lower concentration facilitated more precise comparisons between FBAs because of self-extinguishing of fluorescence and greater variability in exhaustion at the higher level [38]. Structures containing disulphonated anilino groups linked to either diethylamino or morpholino via the triazine rings were characterised by high solubility, poor exhaustion and relatively disappointing increases in whiteness and fluorescence intensity. Conversely, the combination of unsulphonated anilino and methoxy substituents yielded high fluorescence and whiteness values in spite of only moderate exhaustion, especially at the higher concentration. Average performance was characteristic of those products containing monosulphonated anilino and hydroxyalkylamino groups.

The treated fabrics were exposed for various times in an Atlas Weatherometer and typical values of loss in fluorescence intensity and whiteness are given in Table 11.3. Relatively higher photostability was shown by the unsulphonated anilinotriazines, especially if associated with alkoxy substituents. The least stable combinations were disulphonated anilino groups with either diethylamino or morpholino i.e. those exhibiting poor exhaustion and low whiteness index in Table 11.2. As in the latter table, the presence of monosulphonated anilino and hydroxyalkylamino substituents on the triazine rings resulted in average levels of performance.

A detailed study of the photostability of the DAST-type agent CI Fluorescent Brightener 85 on cellophane film was carried out recently. The initial fading reaction is a photosensitised *trans–cis* isomerisation of the stilbene grouping. The subsequent oxidative attack on the molecule is concentrated on the vulnerable ethene linkage at the centre of this moiety [39].

Substituted triazinyl derivatives of DAS are usually chosen for pad–dry–bake application to cotton in conjunction with an easy-care or durable-press finish. In these mildly acidic conditions (pH about 4) the FBA must show appreciable resistance towards the catalyst (usually magnesium chloride) necessary to cure the resin. The less substantive products in the upper half of Table 11.1 are important in this respect, as are compounds of type 11.9 where R = OCH_3 or $CH_3NCH_2CH_2OH$. It is likely that the hydroxyethylamino groups present in many of these compounds participate in condensation reactions with *N*-methylol groups in the cellulose-reactant resin. The performance of an FBA applied in conjunction with a resin finish can be modified and improved by careful formulation of the pad liquor but this lies beyond the scope of the present chapter. Alternatively, FBA and resin can be applied in two separate steps; most DAST-type brighteners would be suitable if applied in this way.

Table 11.2 Exhaustion, fluorescence and whiteness shown by type 11.5 FBAs on cotton [38]

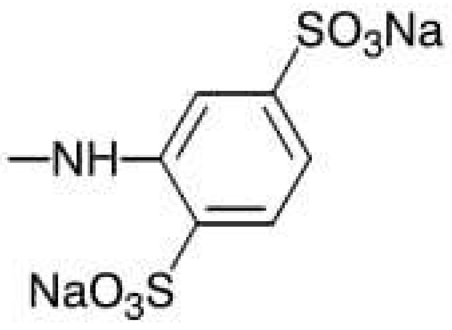
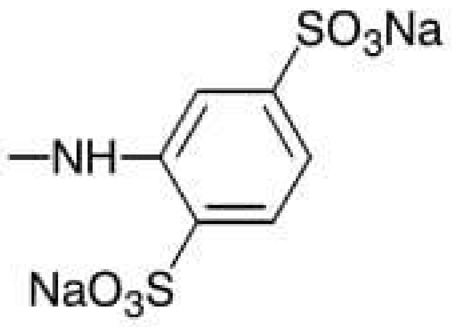
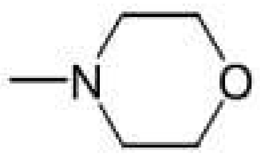
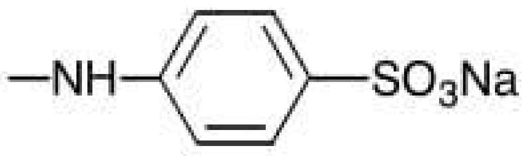
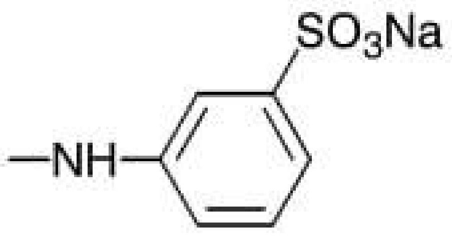
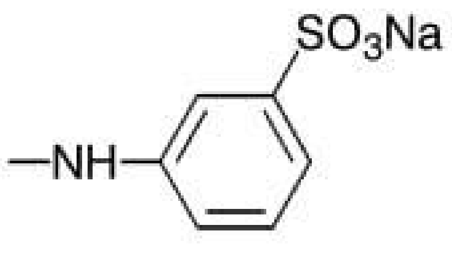
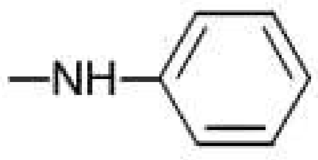
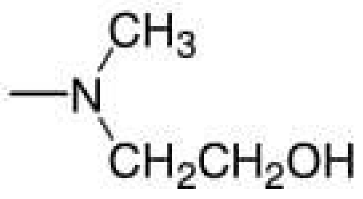
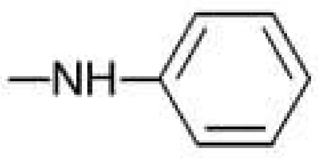
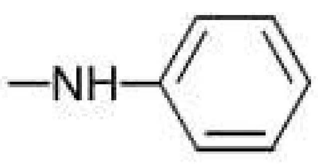
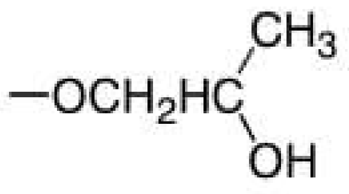
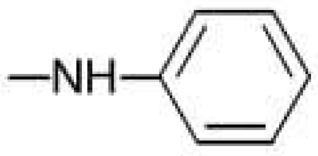
Substituents R_1 and R_2		Exhaustion (%) at 0.05% o.w.f.	Increase in fluorescence intensity at 0.05% o.w.f.	Increase in whiteness index (ASTM) at 0.05% o.w.f.
	$—OCH_3$	80	0.98	43
	$—N(CH_2CH_2OH)_2$	100	0.95	36
	 $—N(CH_3)CH_2CH_2OH$	100	0.88	33
	$—NHCH_2CH_2OH$	60	0.88	32
	 $—OCH_2HC(CH_3)OH$	80	0.83	31
	$—N(CH_2CH_2OH)_2$	80	0.78	28
		40	0.82	26
	$—N(CH_2CH_2OH)_2$	80	0.76	25
	$—N(CH_2CH_3)_2$	40	0.69	19

11.6.2 FBAs for paper

The paper industry is the second most important user of FBAs after the detergent industry, most of the products applied to paper being of the DAST type.

Paper may be brightened during preparation, the FBA being added to pre-bleached pulp before the paper sheet is laid down, or during a subsequent sizing operation. Approximately one-third of the total FBAs used are applied to pulp and two-thirds at the sizing stage. An FBA selected for addition to the pulp must show high substantivity at low temperature, otherwise there would be excessive loss of brightener with the waste water from the process. Resistance towards acidic conditions as low as pH 3 can also be important. Fillers used in

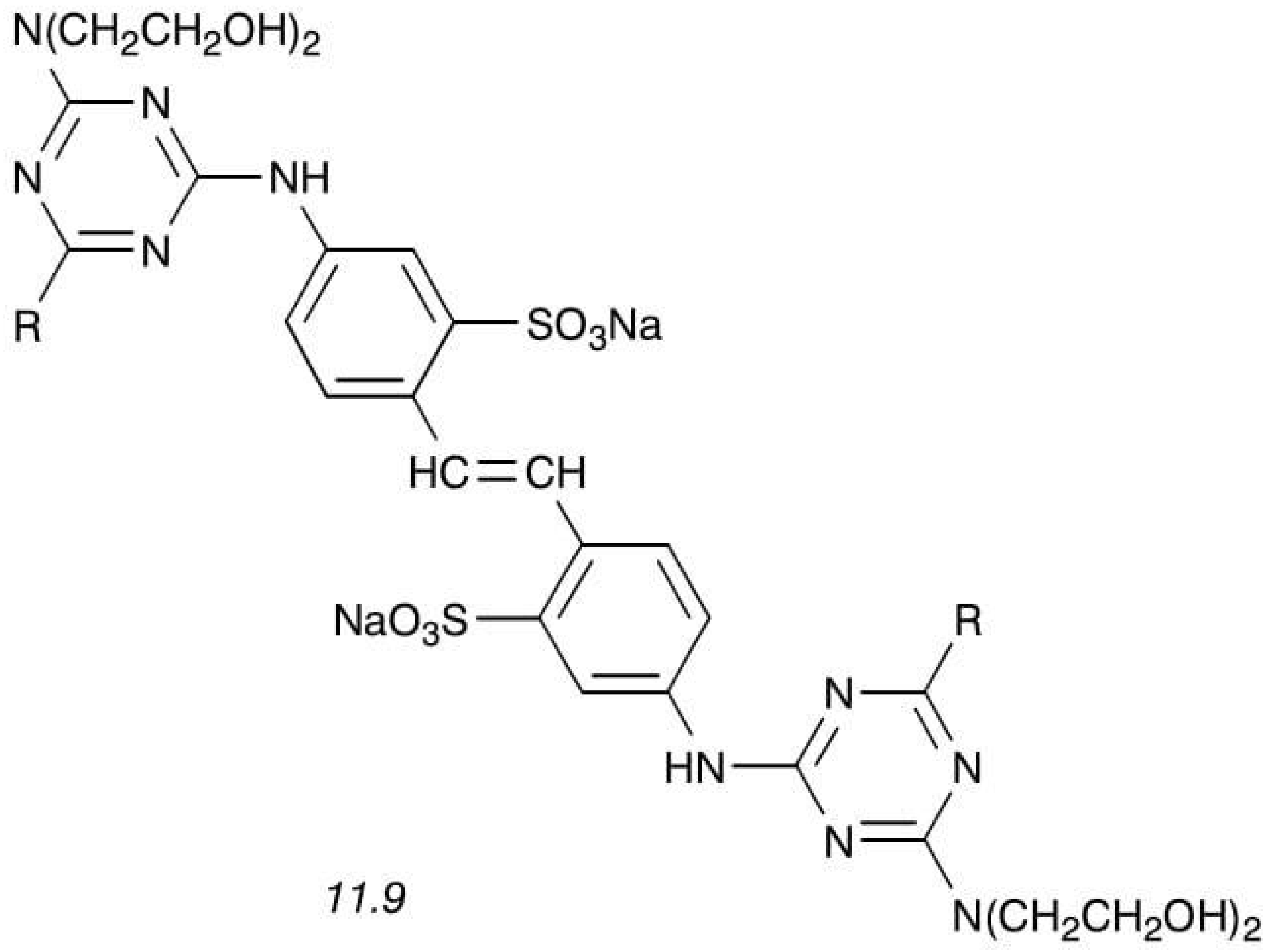
Table 11.3 Loss in fluorescence and whiteness of type 11.5 FBA-treated cotton on exposure to xenon light [38]

		Effect of 40 AATCC fading units	
Substituents R_1 and R_2		% Loss in fluorescence at 0.05% o.w.f.	% Loss in whiteness (ASTM) at 0.05% o.w.f.
	$—N(CH_2CH_3)_2$	70	92
		58	84
	$—N(CH_2CH_2OH)_2$	49	75
	$—NHCH_2CH_2OH$	49	73
	$—N(CH_2CH_2OH)_2$	44	73
	 $—N(CH_3)(CH_2CH_2OH)$	46	69
	$—N(CH_2CH_2OH)_2$	45	67
	 $—OCH_2HC(CH_3)(OH)$	44	66
	$—OCH_3$	44	65

papermaking, such as alum, chalk or china clay, may cause loss of fluorescence and the type and quantity of FBA added may have to be adjusted accordingly.

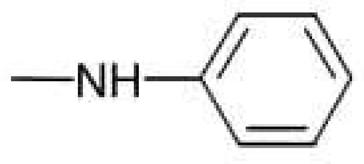
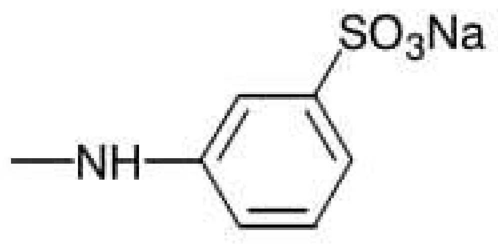
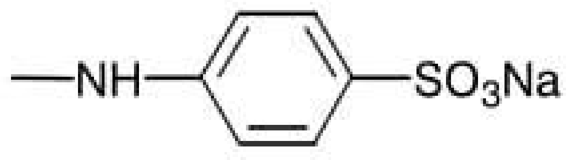
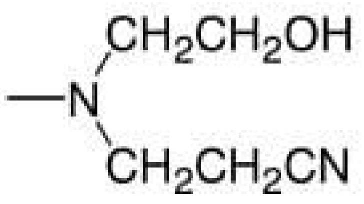
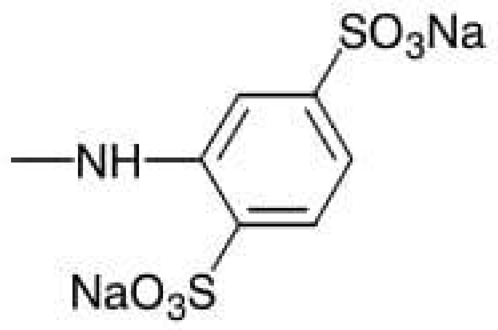
For use from the size press it is necessary for the FBA to be compatible with the chosen size, such as starch, casein or urea-formaldehyde resin. Since sizes tend to be yellowish and to absorb ultraviolet radiation, brighteners are generally less effective in sized paper.

The choice of FBAs and their methods of application to paper is highly complex, being almost as much an art as a science [40]. Examples of important FBAs for use with paper are listed in Table 11.4. This list is far from exhaustive, however, and there are other important products of type 11.5 used as FBAs for paper.



11.9

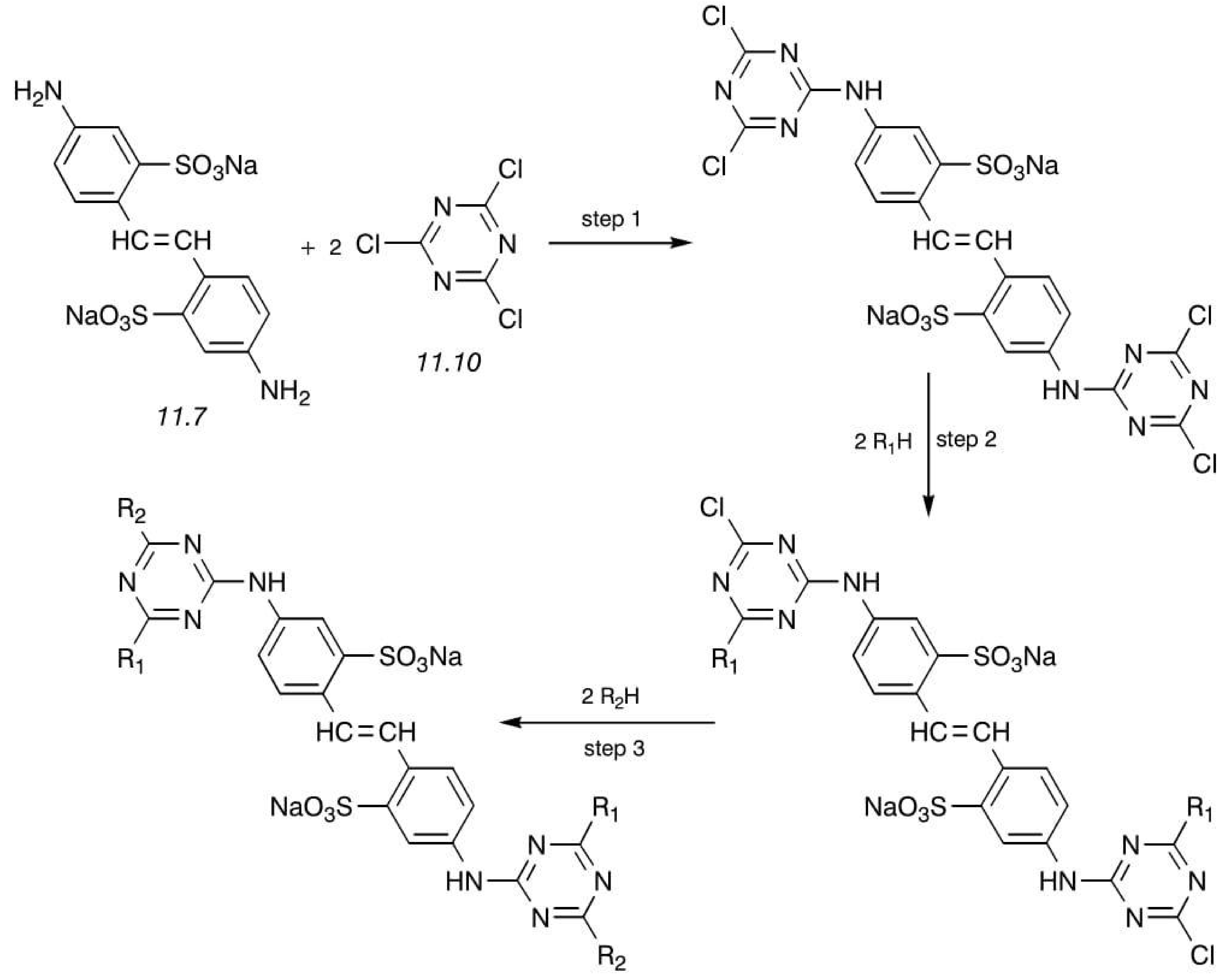
Table 11.4 Important FBAs of type 11.5 used to brighten paper

Substituents R_1 and R_2		Application
	$-N(CH_2CH_2OH)_2$	Pulp
	$-N(CH_2CH_2OH)_2$	Pulp and size press
	 $-N(CH_2CH_2OH)(CH_2CH_2CN)$	Pulp and size press
	$-N(CH_2CH_3)_2$	Size press
$-NH_2$	$-N(CH_2CH_2OH)_2$	Size press

11.6.3 Preparation of DAST-type FBAs

A major reason for the importance of DAST brighteners is their essentially straightforward manufacture from readily available and inexpensive intermediates. Products with widely different substituents and hence showing quite different application properties are easily prepared in a three-step, one-pot synthesis starting from diaminostilbenedisulphonic acid (11.7). The process is illustrated in Scheme 11.2.

By suitable choice of reaction conditions the chloro substituents of cyanuric chloride (11.10) can be replaced in a stepwise fashion. In the first step DAS reacts with cyanuric chloride at a temperature in the 0–20 °C range, ideally at pH 5–6. In the second step an amine or alcohol (R_1H) reacts within the range 20–50 °C under neutral or slightly alkaline



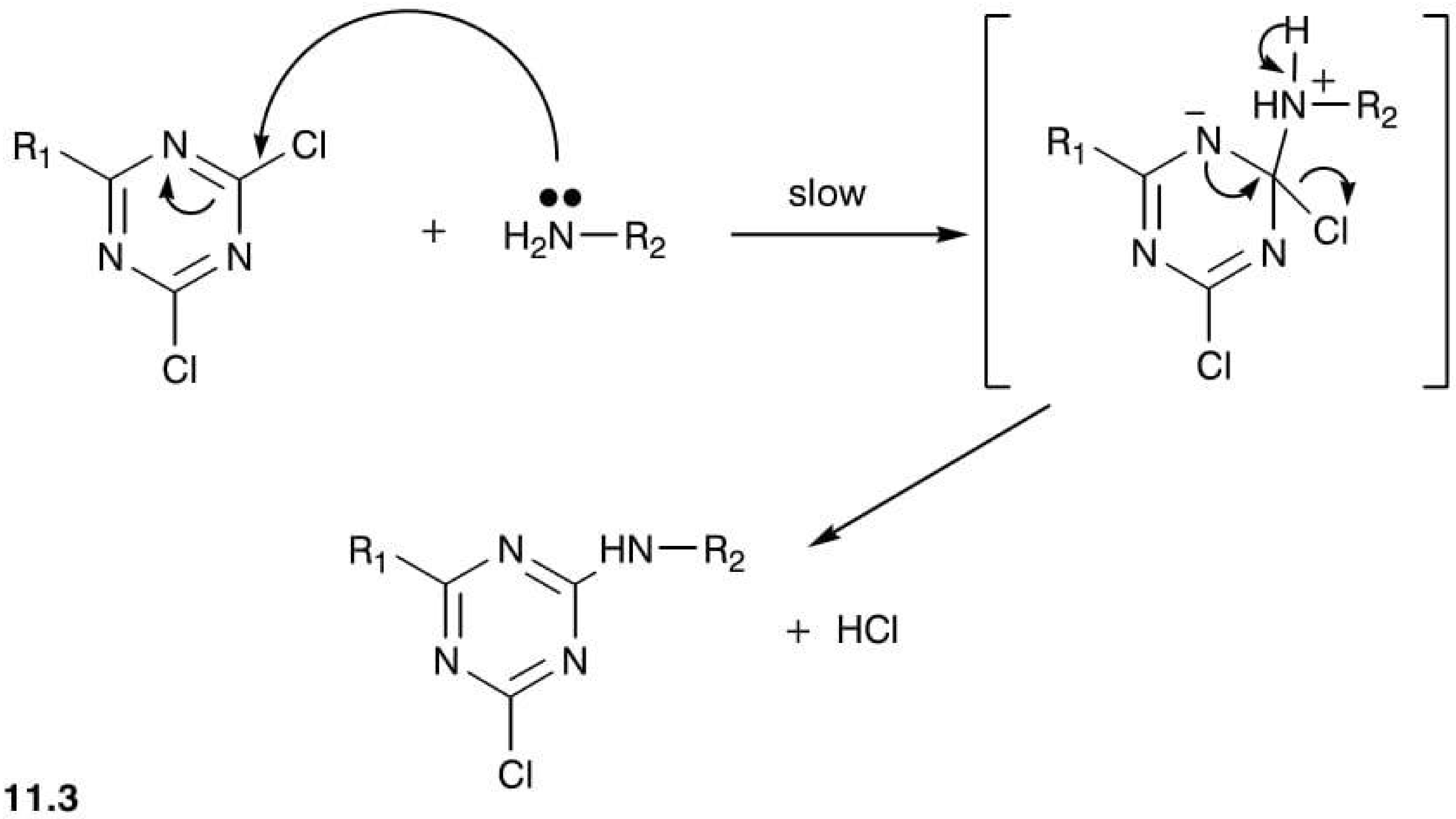
Scheme 11.2

conditions. The third step with another amine or alcohol (R_2H) is completed within the range 50–100 °C under alkaline conditions (pH 8–9). The exact conditions selected for the second and third steps depend on the nature of the attacking nucleophiles (R_1H and R_2H), as well as the substituents already present in the chlorotriazine intermediates.

Scheme 11.2 illustrates the conventional sequence for the manufacture of DAST brighteners. However, it is not always necessary and may not be desirable for DAS to be the nucleophile selected for the first step. In principle the three nucleophiles can be reacted in any order, but it is preferable for the most nucleophilic amine to react last in order to avoid forcing conditions during removal of the last remaining chloro substituents. Alkylamines react more readily than alcohols, thus ensuring that alkanolamines yield their hydroxyalkylaminotriazine derivatives.

The mechanism of these bimolecular nucleophilic substitution reactions is shown in Scheme 11.3 for the reaction between a primary amine and the intermediate dichlorotriazine. A corresponding scheme can be drawn for reaction of a secondary amine, an alcohol or any other nucleophile in any of the replacement steps. It follows from this mechanism that the rate of reaction depends on:

(1) the nucleophilicity of the attacking species, the more nucleophilic reagents reacting more quickly or under milder conditions
(2) the electronegativity of the substituent R_1.

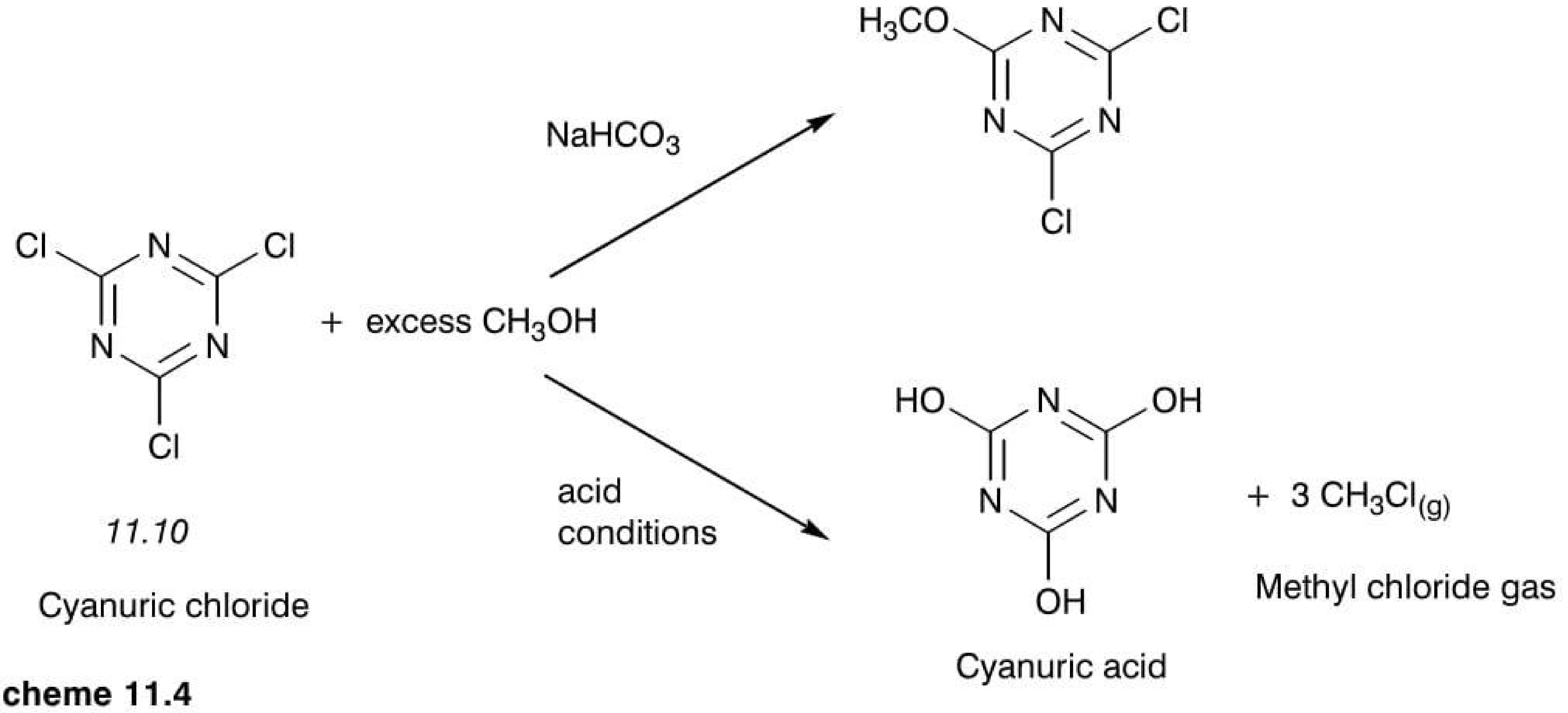


Scheme 11.3

The more electronegative the substituent, the more rapid the reaction or the milder the conditions required. Thus the reaction rate decreases in the order: PhO > MeO > EtO > PhNH > NH_2 > MeNH > EtNH > Me_2N > OH [4].

It also follows that protonation of the triazine ring makes it more susceptible to attack by nucleophilic reagents unless the reagent itself is also protonated. If the triazine ring remains unprotonated when a nucleophilic base, such as an alkylamine, is present as its acid salt the reaction is slower, of course. Cyanuric chloride itself is a very weak base that becomes protonated only under strongly acidic conditions. Thus step 1 in Scheme 11.2 can be carried out in aqueous solution even at pH 2 without risk of undesirable hydrolysis of cyanuric chloride, water being an extremely weak nucleophile.

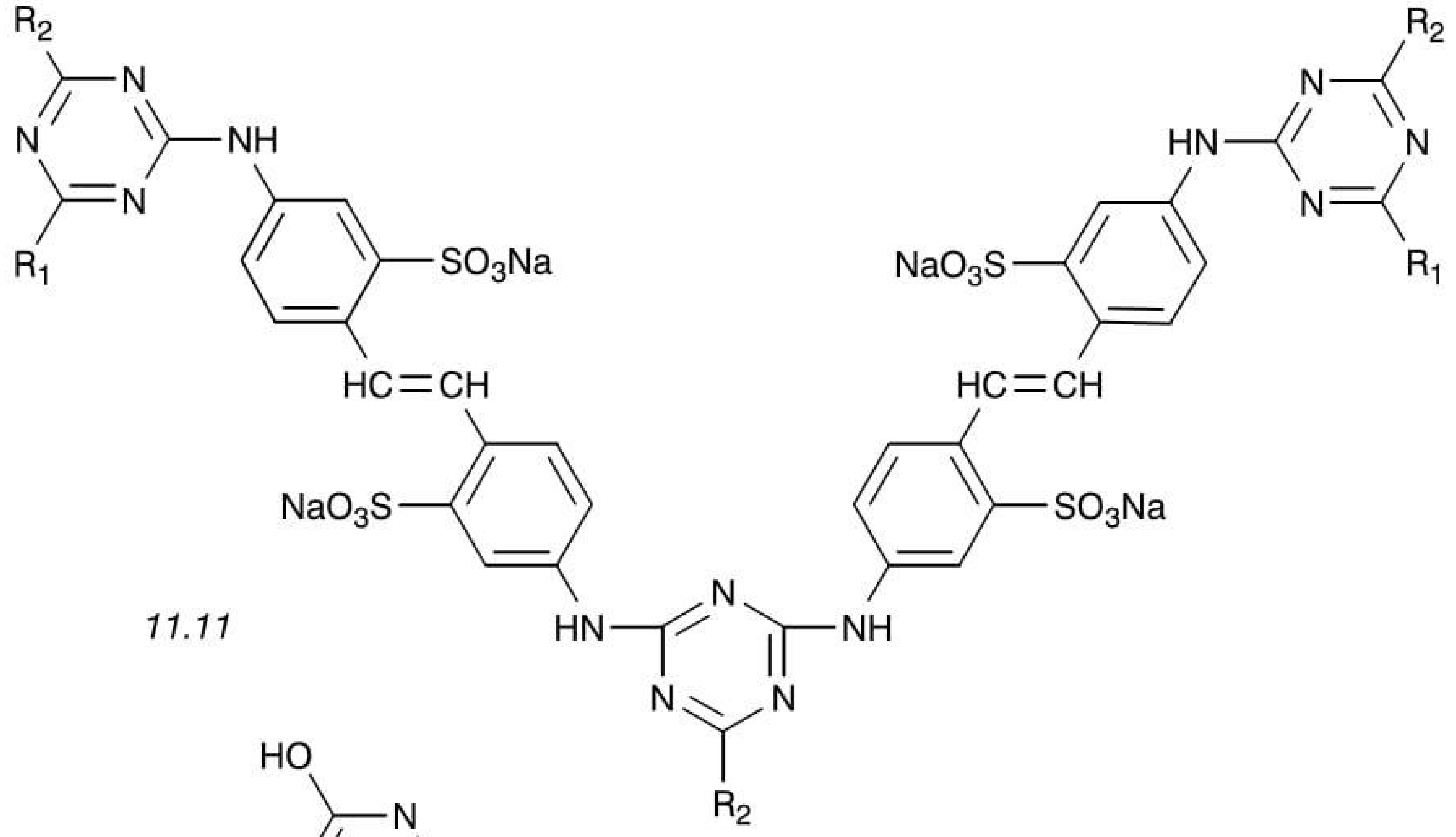
The manufacture of several important brighteners containing alkoxytriazine groups, such as the DAS derivative of highest substantivity in Table 11.1, does not follow the conventional sequence. The first step involves reaction of cyanuric chloride with excess methanol and excess acid acceptor, usually sodium bicarbonate. Under acidic conditions this reaction takes a quite different course and can become dangerously violent (Scheme 11.4).



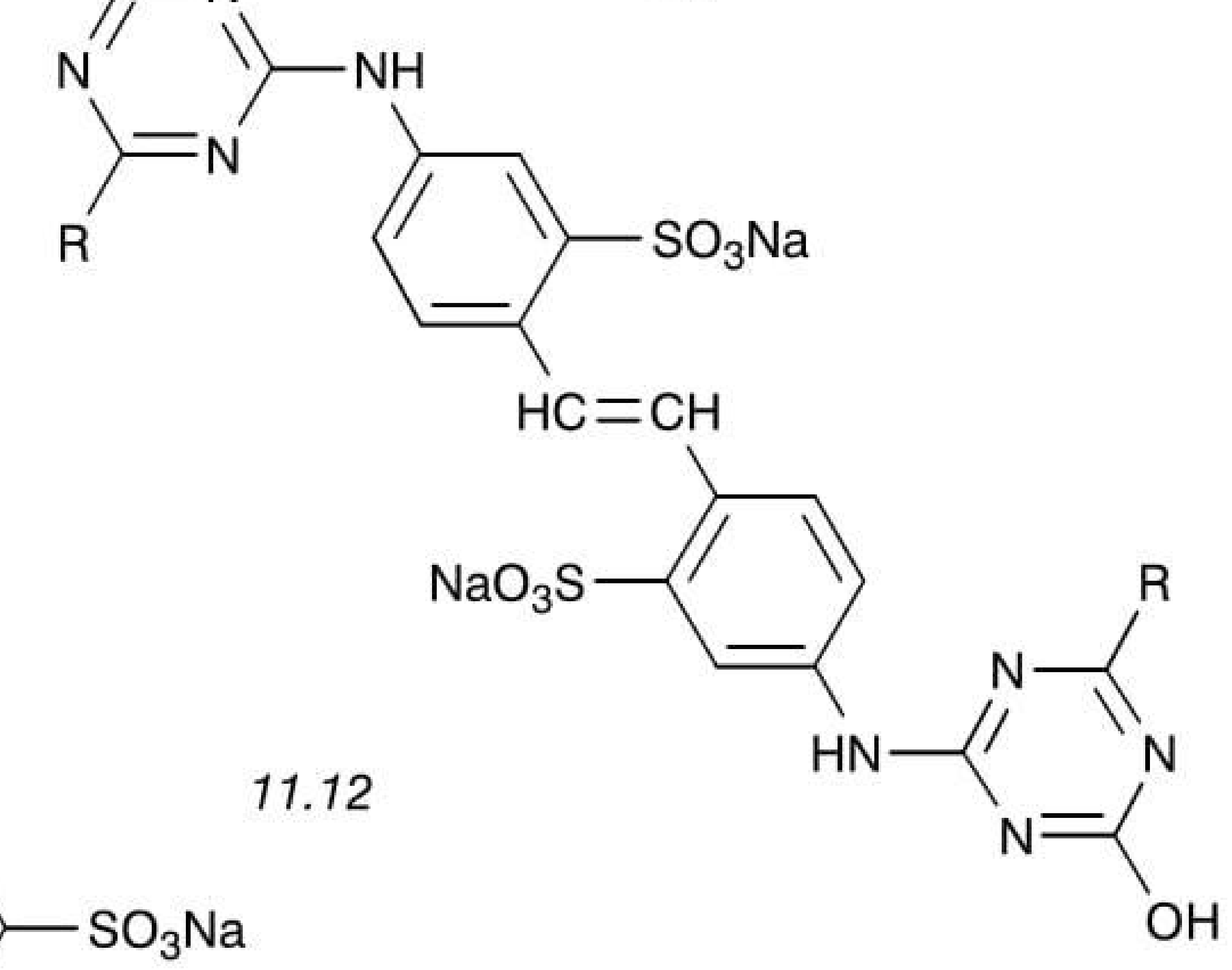
Scheme 11.4

In the preparation of other DAST brighteners it may be advantageous to avoid reacting DAS with cyanuric chloride in the first step. It is difficult to suppress the reactivity of the second chloro substituent completely and undesirable by-products of the general type 11.11 can be eliminated if DAS is made to react with a dichlorotriazine intermediate in the second step. Very careful control of the reaction conditions, especially in steps 1 and 2, is also necessary in order to avoid formation of partially hydrolysed by-products such as structures 11.12 and 11.13.

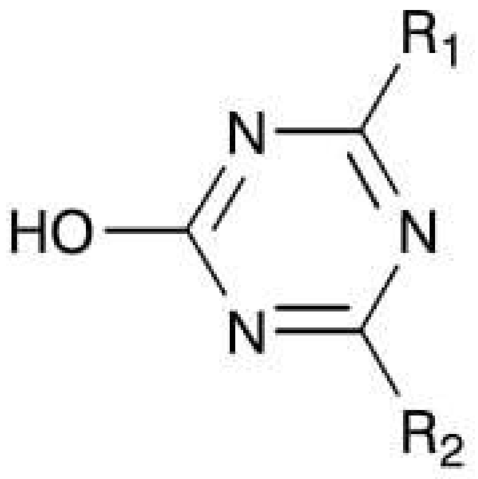
Unsymmetrical products of type 11.14 derived from DAS have been described but these are much more complicated and expensive to prepare than those with symmetrical structures. They have never become commercially important.



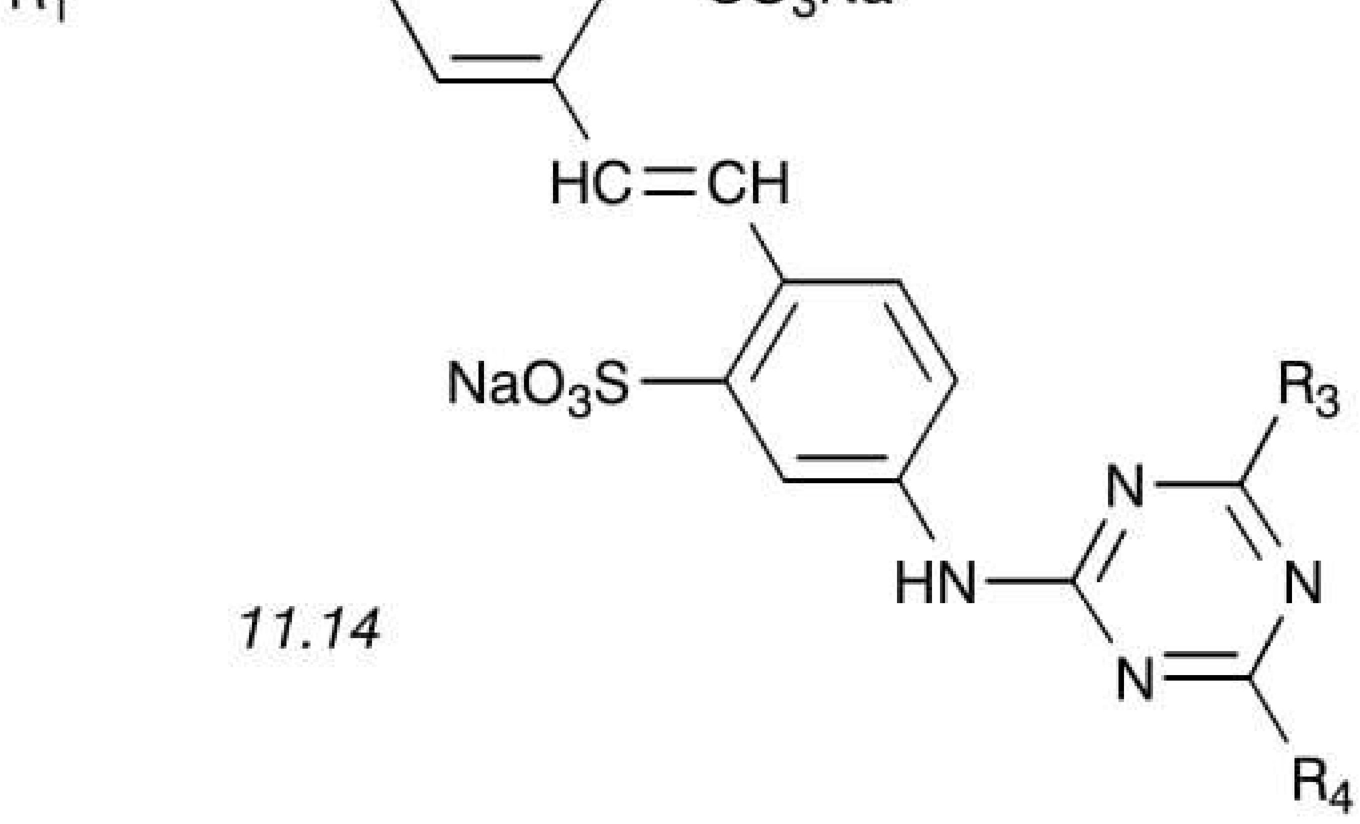
11.11



11.12



11.13



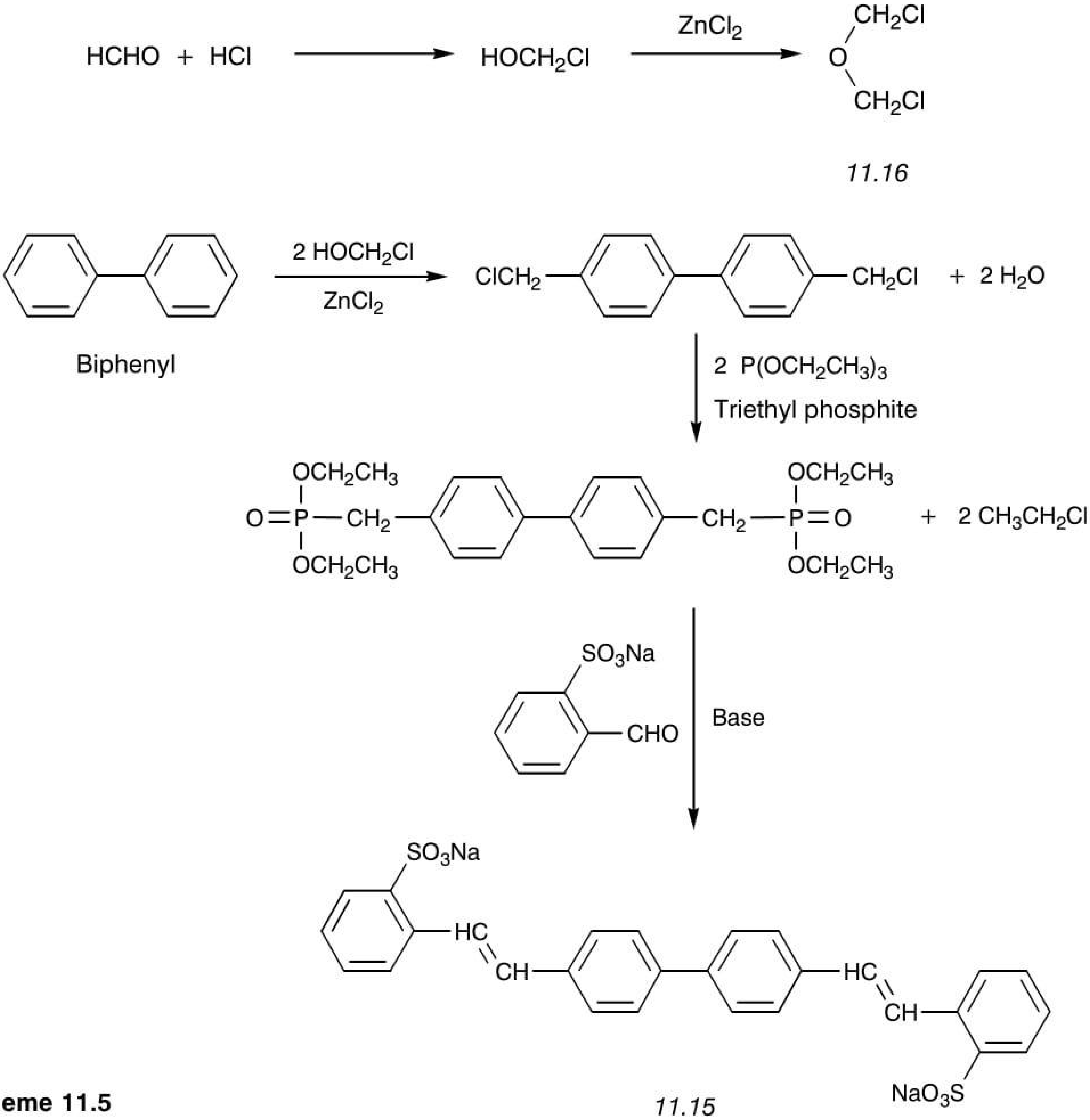
11.14

11.6.4 Speciality FBAs for cotton

Two commercially important brighteners for cotton are not of the DAST type.

The distyryldiphenyl 11.15 is mainly of value for brightening cotton during laundering but it can also be used to brighten cotton by exhaust application. It has high aqueous solubility and has been recommended for use in combination with resin finishes, although its stability at the padding stage is suspect. It has found further uses in the brightening of polyester/cotton and nylon/cotton blends. Both components of a nylon/cotton blend are brightened and on polyester/cotton the cellulosic component is brightened without any undesirable staining of the polyester. Its light fastness on cotton is 4, which is slightly superior to that of DAST brighteners. Compound 11.15 is also resistant to hypochlorite bleach but on cotton it has limited fastness to washing in soft water. The effect of humidity on the photostability of CI Fluorescent Brightener 359, a distyryidiphenyl structure similar to 11.15, has been studied on cellophane film recently. A kinetic analysis of fading rates under these conditions indicated participation in a bimolecular oxidative mechanism [41].

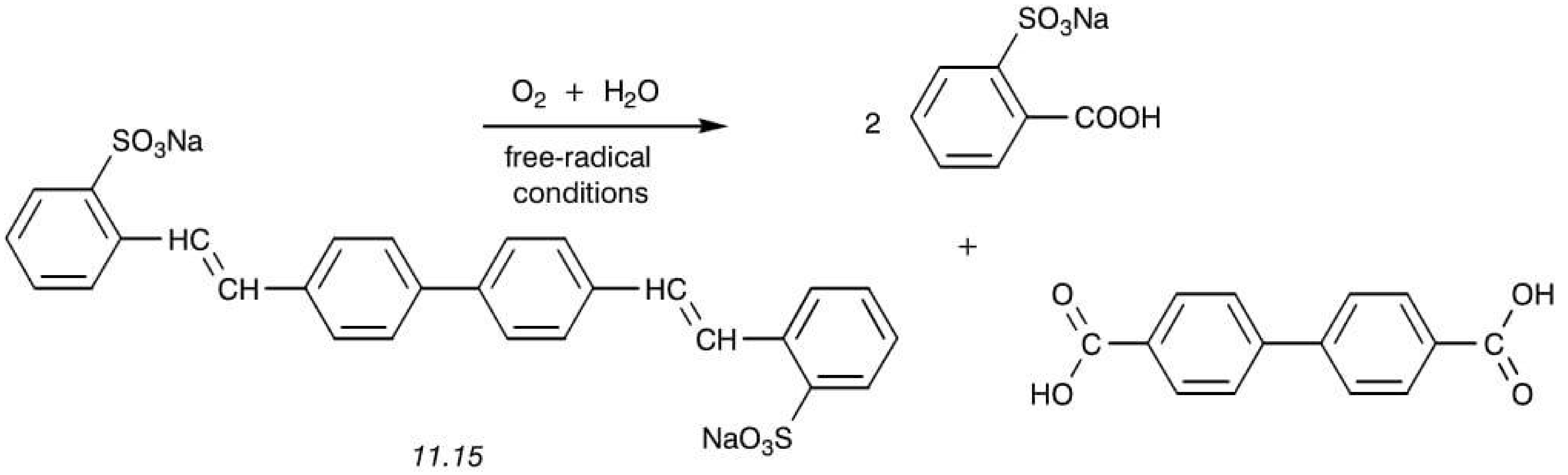
The manufacture of brightener 11.15 is shown in Scheme 11.5. The first chloromethylation stage can only be accomplished safely in a plant specially designed to



Scheme 11.5

ensure that the highly carcinogenic by-product bis(chloromethyl) ether (11.16) formed from formaldehyde and hydrochloric acid does not escape. Otherwise the preparation proceeds without undue difficulty.

A specific advantage of sulphonated distyrylarene brighteners such as 11.15 and similar structures is that the ethene double bonds are readily oxidised during effluent treatment, leading to the formation of soluble acids of low relative molecular mass (Scheme 11.6). Thus it can be inferred that these brighteners and their degradation products are relatively innocuous and are unlikely to accumulate in the environment.



Scheme 11.6

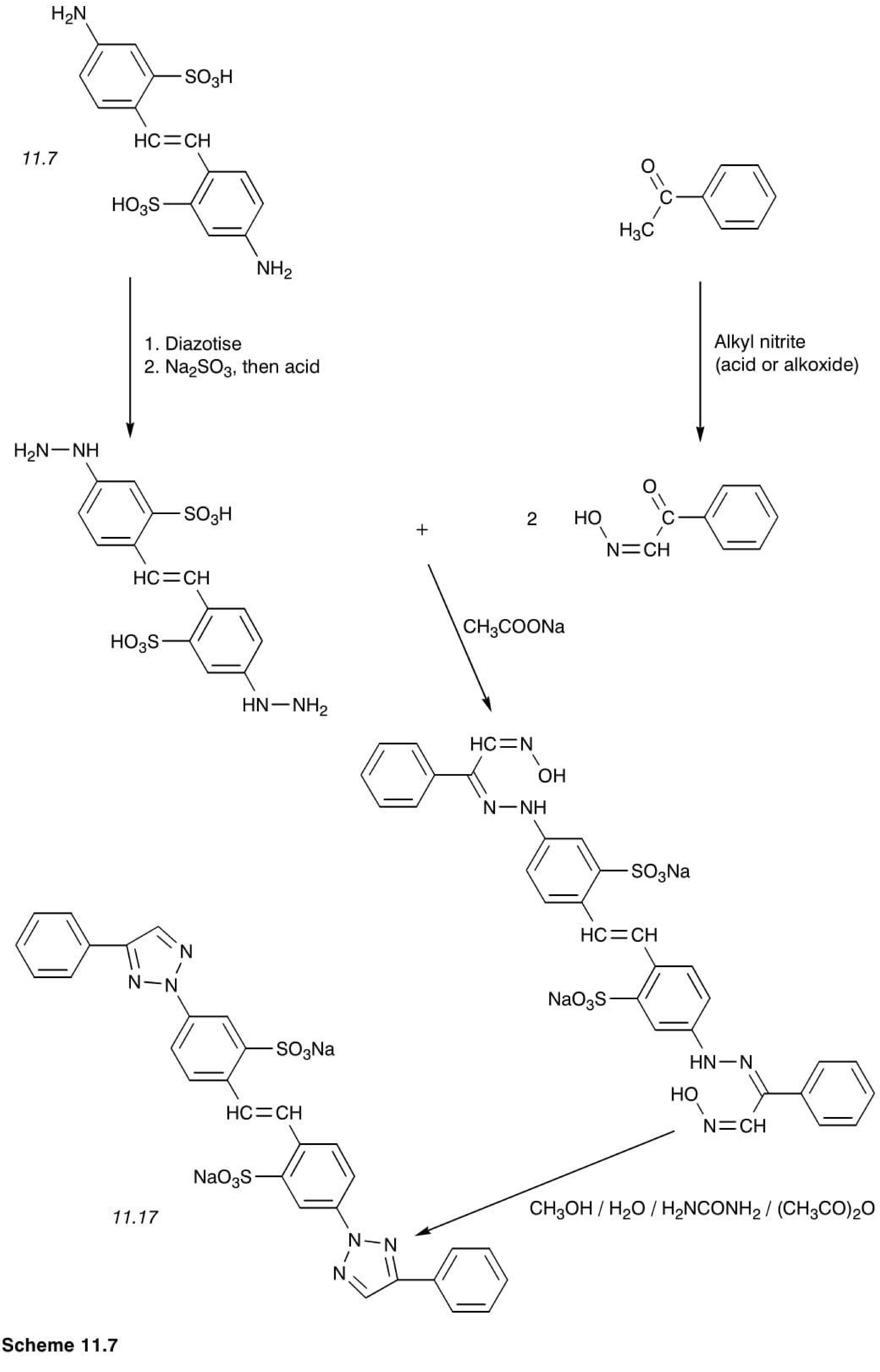
The introduction of heterocyclic rings as terminal groups in the 4,4′-positions of the stilbene nucleus intensifies the fluorescence of the conjugated system and shifts the fluorescence maximum to a longer wavelength. The *vic*-triazole 11.17 is a premium product and cotton brightened with it has a light fastness of 5. This structure is stable to bleaching with hypochlorite or chlorite. It has adequate fastness to washing and a liquid formulation has been marketed for use in combination with a resin finish. It is also of some importance as a component of household detergents. Unfortunately, it is also expensive and its main use is probably as an FBA for nylon, on which fibre it gives better value for money. Its preparation is shown in Scheme 11.7.

A more soluble derivative of compound 11.17, the tetrasulphonated analogue 11.18, has been recommended for application to cotton in combination with a resin finish. Unlike DAST-type FBAs under these conditions, compound 11.18 is compatible with resin formulations containing zinc nitrate as latent acid catalyst. The brightness achieved is not high, however.

Many other products of a variety of structures have been patented for the brightening of cellulosic substrates. The reader is referred to the reviews mentioned earlier for further information.

11.7 BRIGHTENERS FOR CELLULOSE ACETATE AND TRIACETATE FIBRES

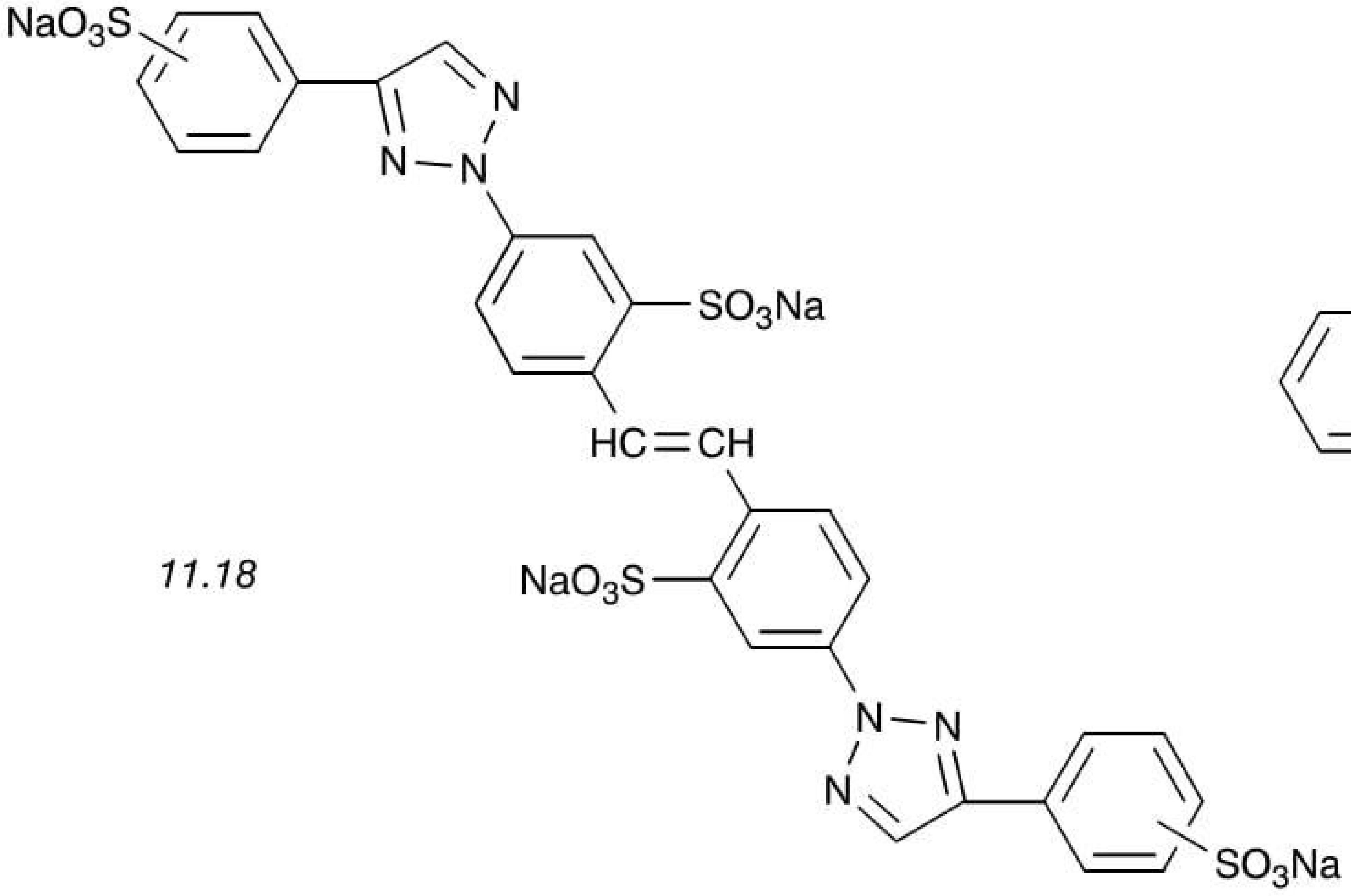
Cellulose acetate and triacetate fibres are brightened with disperse-type FBAs, including derivatives of 1,3-diphenylpyrazoline (11.19). These form a commercially important group of FBAs. If suitably substituted they can be applied to substrates other than acetate and triacetate. The commercially more important products of this type are used to brighten nylon and acrylic fibres. Their preparation and other aspects of pyrazoline chemistry are discussed in section 11.8. Examples of pyrazolines used to brighten acetate and triacetate


11.7
1. Diazotise
2. Na$_2$SO$_3$, then acid
Alkyl nitrite
(acid or alkoxide)
+
2
CH$_3$COONa
CH$_3$OH / H$_2$O / H$_2$NCONH$_2$ / (CH$_3$CO)$_2$O
11.17

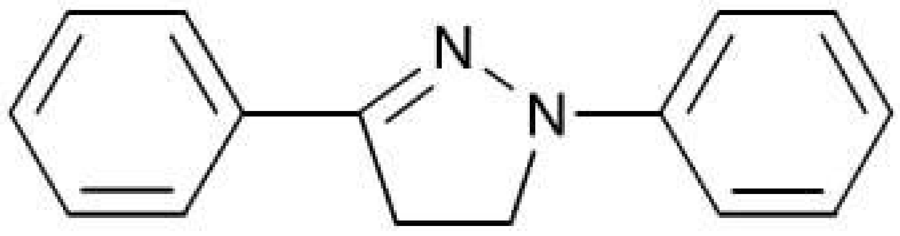
Scheme 11.7

fibres include the sulphonamide 11.20 and the sulphone 11.21, the former giving greenish tones and the latter violet effects.

A pyrene derivative (11.22), a naphthalimide (11.23) and benzoxazoles of smaller molecular size are also used and these are discussed in more detail in section 11.10. The naphthalimide ring system is highly stable, leading to products with good light fastness and stability to chlorite. Their main disadvantage, however, is relatively low fluorescence efficiency, which is primarily a result of low molar extinction coefficients. Stronger fluorescence arises when there is an electron-donating group such as methoxy (as in 11.23) or alkylamino in the 4-position, in which case the absorption and emission properties are associated with intramolecular charge transfer involving the donor group and the electron-withdrawing *peri*-carbonyl groups.

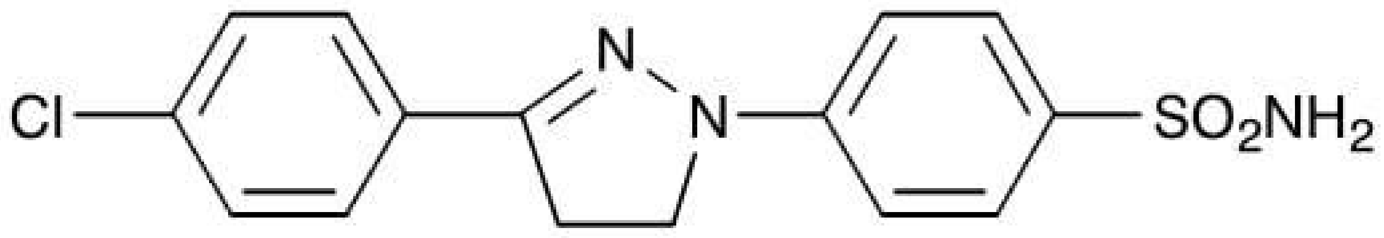


11.18

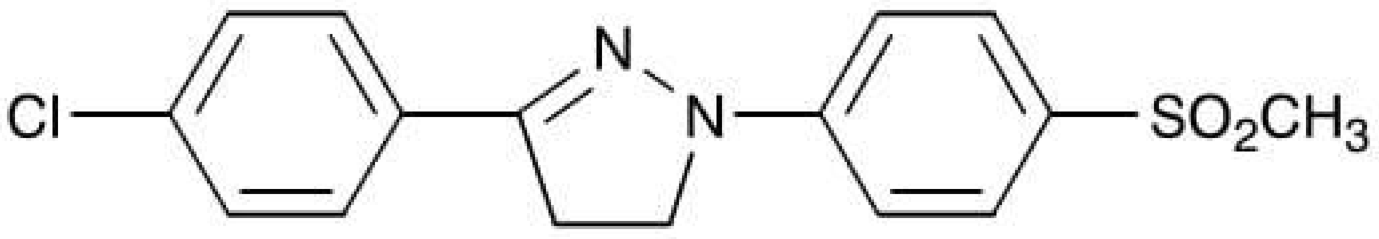


11.19

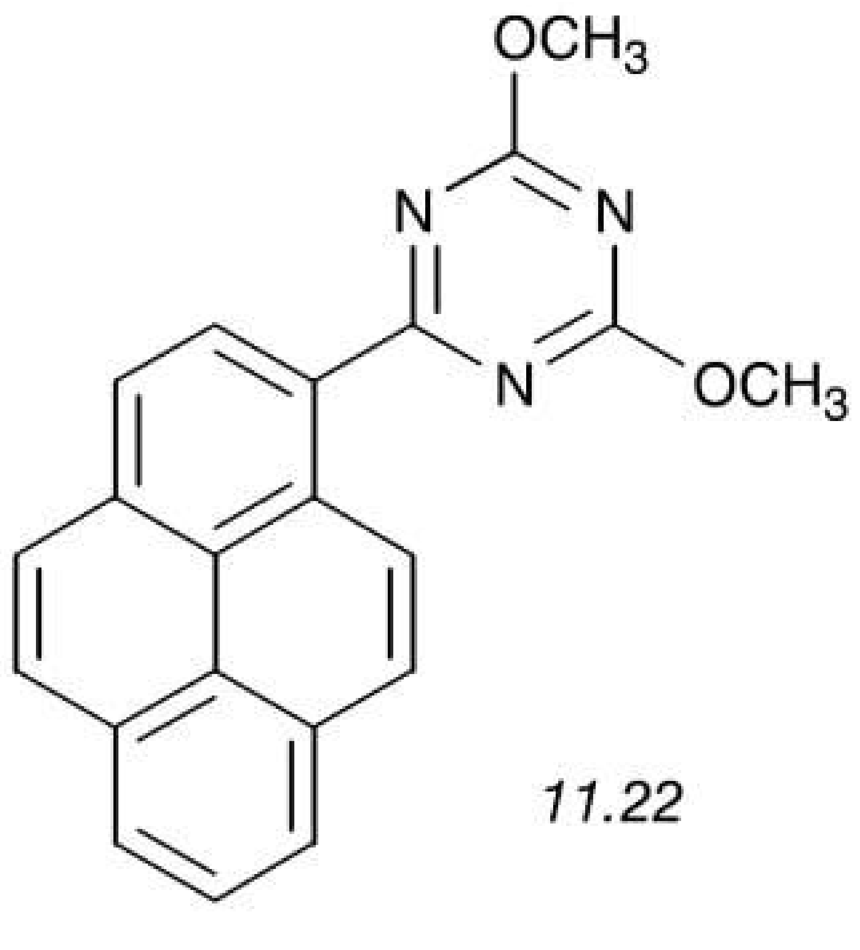
1,3-Diphenylpyrazoline



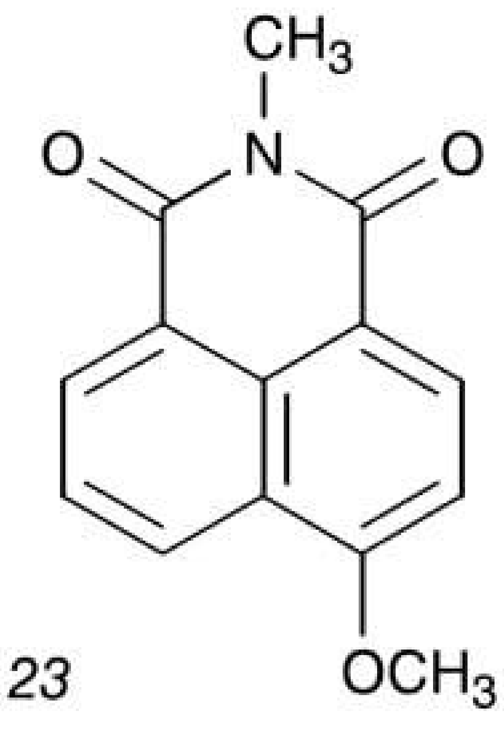
11.20



11.21



11.22

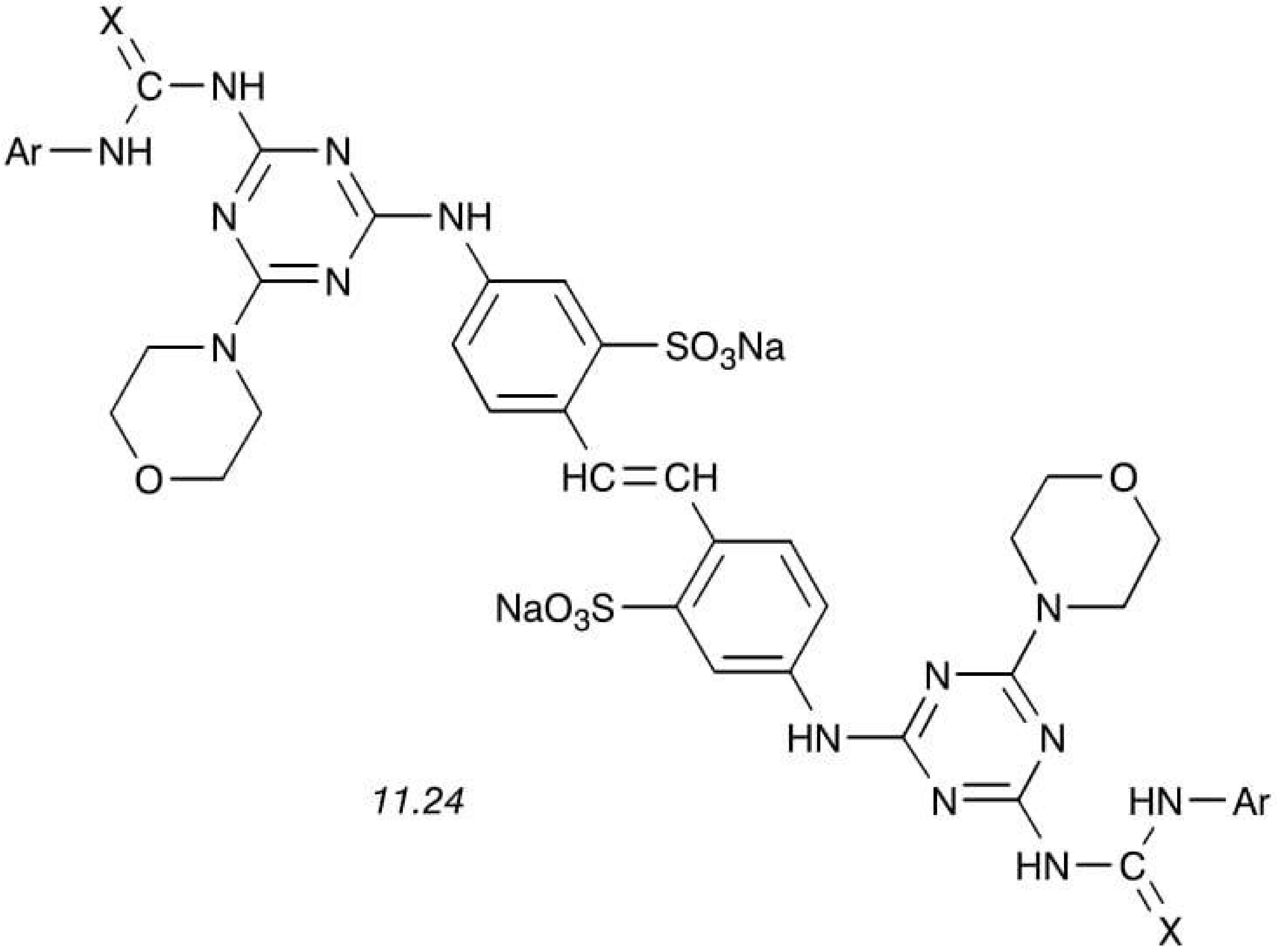


11.23

Several interesting analogues of structure 11.23 were synthesised recently. These derivatives of 4-methoxynaphthalimide contained a triazine ring with an unsaturated polymerisable substituent capable of addition copolymerisation with other vinyl or acrylic monomers. Such brighteners can be incorporated into the synthesis of polymeric finishes and show exceptional durability to organic solvents and wet treatments [42–44].

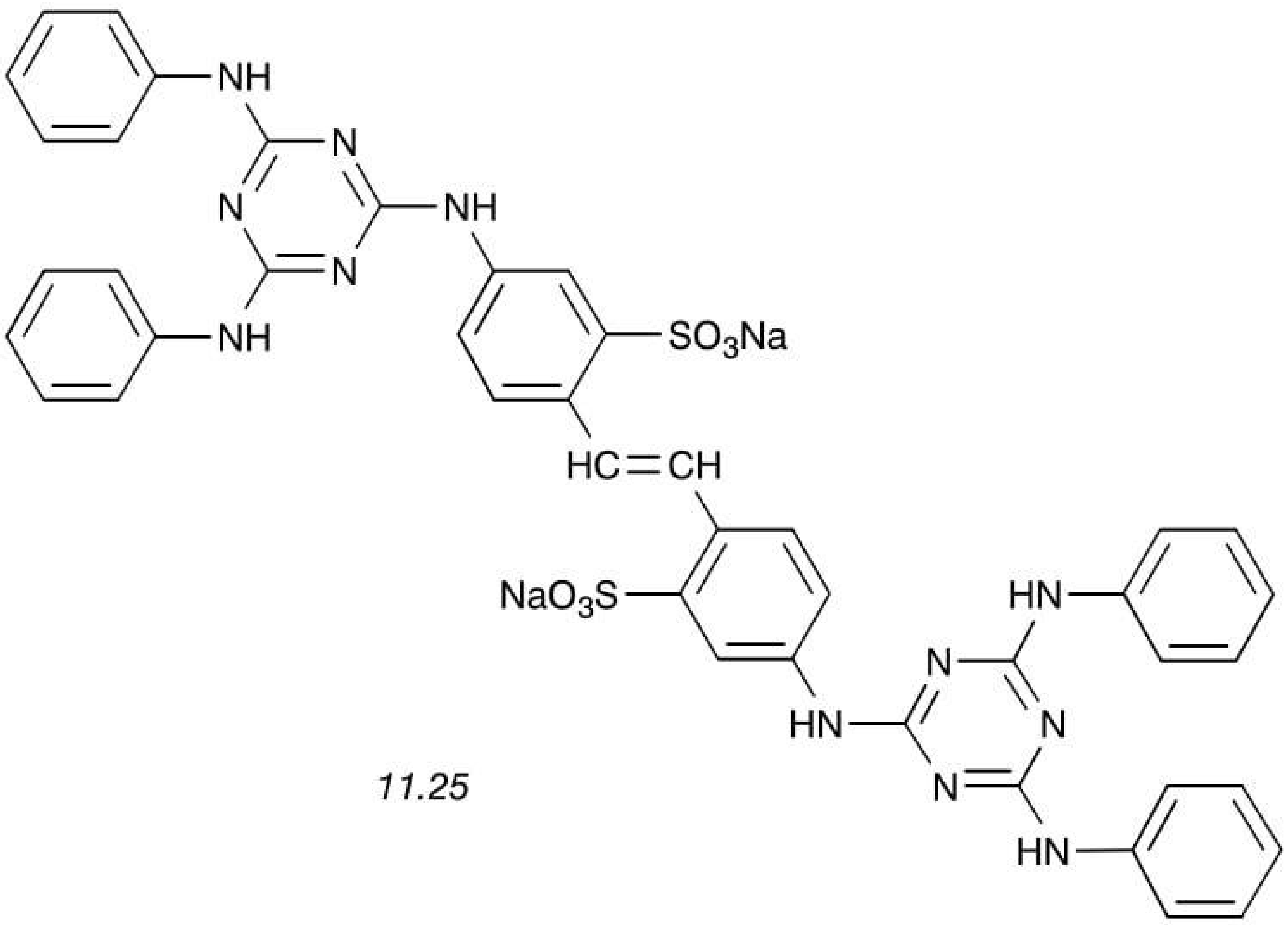
11.8 BRIGHTENERS FOR NYLON

Disperse brighteners of the types used to brighten cellulose acetate, triacetate or polyester fibres can be used to brighten nylon. In practice, however, disperse types are little used and nylon is usually brightened with sulphonated compounds akin to acid dyes. Silk and polyurethane fibres can also be brightened with the FBAs normally used on nylon. Chief amongst these are products of the DAST type already discussed in section 11.6.3. Two series of DAST derivatives of the general structure 11.5 were evaluated recently, in which the R_1 groups were morpholino and the R_2 groups either arylurea or arylthiourea (11.24; Ar = aryl). These products showed high substantivity for both cotton and nylon, the ureido (X = O) or thioureido (X = S) residues providing scope for hydrogen bonding with polar groups in these substrates [45].



11.24

Exhaust brightening of nylon is usually combined with a reduction bleach based on sodium dithionite. Important DAST-type FBAs suitable for this process are exemplified by the four most cotton-substantive compounds listed in Table 11.1. The methoxy-substituted derivative can be applied to nylon successfully at pH 6–6.5 but those with three NH groups attached to each triazine ring are best applied at pH 4–5. All these products show a light fastness rating of only about 3 on nylon. If a reductive bleach is unnecessary the DAST brightener 11.25 can be applied to nylon from an alkaline scouring bath. Good whites are achieved but the light fastness of this tetrakis(anilino) derivative is suspect on nylon.



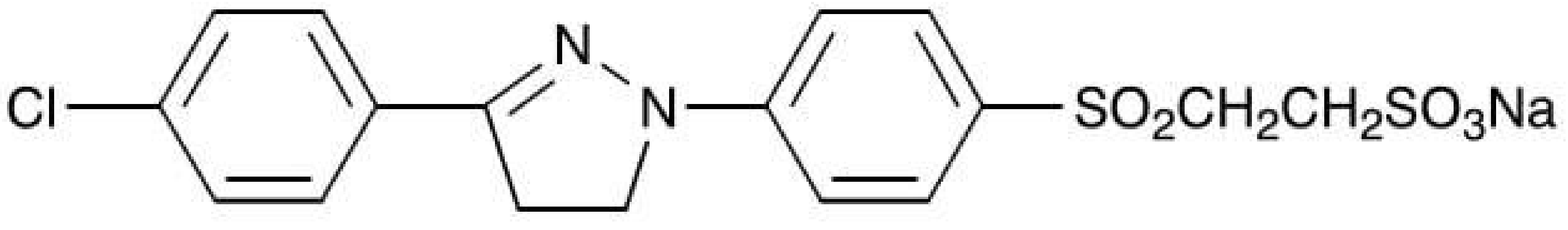
11.25

The premium FBAs 11.15 and 11.17 already mentioned are of importance on nylon because of their superior fastness properties. As on cotton, the distyryldiphenyl structure 11.15 has slightly higher light fastness than the DAST-type brighteners. In contrast to its performance on cotton, however, it has excellent fastness to washing on nylon.

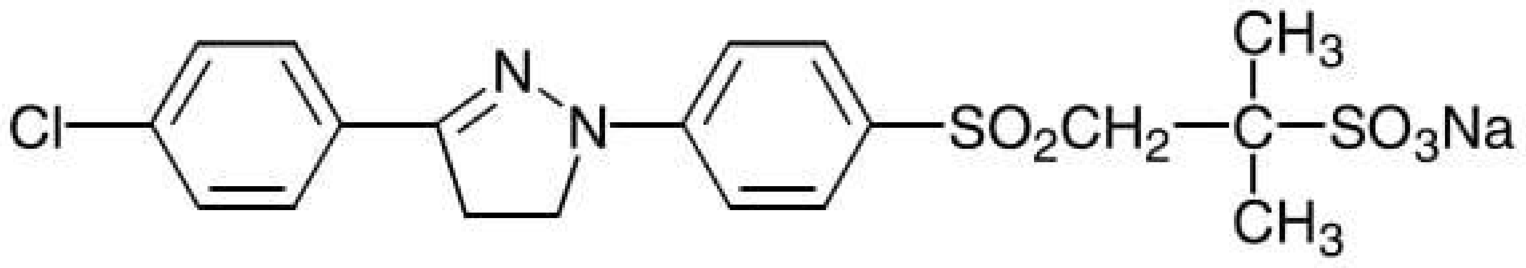
The light fastness of the *vic*-triazole 11.17 on nylon is 4–5; as on cotton this is significantly superior to that of the DAST derivatives. Unlike the DAST types, the *vic*-triazole is also stable towards a sodium chlorite bleach. Applied to nylon in combination with sodium chlorite, compound 11.17 can give exceptionally high whiteness and excellent fastness properties.

Nylon can also be brightened using an anionic derivative of 1,3-diphenylpyrazoline, such as FBA 11.26, 11.27 or 11.28. Although these pyrazolines give excellent whites when applied to nylon by exhaustion, they are usually less cost-effective than the DAST brighteners. For continuous application by pad–thermosol or pad–acid shock methods the situation is reversed, however, and the pyrazoline FBAs are commercially important in this sector.

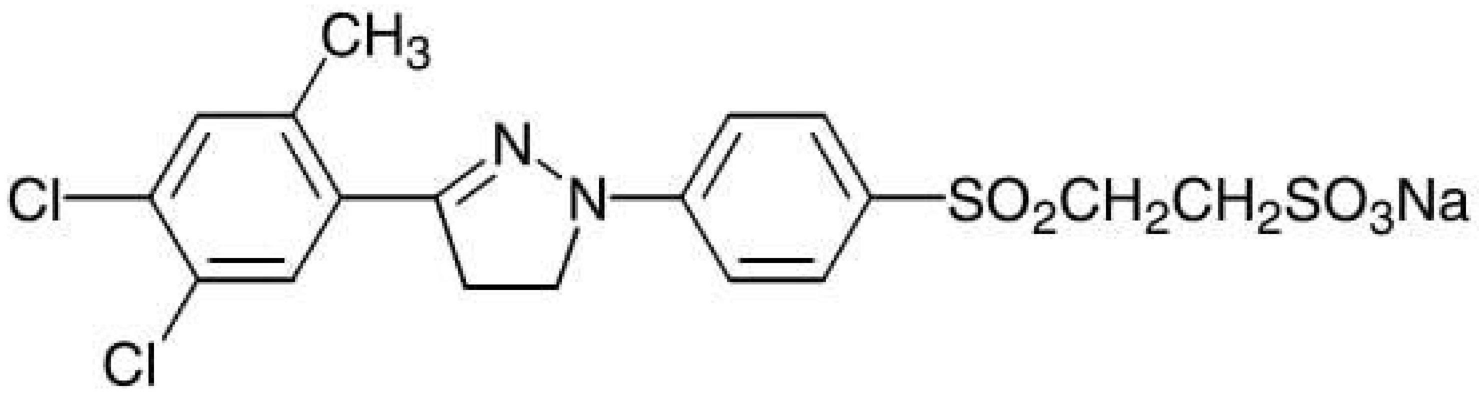
11.26



11.27

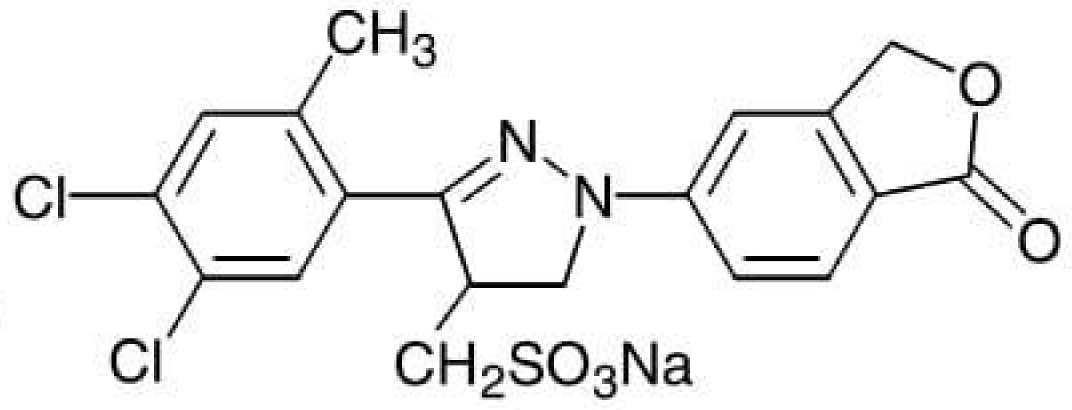


11.28



On nylon these three pyrazolines (11.26–11.28) have light fastness values in the range 3–4, slightly superior to the DAST types. Light fastness in the wet state is generally lower, however, and the pyrazolines suffer more in this respect than the DAST brighteners. Pyrazolines 11.26 and 11.27 in particular have very poor light fastness values of 1–2 in the wet state. The two electron-withdrawing chloro substituents in compound 11.28 have the effect of improving light fastness, especially in the wet state, but at the expense of a loss in solubility and slightly more difficult formulation and application. All three pyrazolines give violet-toned whites on nylon, compound 11.28 being slightly less violet than the other two.

Electron withdrawal by the 3,4-dichloro substituents and the lactone ring in the 3′,4′-positions of the diphenylpyrazoline derivative 11.29 enhances light fastness in both the dry and wet states. Thus the fastness rating of compound 11.29 is slightly higher than those of compounds 11.26–11.28 in the dry state and significantly higher on wet nylon. Pyrazoline 11.29 is also capable of giving brilliant whites of a pleasing bluish hue. It is complicated to manufacture, however. Increasing substitution also reduces solubility and thus adversely affects pad liquor stability, although this problem can be solved by suitable formulation. Pad liquor formulation can be especially important in the pad–thermosol process, where the brightened nylon fabric is often intended as a prepared white ground for colour printing with acid dyes. If too much surfactant has been applied together with the FBA in the pad liquor, 'bleeding' from the fabric at the printing stage can give an unacceptably blurred appearance to the printed design.

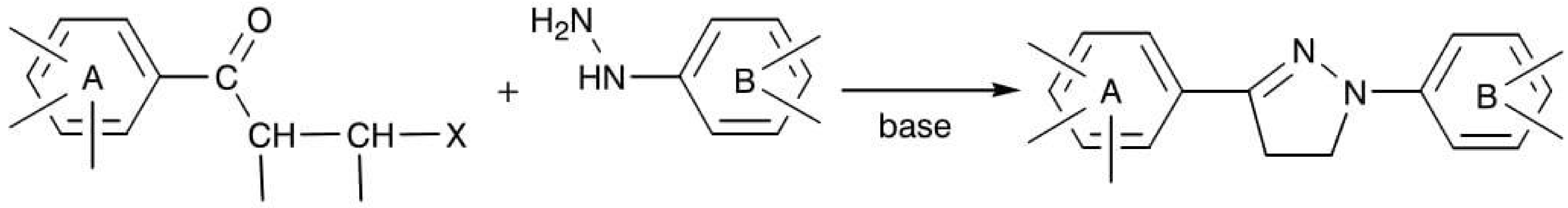


11.29

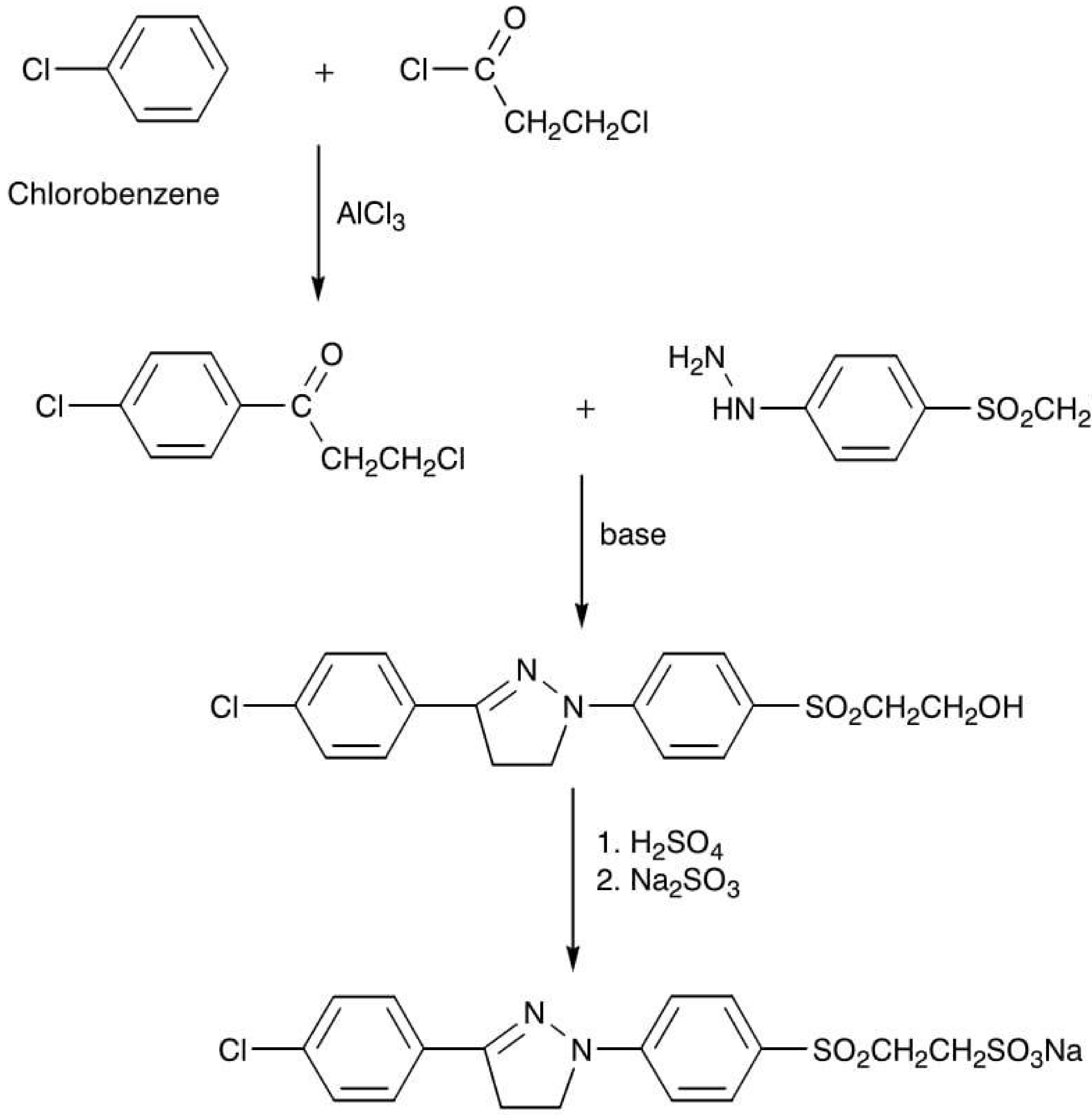
The general method for the preparation of diphenylpyrazolines is shown in Scheme 11.8, in which X is a suitable leaving group, usually chloro but sometimes dialkylamino. This reaction normally proceeds readily, although pH control may be important. Preparation of the substituted ketone and hydrazine intermediates needed for the synthesis may involve lengthy and complicated sequences. Further reactions are often required to modify the substitution in ring B after formation of the pyrazoline ring. The preparation of compound 11.26 shown in Scheme 11.9 illustrates one of the simpler instances.

Derivatives of 1,3-diphenylpyrazoline have been used to brighten cellulose acetate (section 11.7) and acrylic fibres (section 11.11.1) as well as nylon. There has been much study of the effects of substituents on application properties and some general rules can be formulated:

(1) The greater the electron-withdrawing character of substituents in ring A, the greener the hue of brightening.
(2) The greater the electron-withdrawing character of substituents in ring B, the more violet the hue of brightening.
(3) An electron-donating group in the 4-position of the pyrazoline ring has a slight hypsochromic effect, but an electron-withdrawing group has a bathochromic effect.
(4) Light fastness is improved by the introduction of electron-withdrawing substituents into ring A, but is adversely affected by electron-donating substituents.

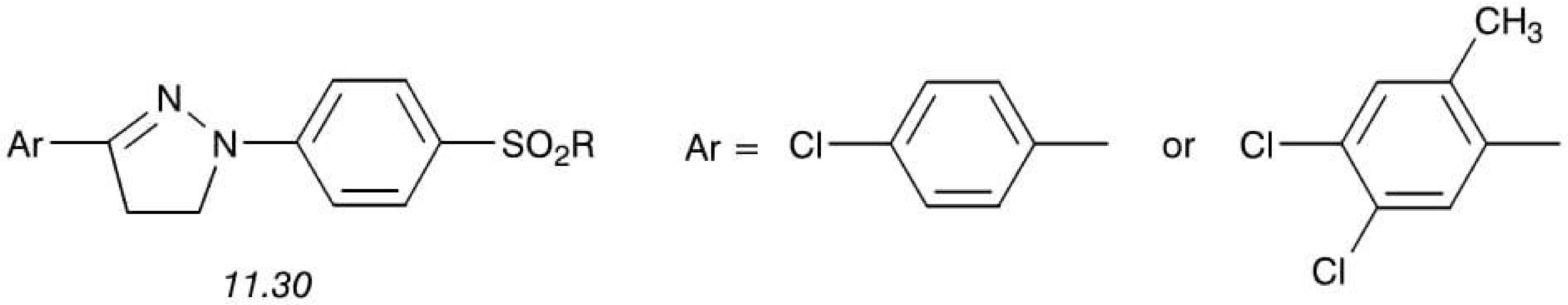


Scheme 11.8



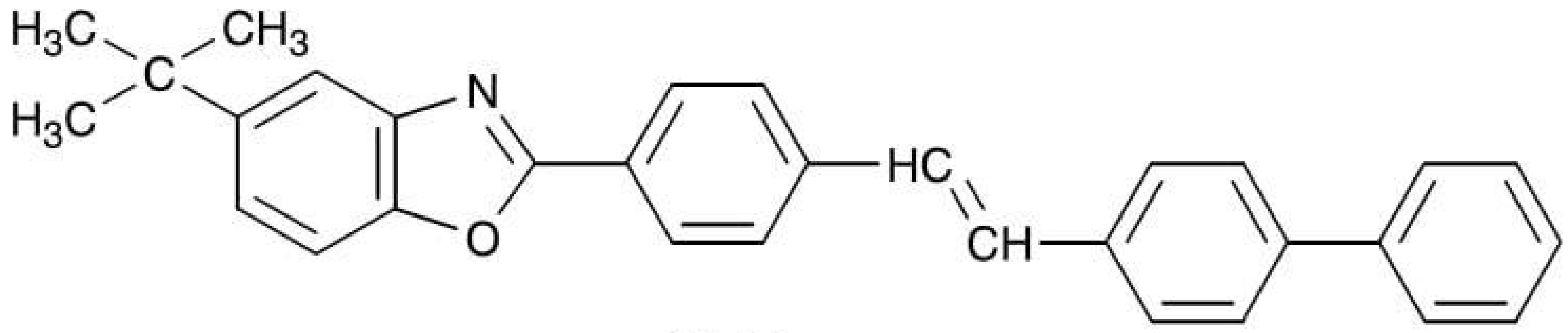
Scheme 11.9 *11.26*

Theoretical explanations for the effects of substituents on the hue of diphenylpyrazoline brighteners have been published by Güsten and co-workers [46,47]. In practice almost all commercially important diphenylpyrazoline FBAs have the general structure 11.30, in which SO_2R is a sulphone or sulphonamide grouping.



11.30

Since pyrazoline FBAs tend to stain cotton they cannot be used to brighten nylon/cotton blends, which require an FBA of the DAST type, the distyryldiphenyl 11.15 or the *vic*-triazole 11.17. The two most important of these are probably the methoxy-substituted DAST product in Table 11.1 and the distyryldiphenyl derivative. By careful adjustment of the dyebath pH these products will exhaust onto both nylon and cotton to give a good solid white. Nylon can also be brightened by incorporation of a thermally stable FBA in the melt, the FBA being added to the polymer before extrusion or shaping. Structure 11.31 is typical of the compounds selected for this purpose. The benzoxazole ring system is particularly important in intensifying the fluorescence of the stilbene system and conferring high fastness to light.



11.31

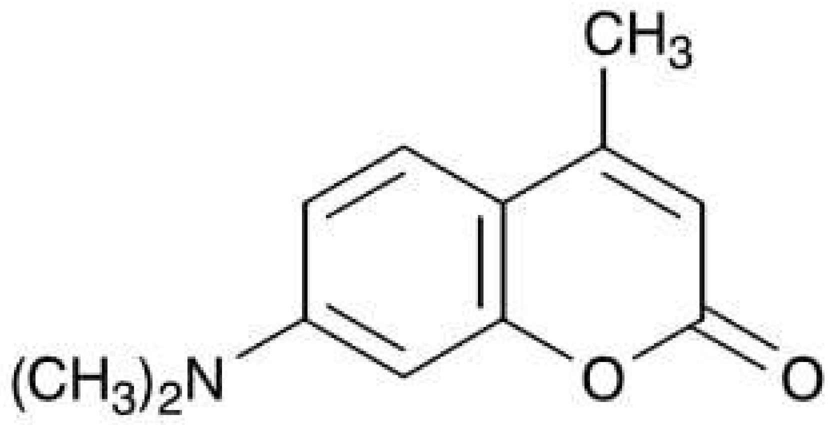
11.9 BRIGHTENERS FOR WOOL

Wool is naturally yellower than other textile substrates and bleached wool gradually becomes yellow again when exposed to sunlight or other ultraviolet sources. The effect of light on wool is complex and depends on the conditions of exposure. The problem of yellowing is accentuated if the wool is left wet in sunlight. Since FBAs absorb ultraviolet light they accelerate this photo-initiated yellowing. The rate of yellowing of bleached wool increases with decrease in wavelength of the incident radiation, 300 nm being the approximate lower limit of ultraviolet reaching the earth from the sun. In contrast, the most important wavelengths for yellowing FBA-treated wool are within the range 340–420 nm. Maximum free-radical formation and acceleration of yellowing occurs in the region 350–410 nm, where brightener excitation takes place [48].

For satisfactory whiteness on wool, it is essential for the fibre to be well scoured and bleached, either oxidatively with hydrogen peroxide or by reduction using stabilised sodium dithionite. Brightener is usually applied together with the dithionite bleach. To achieve the highest possible whiteness, the wool should first be scoured to remove natural waxes and other contaminants, then bleached with peroxide and finally treated with FBA during a second bleach with dithionite.

If wool containing a reducing agent is exposed to irradiation, the rate of yellowing is slower than on untreated wool. Thiourea dioxide is particularly effective in this regard, especially when used in conjunction with formaldehyde. Although thiourea dioxide retards the yellowing of wool treated with an FBA, it does not prevent destruction of the latter. It was shown that this reducing agent minimises yellowing by reducing the coloured products formed on photodegradation of the FBA and certain amino acid residues in the substrate [49].

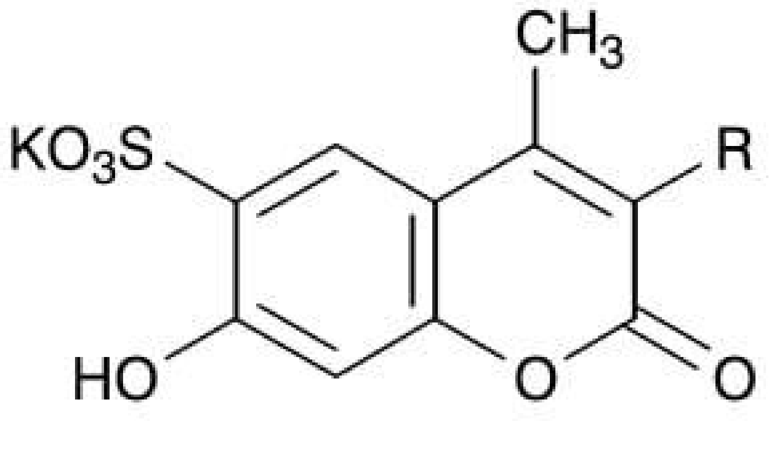
The FBAs used to brighten wool are mainly DAST types and pyrazolines of the acid dyeing type already discussed in section 11.8. Examples include the three most cotton-substantive DAST brighteners listed in Table 11.1, although on wool these give light fastness ratings of only approximately 2. The pyrazolines 11.26–11.28 have light fastness of 3–4 on dry wool, but very poor light fastness in the wet state. The coumarin derivative 11.32 is sometimes used on wool and can give exceptional brilliance, but unfortunately its light fastness is only 1. The important fluorescent coumarin derivatives almost invariably contain an electron-donating substituent in the 7-position, for example a dialkylamino group as in compound 11.32. Furthermore, an electron-withdrawing substituent in the 3- or 4-position, such as a cyano group, leads to shifts of the absorption and emission bands to longer wavelengths [50].



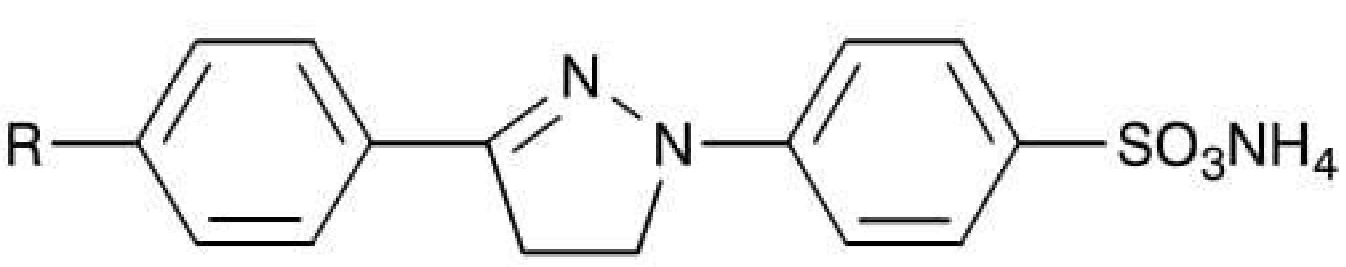
11.32

Although wool is most often brightened using FBAs containing stilbene or pyrazoline fluorescent systems, such compounds degrade rather quickly on exposure to sunlight and also sensitise photodegradation of the wool. Degradation on the surface of wool appears to involve interaction of the stilbene with wool keratin and this is not necessarily a photo-oxidative process. There is good evidence that adsorbed stilbene derivatives can sensitise the formation of singlet oxygen, which then reacts with indole rings (tryptophan residues) in wool. Like the pyrazolines, stilbenes have the facility to self-destruct in photochemical processes [51].

Novel fluorescent anionic surfactants of the types 11.33 and 11.34, where R represents alkyl groups of various lengths, have been applied to wool in order to study their distribution and effects on the physical and chemical properties of the fibre. Sections of the treated fibres were examined under a fluorescence microscope. The intercellular and cell remnant regions appeared to be the preferred locations of the adsorbed surfactants, but the distribution pattern was dependent on the length of the R chain of the surfactant and the conditions of application to wool [52].



11.33



11.34

Fluorescence quenching studies of these alkylated FBAs in aqueous solution were carried out using spectroscopic techniques. For the higher members of each series, plots of fluorescence quantum yield against agent concentration showed a sharp decrease in fluorescence intensity at a specific concentration, in contrast to the smoothly decreasing curve characteristic of the lower alkyl or unsubstituted FBAs. The kinetics of fluorescence quenching were consistent with the formation of micelles from the more surface-active higher alkyl derivatives [53].

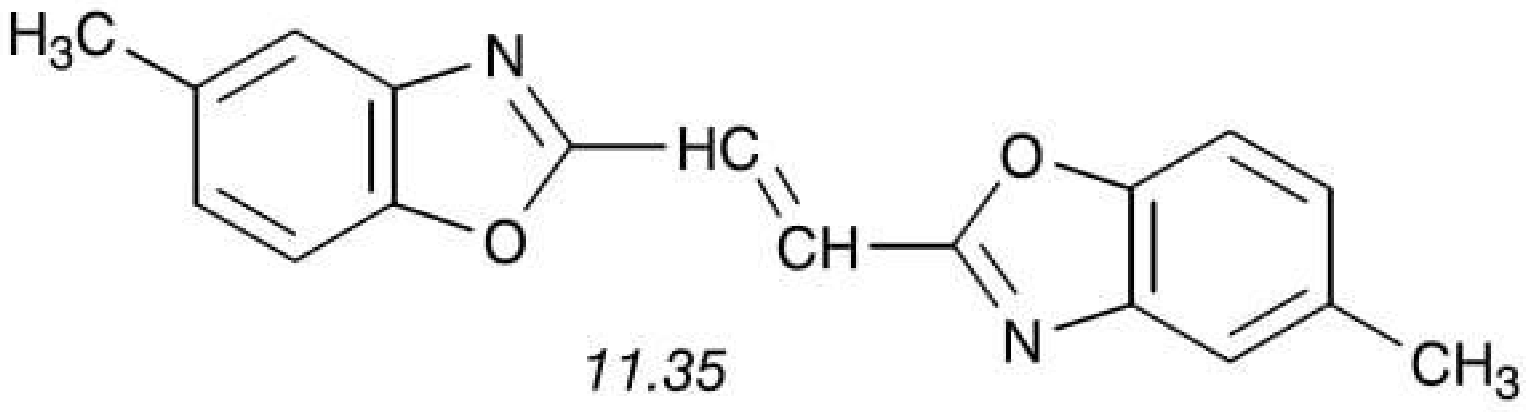
Long-lived transient species have been detected during laser flash photolysis of solutions of the disulphonated distyryldiphenyl derivative 11.15. These transients are readily quenched by reducing agents but their yield is enhanced in the presence of oxidising ions. Such species are believed to be radical cations formed following monophotonic photoionisation. Transient quenching is observed in the presence of indole, tryptophan and tryptophyl peptides. These results are indicative of the sensitised photodegradation of wool keratin in the presence of FBAs of the distyrylarene class [54].

11.10 BRIGHTENERS FOR POLYESTER FIBRES

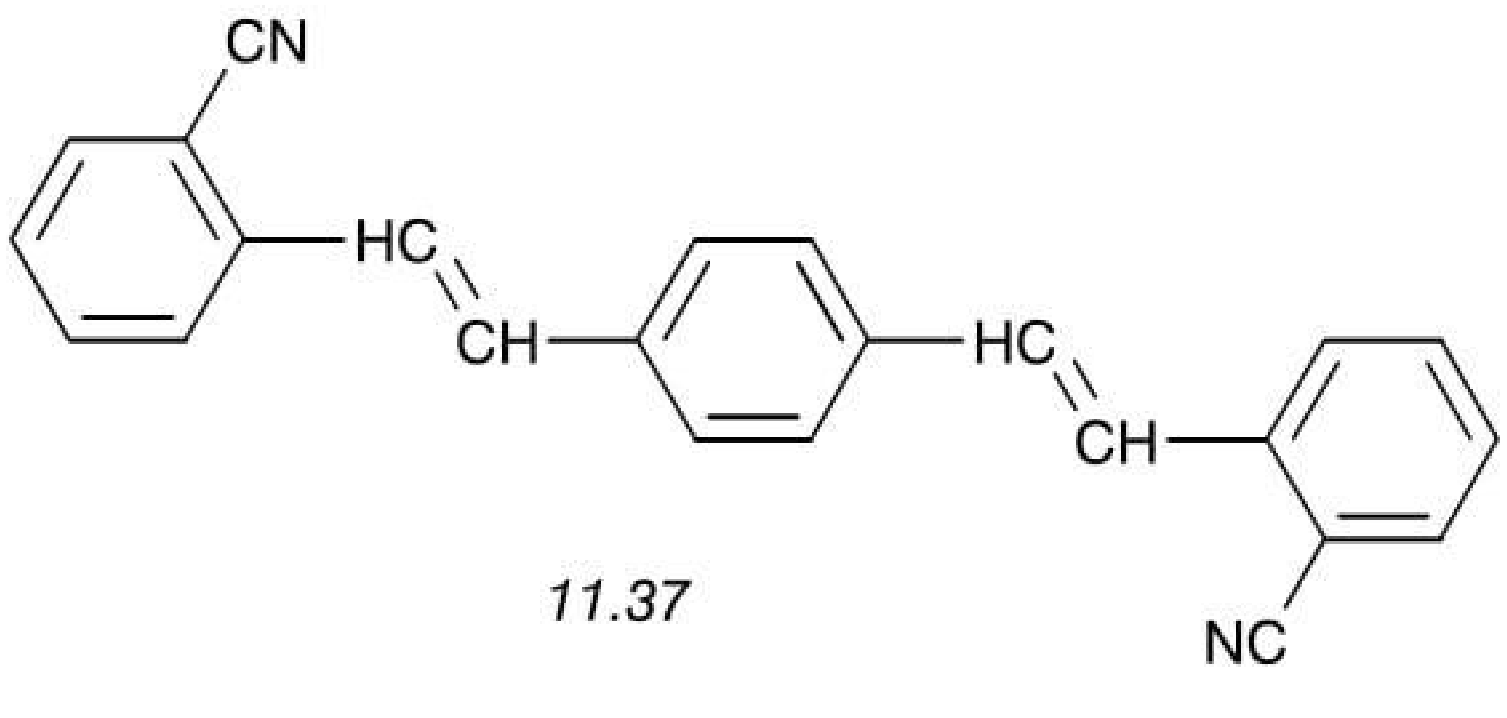
Much research has focused on the development of better brighteners for application to polyester. Huge numbers of patents have appeared and it is impossible to cover all the chemical variations in this chapter. Many of the more important commercial products and chemical types are discussed here but the reader is referred to published reviews [5,6,10,11] for more detail.

Although polyester is always brightened with disperse-type products, the methods of application vary. FBAs are marketed for incorporation in the polymer mass, for exhaust application with or without carrier and for use in the pad–thermosol process at a temperature within the range 160–220 °C. Most products are applicable by more than one method, although none can be applied satisfactorily by all methods and cost-effective products introduced in the 1950s still remain important today.

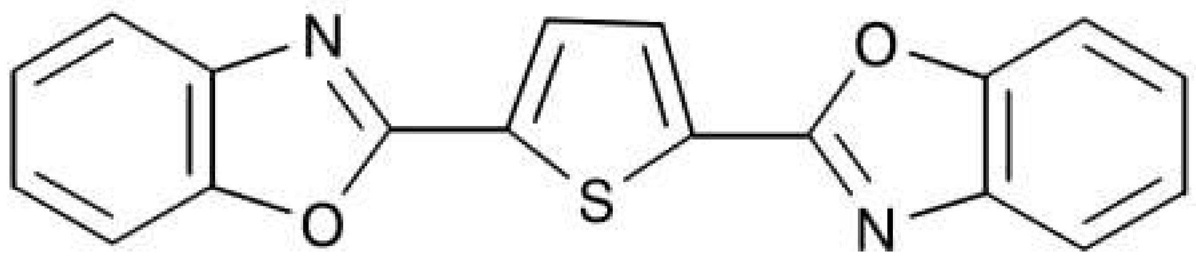
In general and as expected, brighteners of relatively small molecular size are most suitable for application by exhaustion. Less volatile compounds of larger molecular size tend to be preferred for pad–thermosol application or for incorporation in the polymer mass. Commercially important for exhaust application are the previously mentioned pyrene derivative 11.22, the naphthalimide 11.23, the bis(benzoxazolyl)ethene 11.35, the bis(benzoxazolyl)thiophene 11.36, the distyrylbenzene 11.37 and the stilbene bis(acrylic ester) derivative 11.38. Products of the 11.35 type show excellent light fastness but only moderate fastness to sublimation. In view of this volatility they can be used in the transfer printing of polyester.



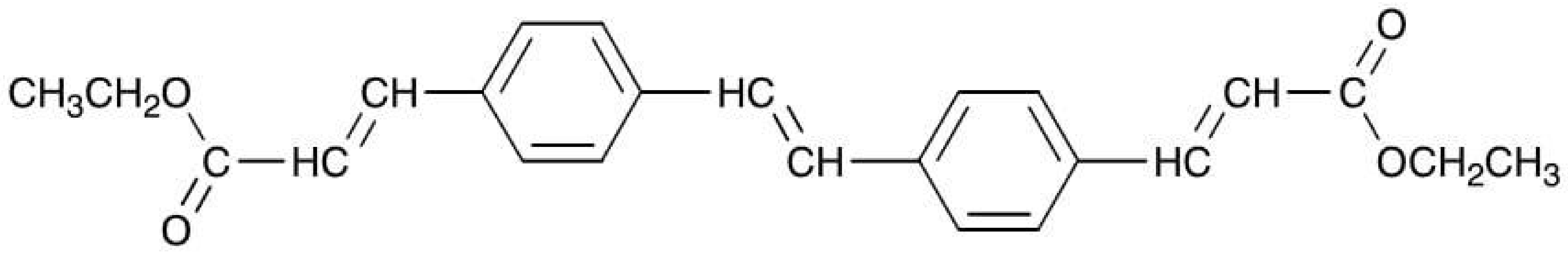
11.35



11.37



11.36

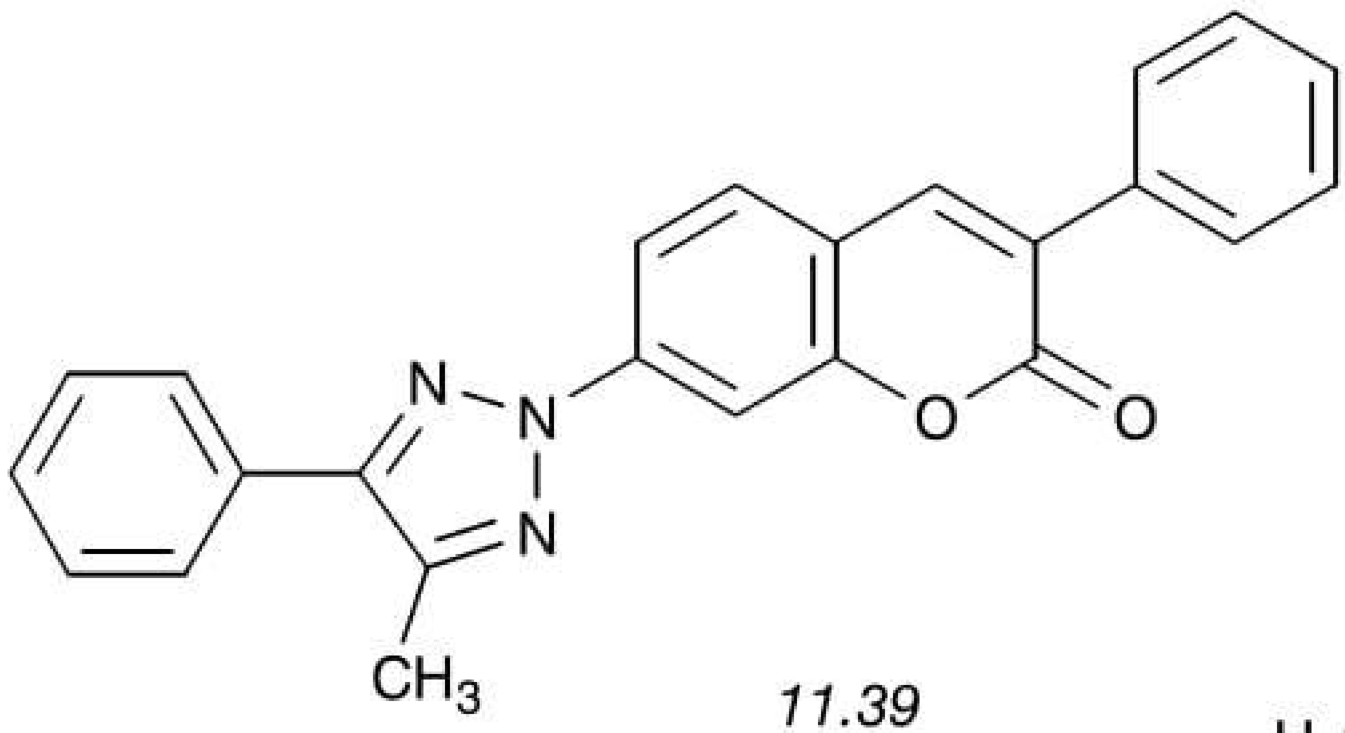


11.38

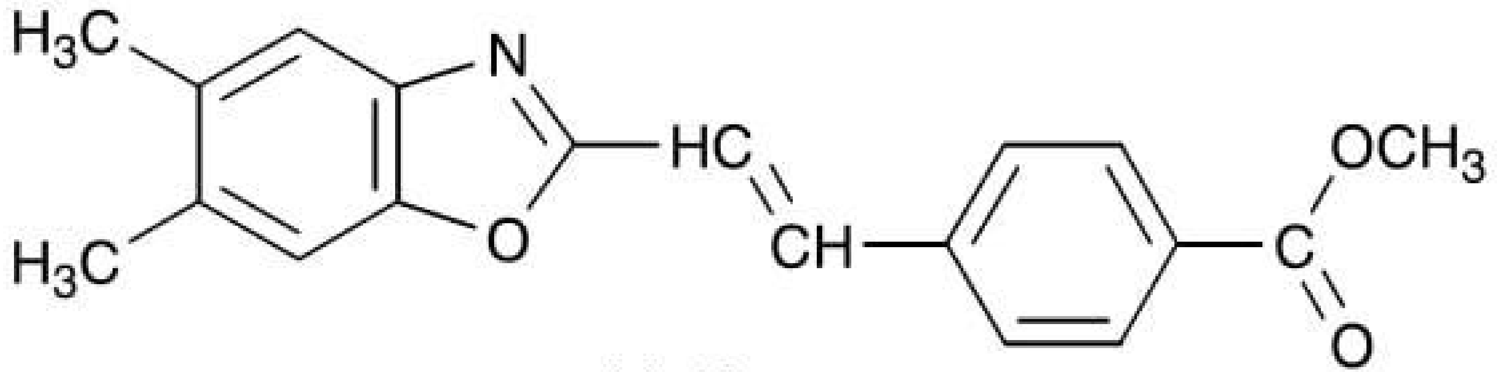
Polyester is brightened more effectively by exhaustion either in pressurised equipment at 125–130 °C or at the boil in the presence of a carrier. Small amounts of carrier may be added to assist levelling in the high-temperature process but the use of carriers is increasingly deprecated for environmental reasons. Commercially satisfactory results are obtained at the boil in the absence of carrier using rapidly diffusing FBAs of relatively small molecular size, such as the naphthalimide 11.23 or the benzoxazole derivatives 11.35 and 11.36. Polyester FBAs that are suitable for exhaust application are normally stable to sodium chlorite bleaching, although the pyrene derivative 11.22 and the bis-ester 11.38 are exceptions.

Most of the FBAs used to brighten polyester by exhaustion may also be applied successfully by the pad–thermosol method at a baking temperature up to 190 °C. At temperatures higher than this the more volatile brighteners sublime and give poor yields. Compounds suitable for use with a baking temperature that exceeds 190 °C include the pyrene derivative 11.22, the benzoxazole 11.31, the distyrylbenzene 11.37 and the stilbene bis-ester 11.38. The temperature used during the baking stage in this process depends largely on the equipment available to the finisher. Thus FBAs showing optimum performance at temperatures ranging from 160 to 220 °C all have a niche in the market. Shorter baking times, leading to greater throughput of brightened fabric, are possible at the higher temperatures, although energy costs are greater. Products capable of giving good whiteness at relatively low thermosol temperatures appear to be gaining in importance [12].

Many other compounds have been marketed as polyester brighteners for application by exhaustion or in the pad–thermosol process. No account would be complete without mention of the important class of coumarin disperse FBAs, of which structure 11.39 is a typical example. Many commercial brighteners for polyester contain one or two benzoxazole groups, including compounds 11.31, 11.35, 11.36, 11.40 and 11.41.



11.39



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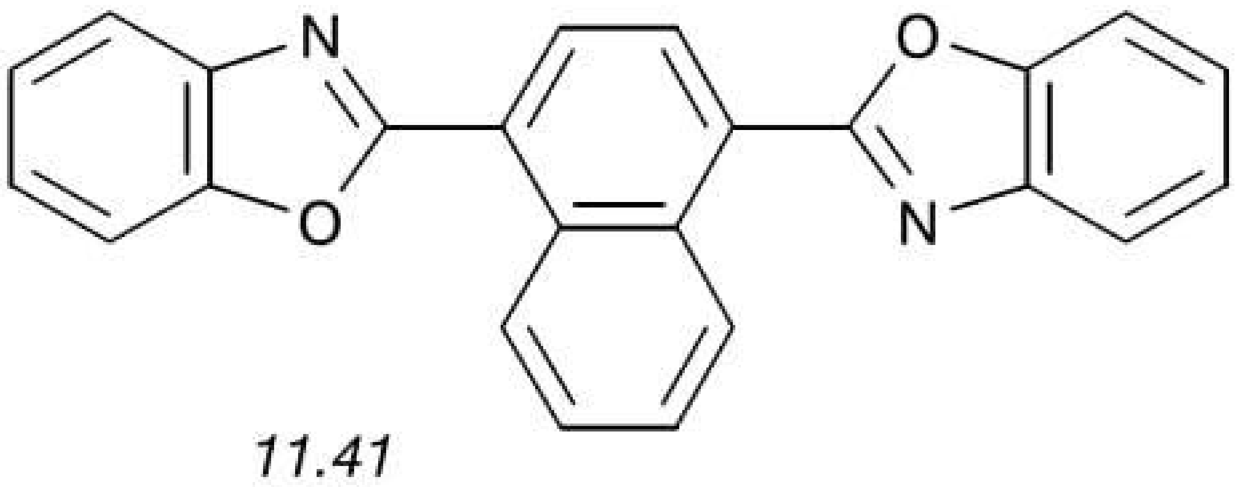

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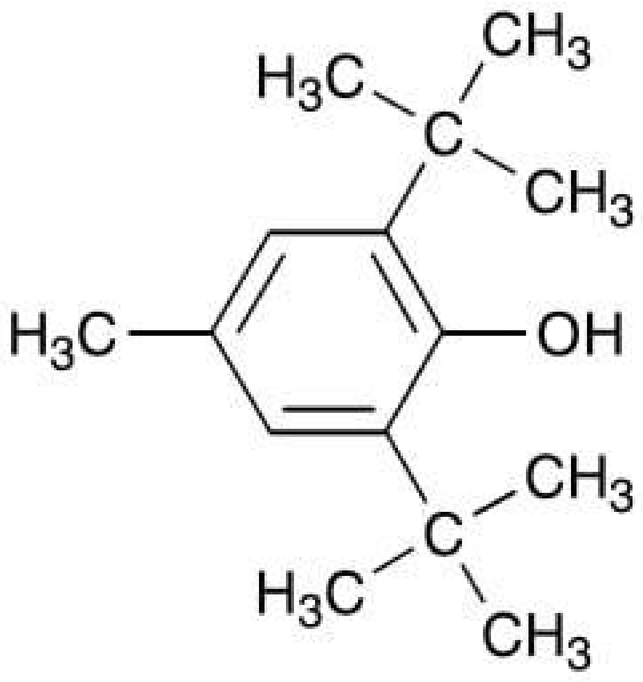


11.42

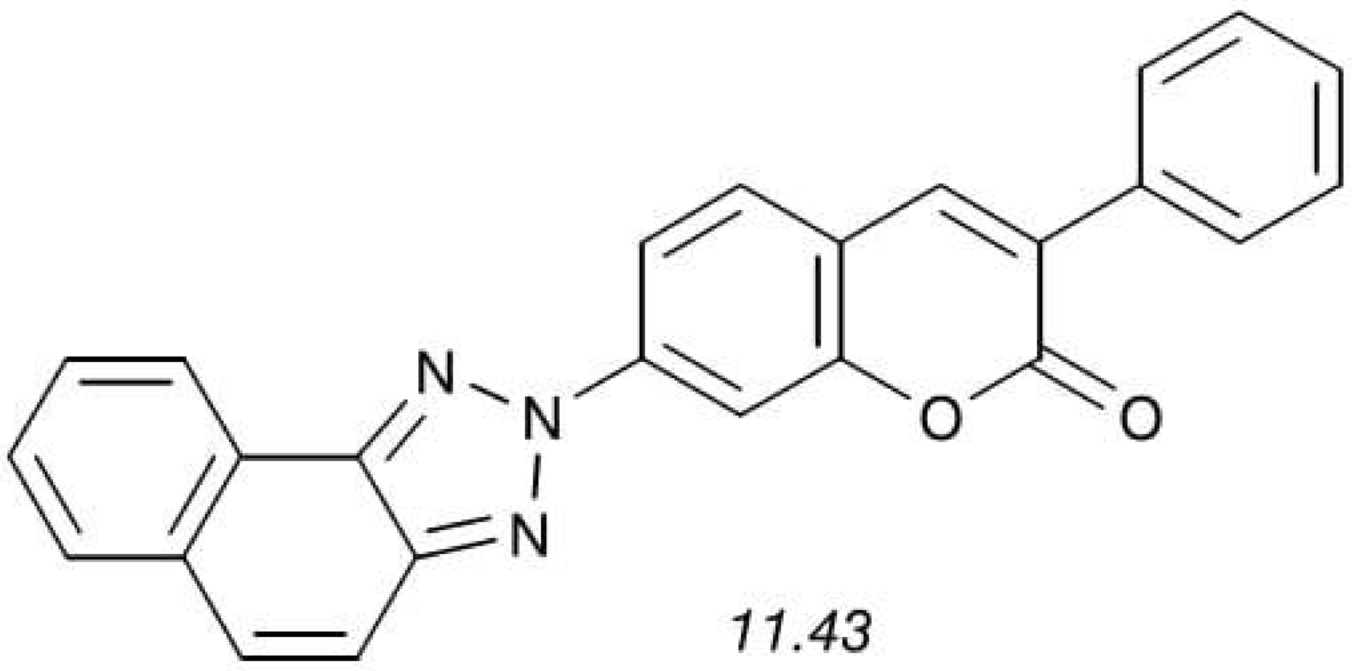
Polyester brighteners typically show excellent fastness properties. Light fastness is usually 5–6, the pyrene derivative 11.22 being an exception with light fastness of only 2–3. Although this compound gives a distinctly greenish brightening tone it is capable of producing remarkably brilliant whites and remains an important commercial product.

Yellowing of white textiles in the presence of gas fumes (nitrogen oxides) has become important in recent years. The yellowing is often attributable to the formation of quinonoid compounds arising from reaction between the oxides of nitrogen and antioxidants such as di-t-butyl-*p*-cresol 11.42 present in packaging materials. Reinehr and Schmidt have shown that several polyester FBAs yellow in the presence of exceptionally high concentrations of nitrogen oxides, but they were unable to detect any significant yellowing at concentrations likely to be approached in practice [55].

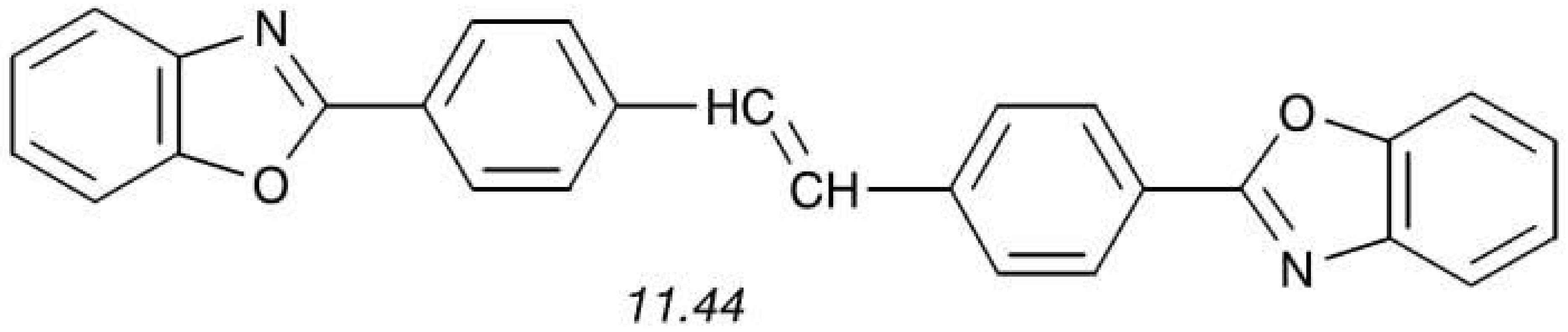
Synergistic effects can often be observed with polyester brighteners and formulated mixtures of brighteners are increasing in importance. For example, mixture products containing the pyrene derivative 11.22 with either the naphthalimide 11.23 or the benzoxazole 11.35 have been marketed. This property may be exploited either to increase the maximum whiteness achievable or to attain a desired level of whiteness by applying a lower concentration of the synergistic mixture. The subject has been discussed by Martini and Probst [56], but the mechanism by which the synergy operates is not completely understood.

In a recent evaluation of this phenomenon, the whiteness indices given by eleven individual brighteners on polyester were compared with those of their binary mixtures in various ratios. In many cases the whiteness performance of a mixture was markedly superior to that shown by the individual components [57]. A more specific investigation was confined to a series of benzoxazole FBAs. Their fluorescence spectra and fluorescence lifetimes were determined individually and in mixtures. The relationships between molecular structure and photophysical properties were discussed [58].

Much polyester fibre intended for curtain net or other white goods is sold in pre-brightened form. The brightener is added to the polymer melt before or during extrusion, so it must exhibit high thermal stability. Two important FBAs used in this way are the triazolylcoumarin 11.43 and the bis(benzoxazolyl)stilbene 11.44. The latter structure provides brilliant whiteness with a violet tone, more pleasing to most observers than the slightly greenish hue given by compound 11.43. The coumarin, however, is stable under the conditions of condensation polymerisation and can be incorporated before polymer manufacture. The benzoxazole is not entirely stable and this has to be added to the polymer granules immediately before extrusion. Polyester brightened with the coumarin has a light fastness rating greater than 7, making it very important commercially. The presence of the phenyl and naphthotriazolyl groupings, contributing π-electron mobility in positions 3 and 7 respectively, markedly amplifies the fluorescence intensity, as well as conferring exceptional photostability.



11.43



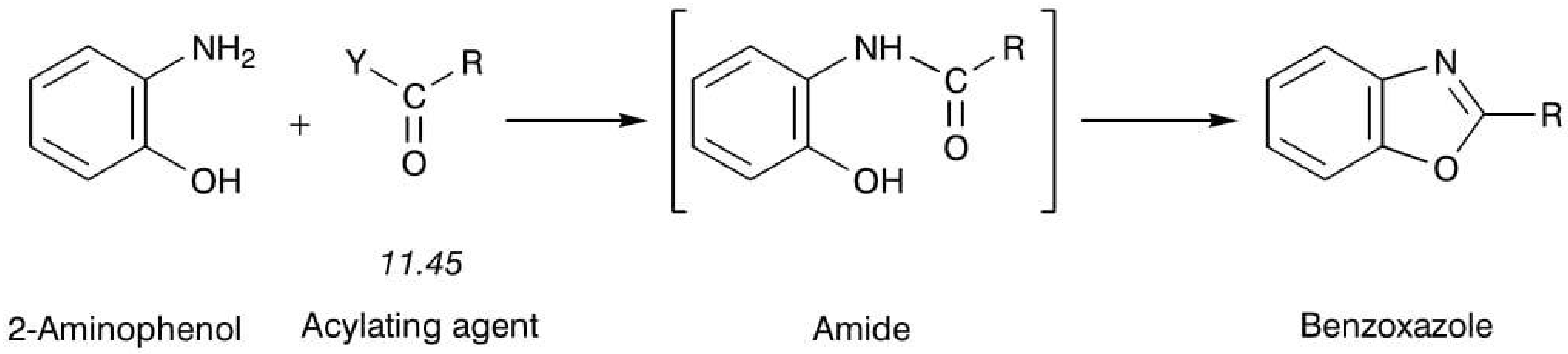
11.44

The photochemical fading of disperse dyeings on polyester is retarded if an FBA has been applied by mass pigmentation before extrusion. The higher the concentration of FBA present, the greater is the protective effect on the light fastness of the disperse dyes [59]. Studies of the mechanism of photochemical decomposition of DAST-type brighteners have shown that stilbenes may act not only as sensitisers to produce singlet oxygen, but also as physical and chemical quenchers [60]. Owing to their capacity to self-destruct by such mechanisms, certain types of FBA can be preferentially destroyed in the presence of the photochemically more stable disperse dye molecules [59].

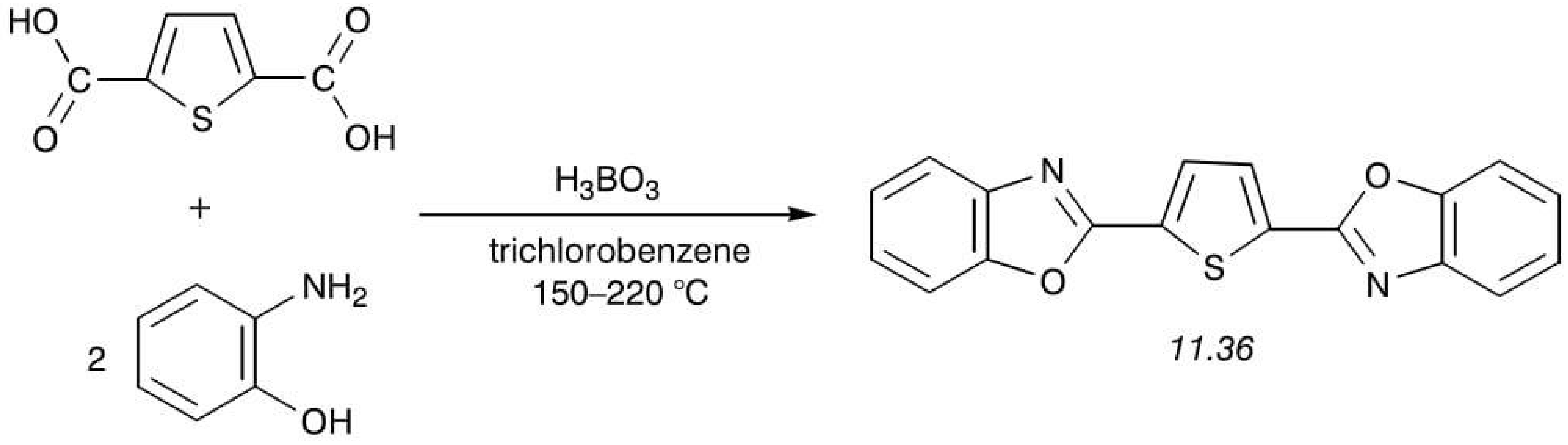
Since the structures of polyester FBAs are so varied, the reactions employed in their synthesis are also diverse. The organic chemistry can be complex and the intermediates required are often difficult to prepare. A full discussion is beyond the scope of this chapter. The reader is referred, in the first place, to the reviews mentioned in the introduction for further information [3–13]. A summary of the more important methods of manufacture follows.

Those polyester FBAs containing a benzoxazole group are usually prepared from the appropriate *o*-aminophenol and carboxylic acid (11.45; Y = OH) or one of its derivatives, as shown in Scheme 11.10. The reaction proceeds via an intermediate amide and it can be advantageous to start from an acid derivative such as the acid chloride (11.45; Y = Cl) or ester (11.45; Y = OEt), which are both more effective acylating agents. The preparation of compound 11.36, shown in Scheme 11.11, illustrates this process, but the optimum conditions for ring closure vary considerably from one structure to another. The article by Gold contains a valuable and detailed summary [4].

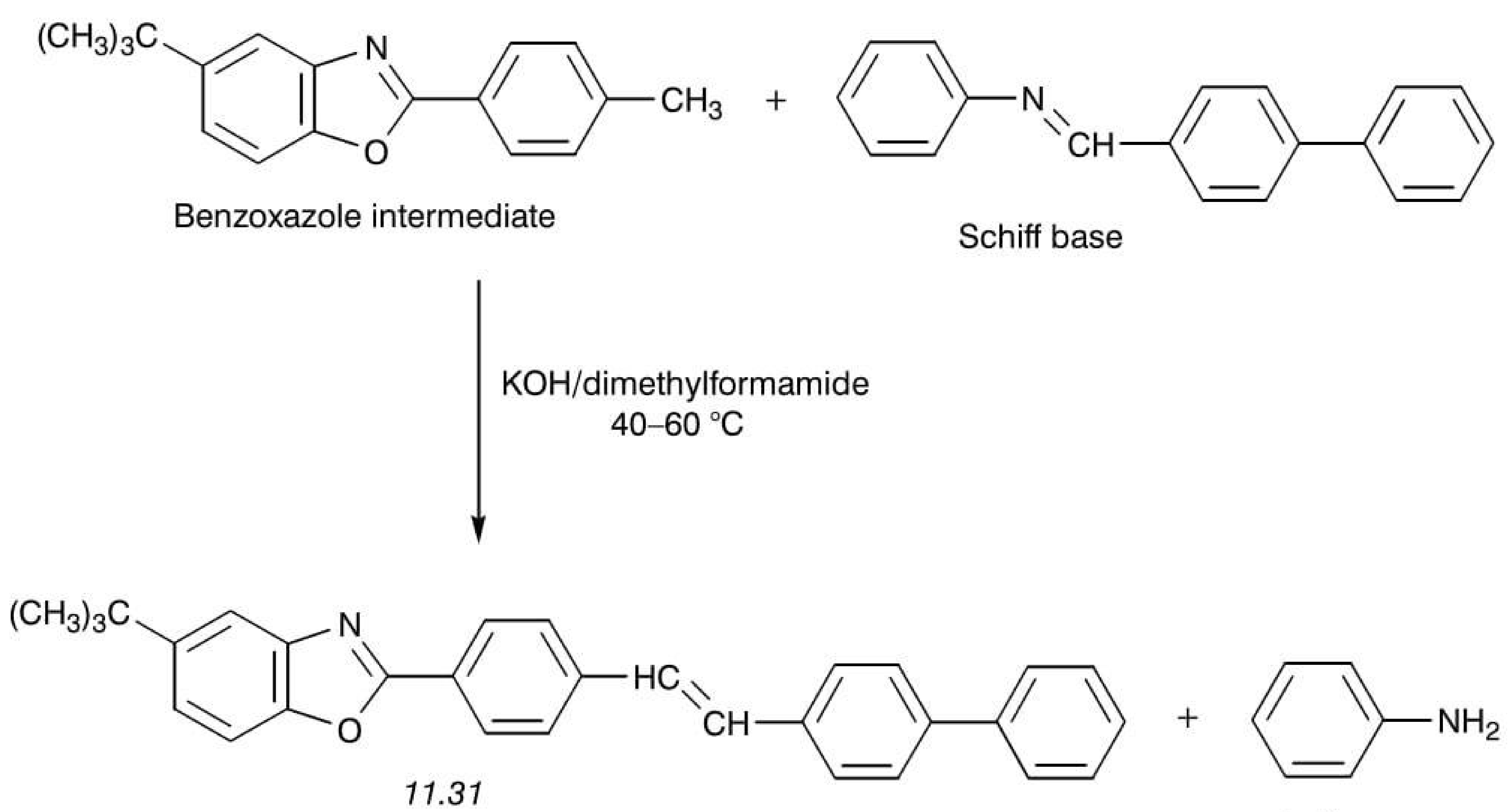
Formation of the oxazole ring is not always the last step in synthesis of the brightener. Unsymmetrical compounds that contain both a benzoxazole group and an ethene linkage can be prepared by the anil synthesis [51], in which a compound possessing an activated methyl group reacts with a Schiff base. The preparation of brightener 11.31 is an illustration of this method (Scheme 11.12).



Scheme 11.10



Scheme 11.11



Scheme 11.12

Most of the important class of coumarins used as polyester FBAs are made via 7-amino-3-phenylcoumarin (11.46), which can be prepared by the Pechmann procedure from *m*-aminophenol. Conversion of intermediate 11.46 to FBAs may be achieved in various ways, two of which are shown in Scheme 11.13.

The naphthalimide 11.23 is manufactured from acenaphthene by sulphonation, oxidation to the naphthalic anhydride derivative and conversion to 4-methoxy-*N*-methylnaphthalimide as outlined in Scheme 11.14.

A Michaelis-Arbusov rearrangement followed by a Wittig-Horner reaction is involved in preparation of the distyrylbenzene derivative 11.37, as shown in Scheme 11.15. Precautions must be taken in the first stage to minimise formation of the carcinogenic by-product bis(chloromethyl) ether 11.16. The stilbene bis-ester 11.38 can be made by a similar procedure, or alternatively by the reaction of ethyl acrylate with 4,4′-dibromostilbene in the presence of a palladium-based catalyst (Scheme 11.16), a synthesis that yields the required *trans* form of the brightener.

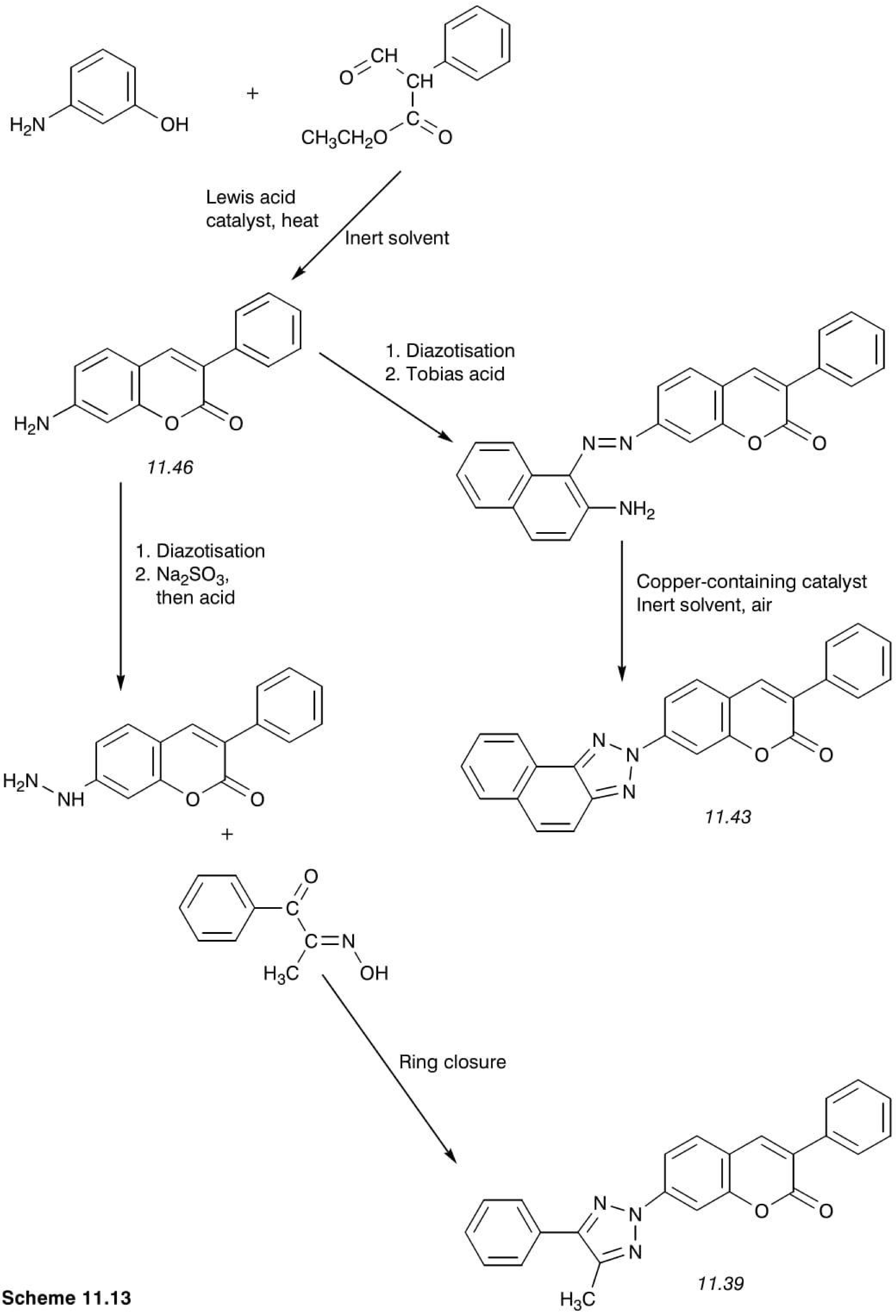
The important bluish mixing component 11.22 for whitening polyester is made by Friedel-Crafts acylation of pyrene (Scheme 11.17). This tetracyclic hydrocarbon is not unlike anthracene in its susceptibility to substitution reactions. The most stable bond arrangement in pyrene appears to be that shown as form 11.47a, which contains three benzenoid (b) rings. Canonical form 11.47b, containing only two such rings, contributes to a lesser extent (Scheme 11.18). In all monosubstitutions, pyrene is attacked initially at the 3-position, corresponding to the α-positions in anthracene or naphthalene.

Brightener structures of only moderate molecular size are of interest for white grounds in the transfer printing of polyester fabrics. Derivatives of 6-acetamidoquinoxaline with an electron-donating substituent (X) in the 2-position (11.48) were prepared by converting quinoxalin-2-one to 2-chloro-6-nitroquinoxaline and condensation with amines (X = RNH), alcohols (X = RO) or phenols (X = PhO), followed by reduction and acetylation (Scheme 11.19). The nitro intermediates (11.49) are also of interest as low-energy disperse dyes for polyester [61].

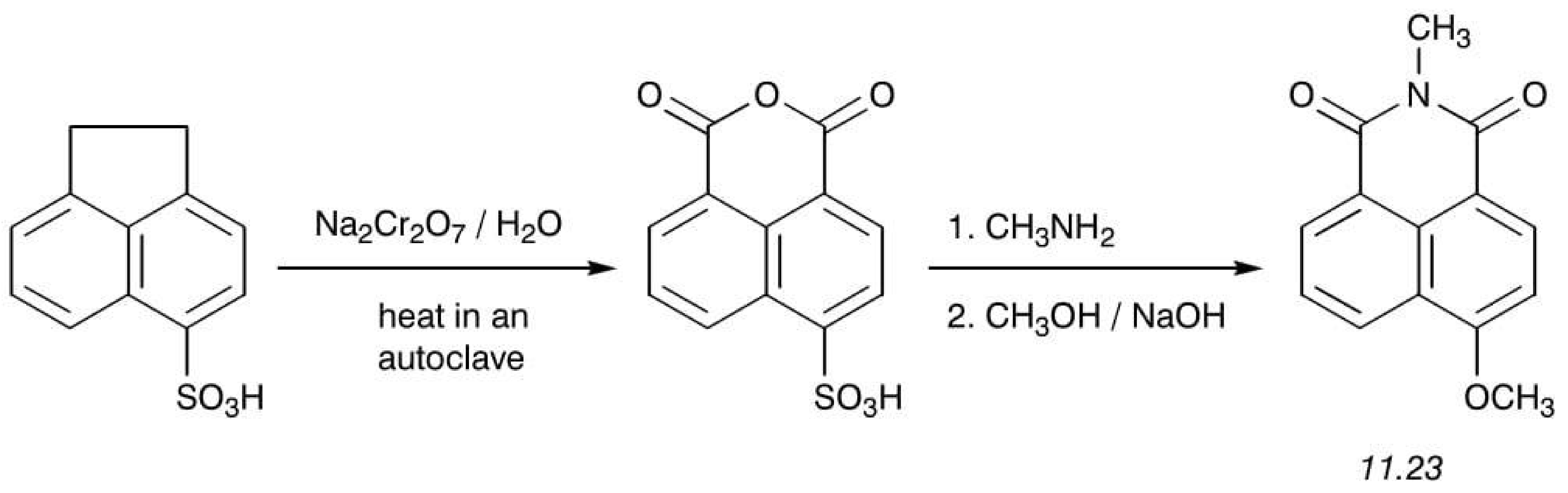
FBAs for incorporation in the polymer melt are usually sold as the pure brightener without diluents. Most polyester FBAs, however, are supplied in the form of an aqueous dispersion. Considerable care is required in formulating these dispersions; not only must the dispersion be stable in transportation and storage, but the dispersing agents selected must not adversely affect the properties (such as light fastness) of the goods treated with the brightener. An FBA must be correctly formulated if it is to succeed commercially.

White polyester/cotton fabrics represent a substantial segment of the market. Such blends can be brightened either by exhaustion or continuously by pad–thermosol or pad–steam processes. Suitable brighteners are selected from those intended for use on polyester or cellulosic substrates. Most polyester/cotton fabrics are woven constructions and it is essential to desize them before application of an FBA. Fabrics produced for sale as white goods must be chemically bleached before, during or after FBA treatment. In order to achieve the most solid white effects both fibre components of the blend require a brightener. The disperse and anionic brighteners selected must be compatible in hue. It is common practice, however, to brighten only one of the blend components for less critical end-uses.

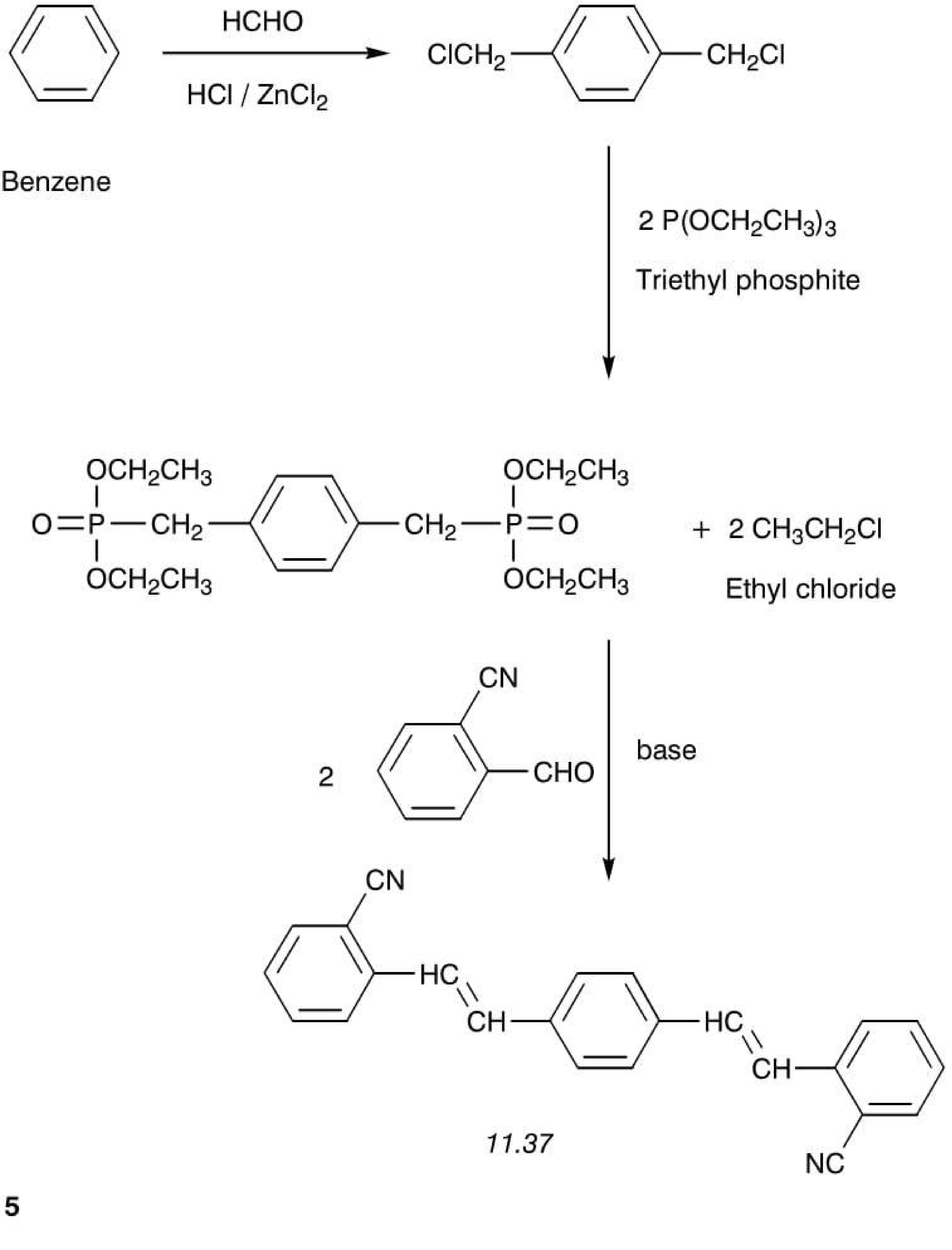
In a recent detailed evaluation of CI Fluorescent Brightener 393 on polyester, this product was incorporated into the polymer melt. The prebrightened fibre was blended with cotton and fabric knitted from these yarns was scoured and bleached. It was demonstrated


H2N
OH
+
O
CH
CH
C
O
CH3CH2O
Lewis acid catalyst, heat
Inert solvent
H2N
O
O
11.46
1. Diazotisation
2. Tobias acid
N=N
NH2
O
O
1. Diazotisation
2. Na2SO3, then acid
Copper-containing catalyst
Inert solvent, air
H2N
NH
O
O
+
N
N
N
O
O
11.43
O
C
C=N
H3C
OH
Ring closure
N
N
N
O
O
H3C
11.39

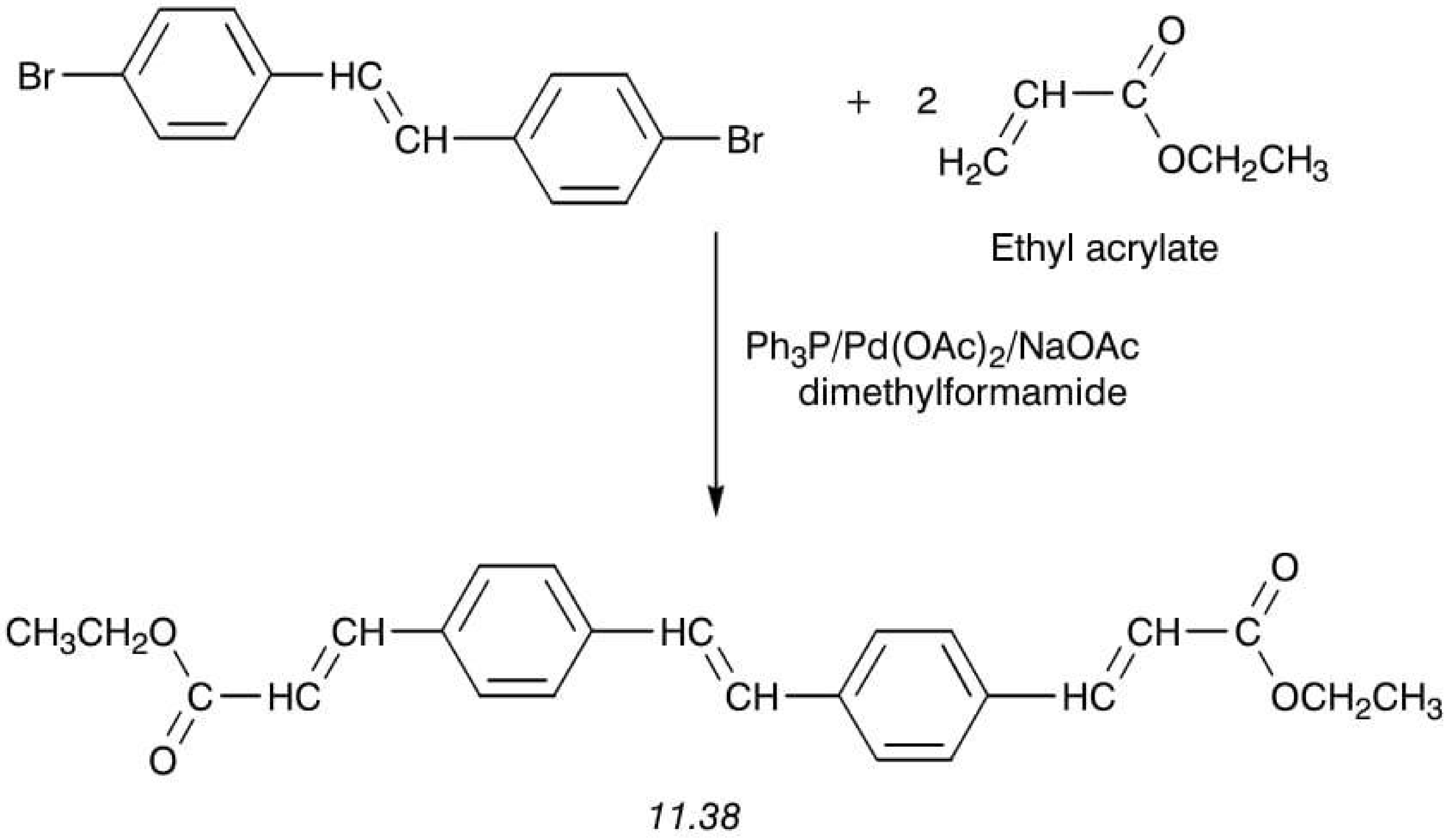
Scheme 11.13



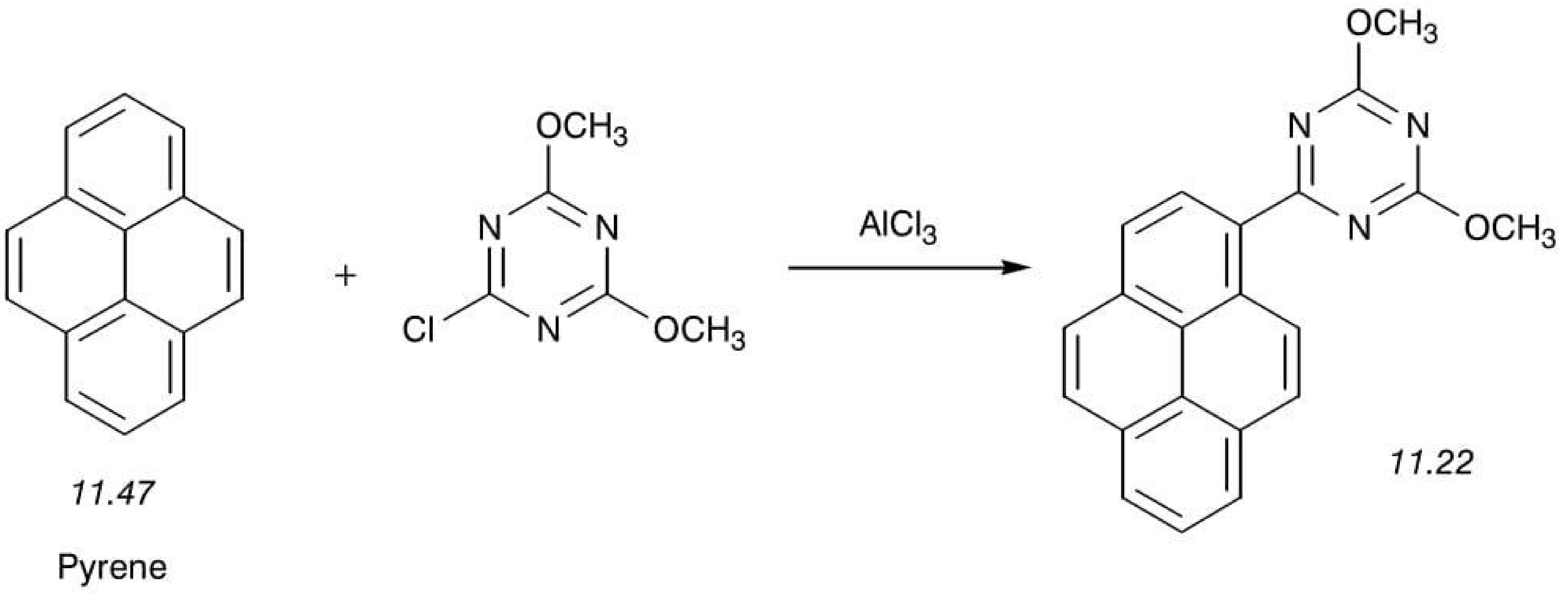
Scheme 11.14



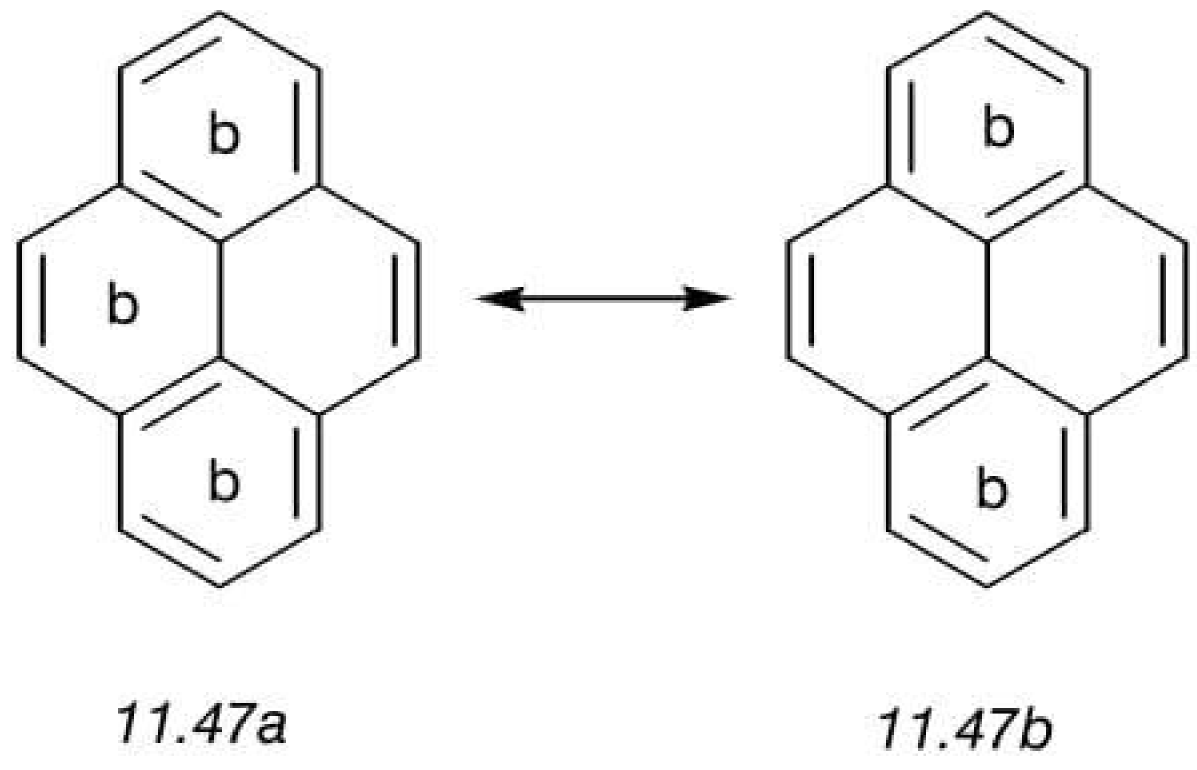
Scheme 11.15



Scheme 11.16



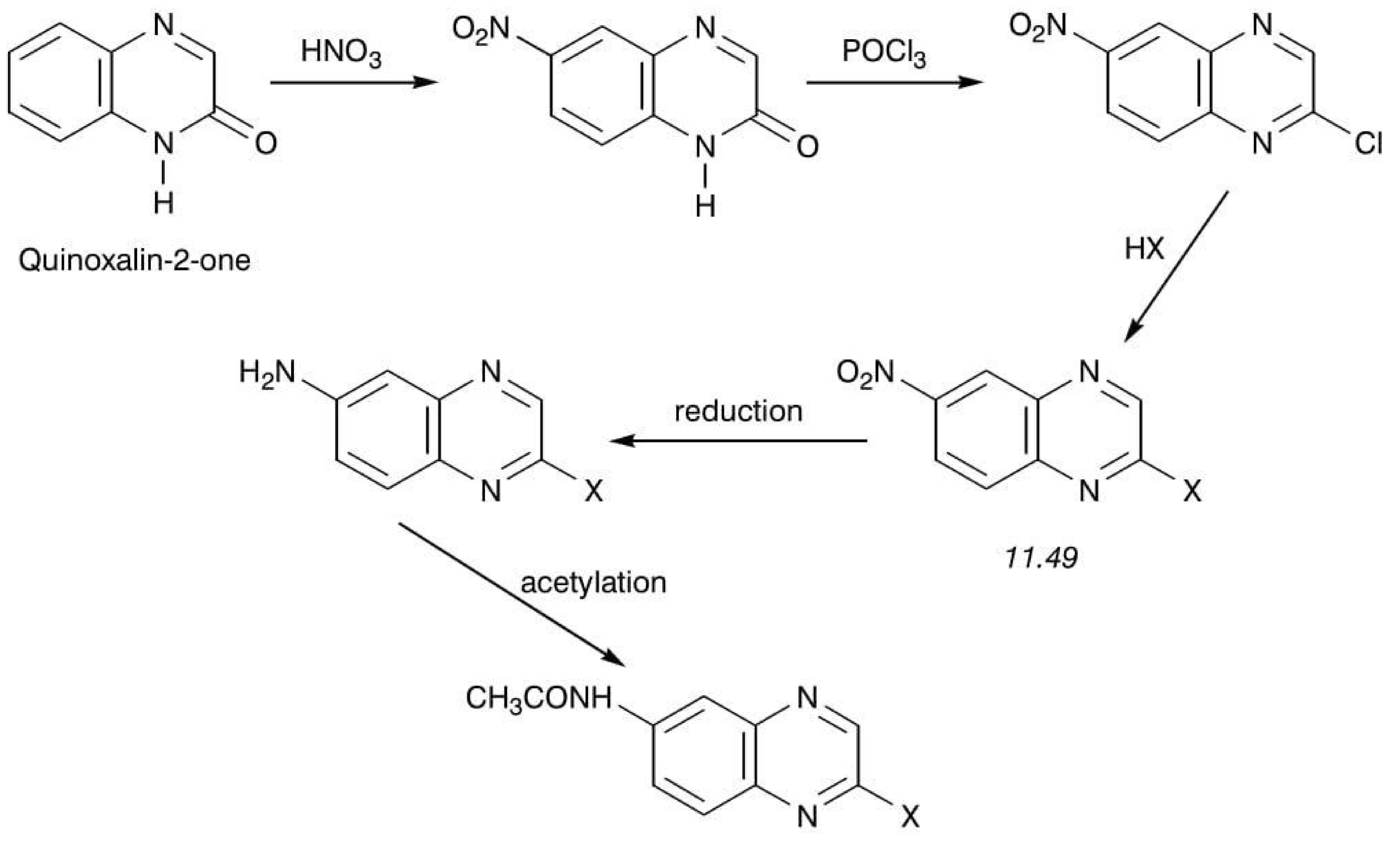
Scheme 11.17



Scheme 11.18

that if an effective cotton bleaching process is applied in combination with producer-brightened polyester, the final degree of whiteness is sufficiently high to avoid the use of a cotton-substantive fluorescent brightener [62].

If a padding process is used to brighten a polyester/cotton blend, both the disperse and anionic brighteners may be applied from the same pad bath, even when a resin finish is applied simultaneously to the cellulosic component of the blend. Similarly, both types of



Scheme 11.19

FBA may be applied by exhaustion from the same bath. If the polyester portion of the blend is to be bleached with sodium chlorite, the cotton is usually brightened in a second step since most FBAs for cotton are destroyed by sodium chlorite. Both types of FBA are normally compatible with a hydrogen peroxide bleaching process.

11.11 BRIGHTENERS FOR ACRYLIC FIBRES

At one time disperse-type FBAs, such as pyrazoline, coumarin or naphthalimide derivatives, were commonly used to brighten acrylic fibres. Today all the important brighteners for these fibres are cationic in character and can be divided into two main categories:

- type A: products that are oxidised by sodium chlorite
- type B: products that are stable to sodium chlorite.

Type B brighteners can be applied in the absence of bleach, of course, but show their best results when applied simultaneously with sodium chlorite, where they are capable of giving exceptionally high whiteness.

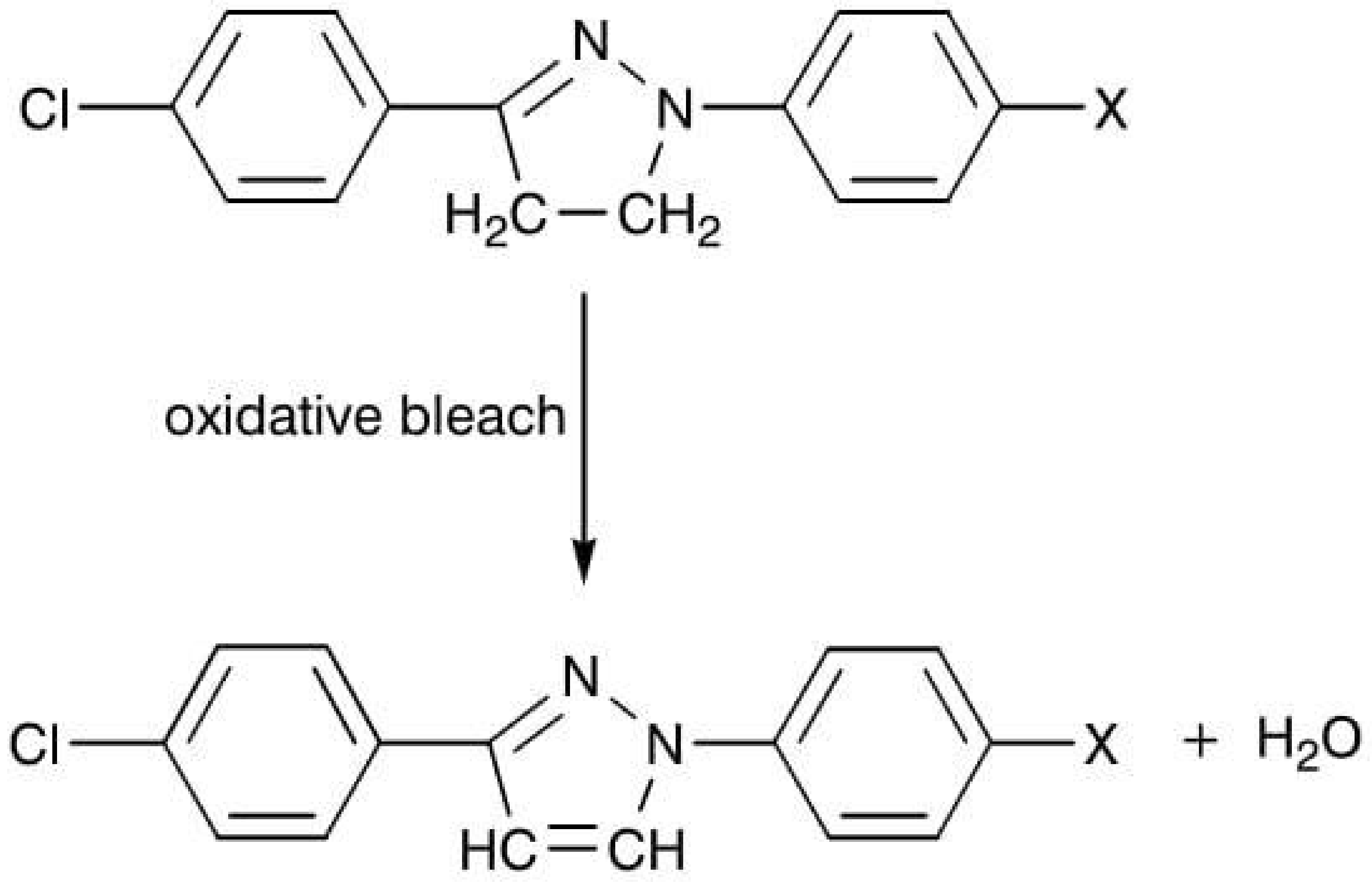
Acrylic fibres are usually brightened from an exhaust bath in the presence of dilute organic acid. Application of brightener by a padding method, such as pad–roll or pad–steam, can be used but is uncommon. When these fibres are brightened from an exhaust bath, careful control of application conditions is necessary. Most acrylic fibres have a glass-transition temperature in the region of approximately 80 °C and the rate of absorption accelerates rapidly with increase in temperature over this critical region. Too rapid an increase in temperature can lead to unlevel absorption of the FBA.

As an alternative to oxidative bleaching with sodium chlorite, acrylic fibres may be given a reductive bleach using sodium bisulphite in the presence of oxalic acid. This method is necessary with Courtelle (Courtaulds) because this fibre would be damaged by chlorite bleaching. Both types of acrylic brightener can be applied with a bisulphite bleach.

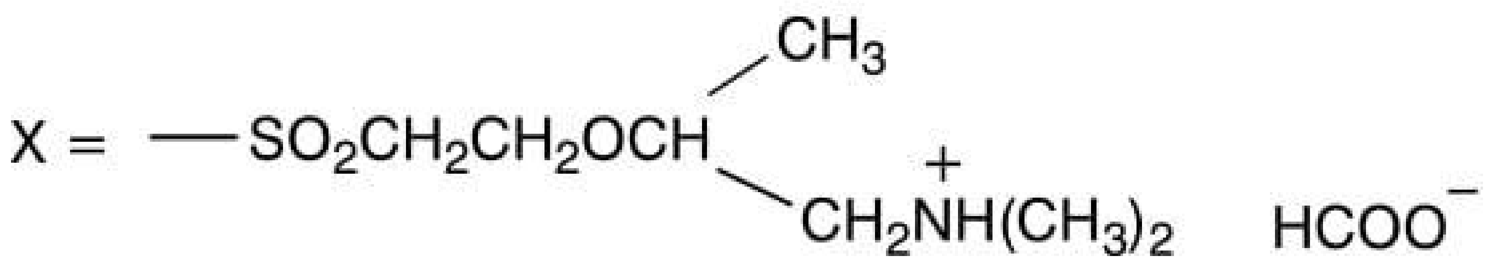
11.11.1 Type A products

This category mainly consists of derivatives of 1,3-diphenylpyrazoline, such as compounds 11.50–11.52. None of these substituted pyrazolines shows significant resistance to oxidative bleaching. The fluorescence stemming from the central ring disappears owing to dehydrogenation to the corresponding pyrazole (Scheme 11.20). The sulphones 11.50 and 11.51 are marketed as aqueous solutions of their formate salts. They produce violet brightening effects of light fastness 4 and are capable of producing excellent whiteness. The sulphonamide 11.52 gives greener effects and is incapable of producing the levels of whiteness attainable using either 11.50 or 11.51. In order to suppress the violet tone slightly and to achieve a higher visual level of whiteness from a given amount of FBA, the sulphone types are sometimes formulated with a small amount of a shading dye.

The general method for the preparation of diphenylpyrazoline FBAs has already been discussed (Scheme 11.8). As a further illustration, the synthesis of the sulphone 11.51 is shown in Scheme 11.21.



Scheme 11.20



$X = -SO_2CH_2CH_2OCH(CH_3)CH_2\overset{+}{N}H(CH_3)_2\quad HCOO^-$

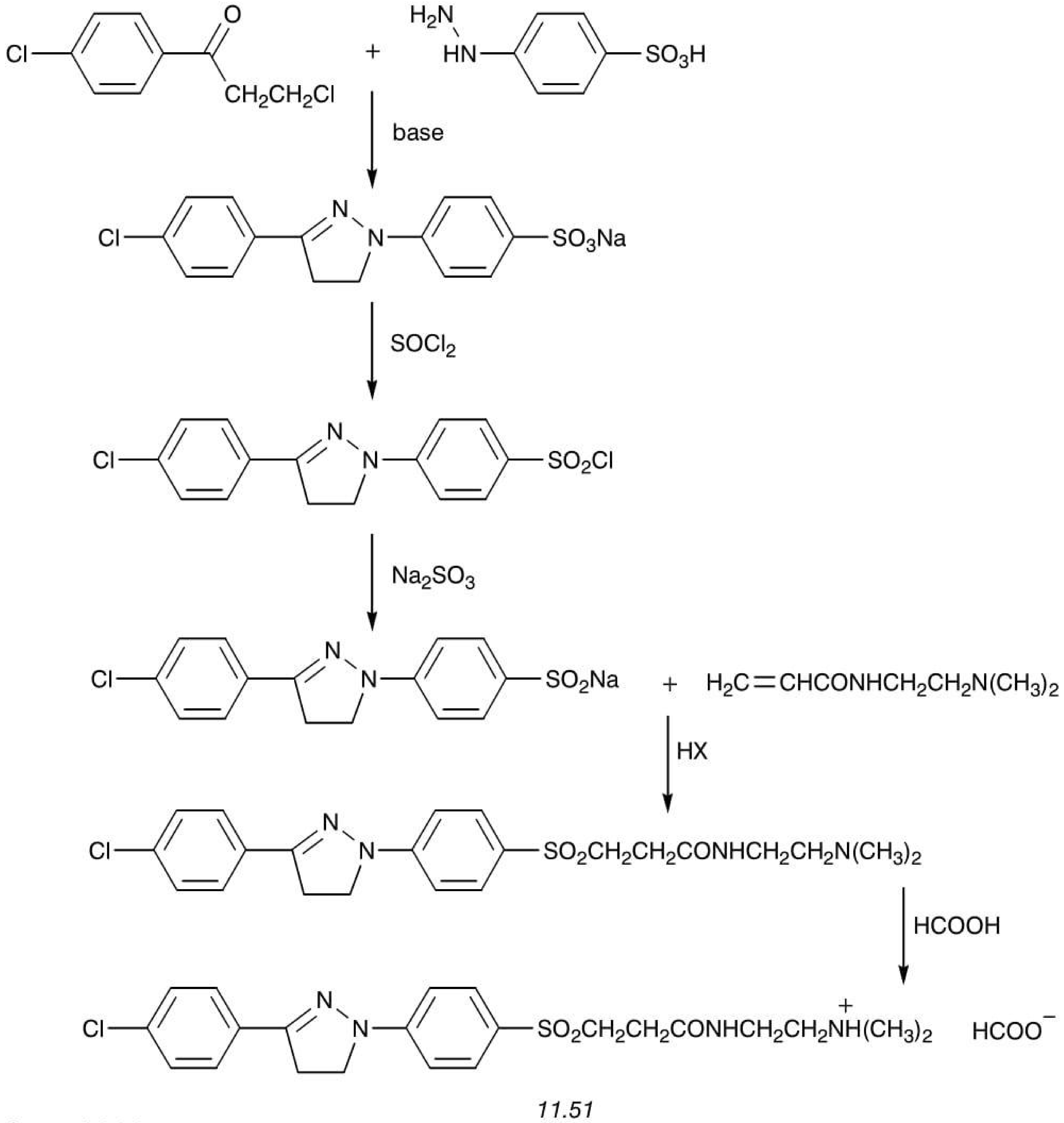
11.50 Cationic grouping Anion

$X = -SO_2CH_2CH_2CONHCH_2CH_2\overset{+}{N}H(CH_3)_2\quad HCOO^-$

11.51 Cationic grouping Anion

$X = -SO_2NHCH_2CH_2CH_2\overset{+}{N}(CH_3)_3\quad Cl^-$

11.52 Cationic grouping Anion



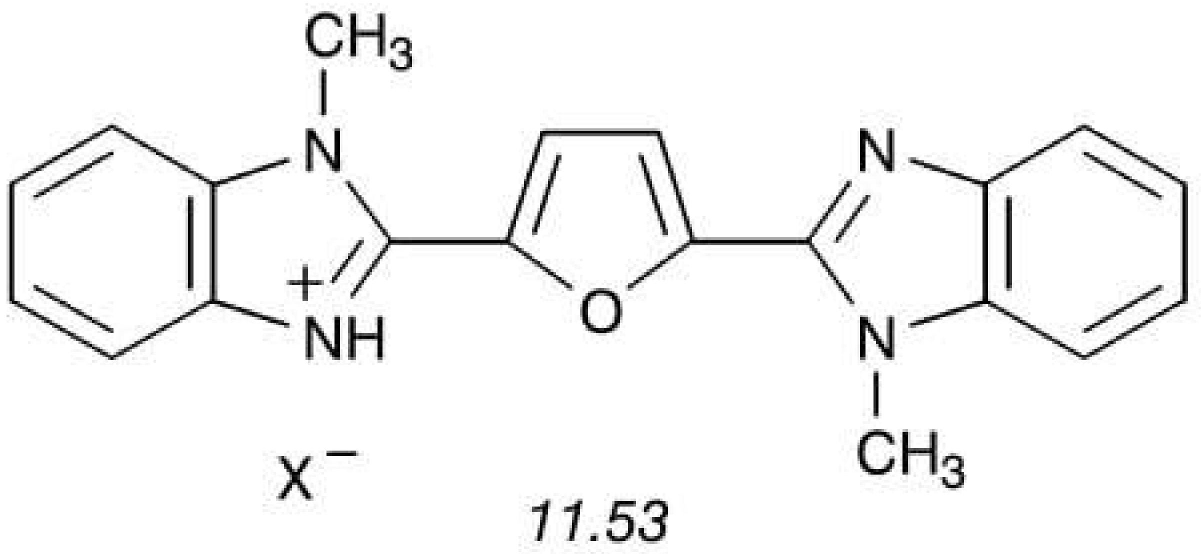
11.51

Scheme 11.21

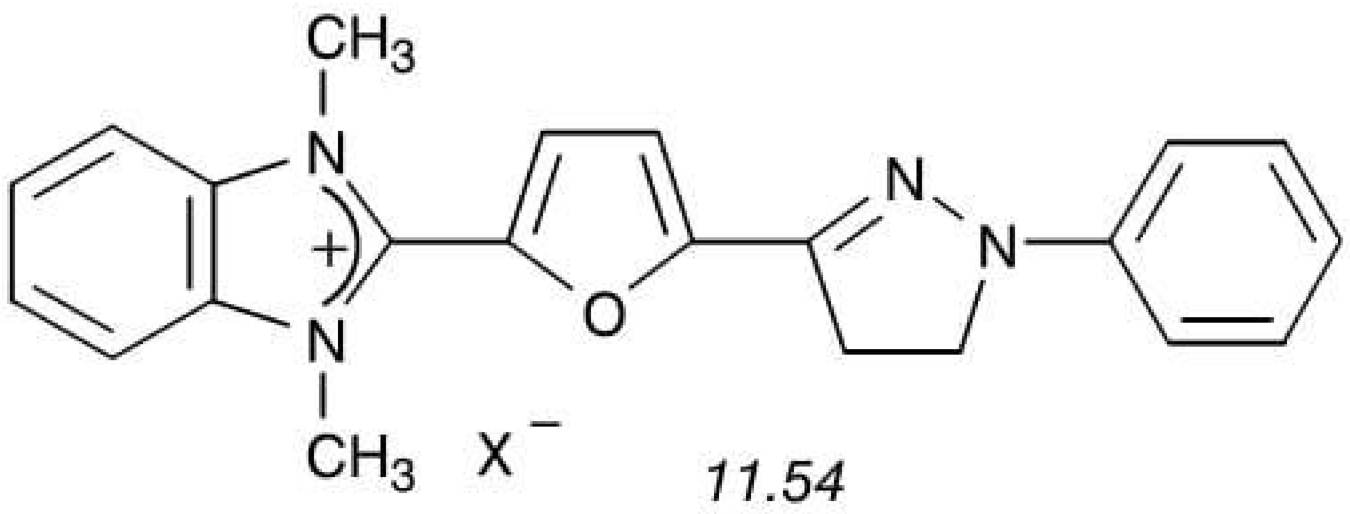
11.11.2 Type B products

The benzimidazoles 11.53 and 11.54, both of which gave greenish brightening effects, were formerly used widely in the chlorite bleaching of acrylic fibres. The first of them to be introduced, the bis(benzimidazolyl)furan 11.53, gave excellent whites of light fastness 4 but a strongly acidic dyebath was recommended to give the best results. More recently, compounds 11.53 and 11.54 were supplanted by the improved benzofuranyl (11.55) and benzoxazolyl (11.56) benzimidazole derivatives, which give neutral shades of white with light fastness ratings slightly higher than the bis-benzimidazole 11.53. They are also easier to apply and are capable of producing a higher level of whiteness.

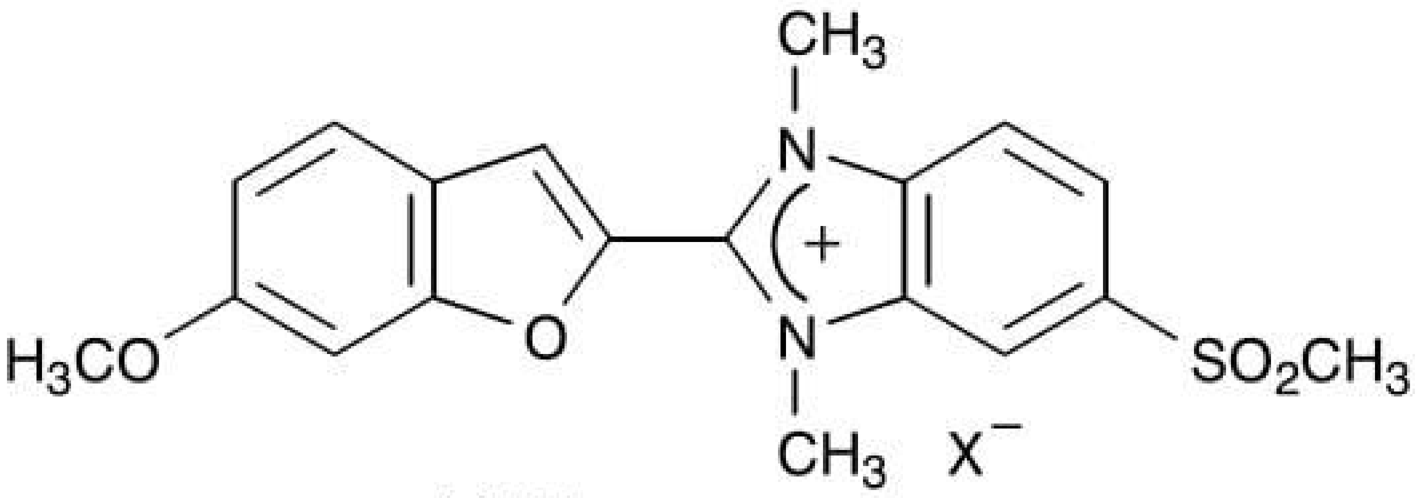
For a time the parent compound 11.57, easier to prepare than its methylsulphonyl derivative 11.55, was also marketed. This was capable of producing brilliant whites on acrylic fibres that were exceptionally violet in tone. If violet brightening effects of good light fastness are required they can be achieved in combination with sodium chlorite using the



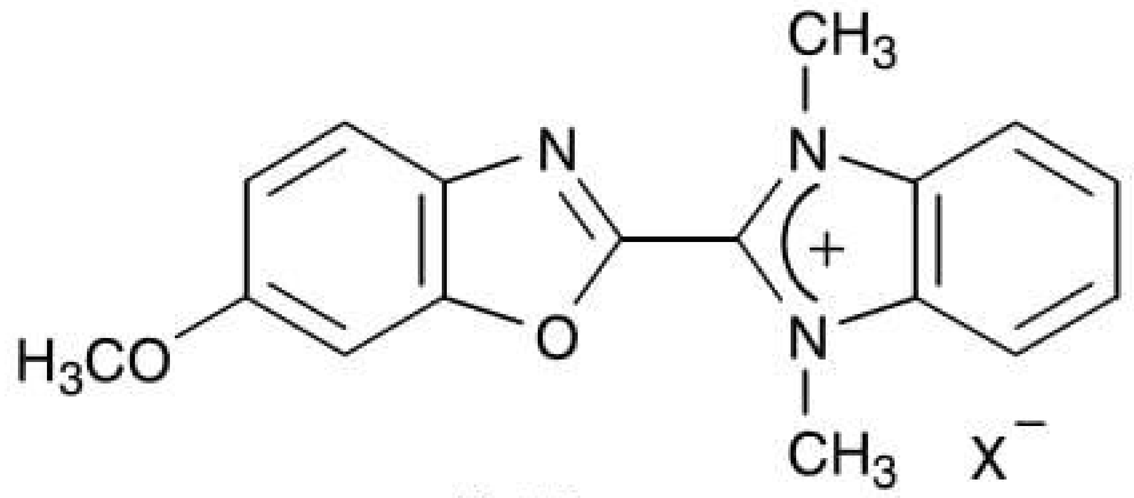
11.53



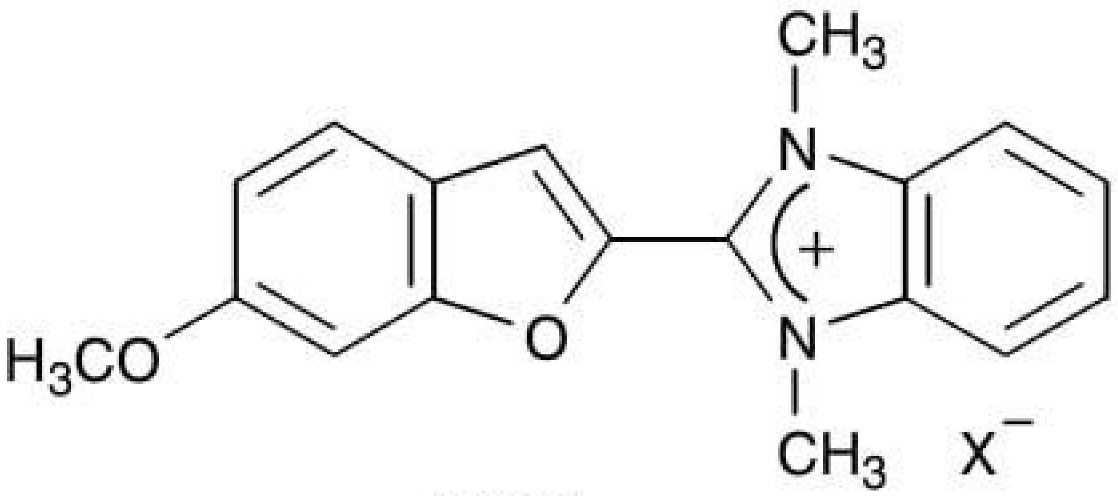
11.54



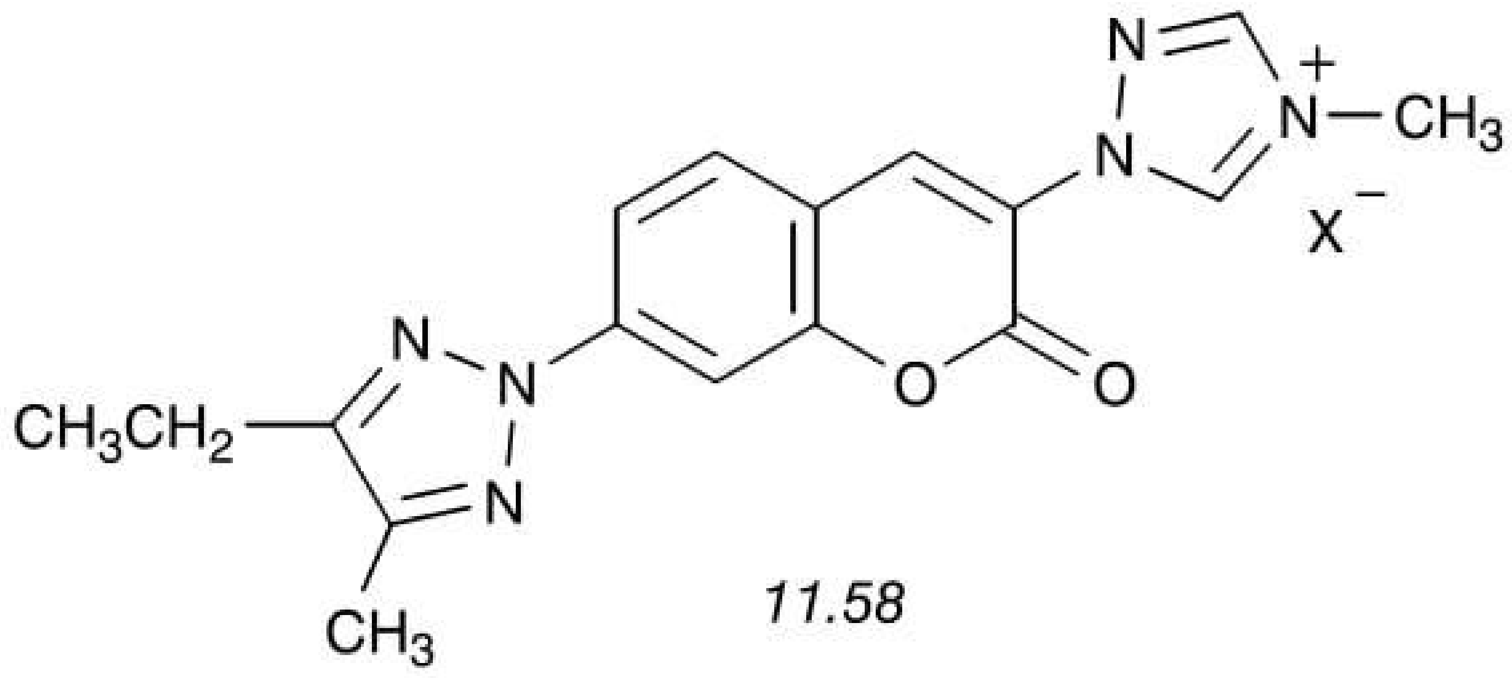
11.55



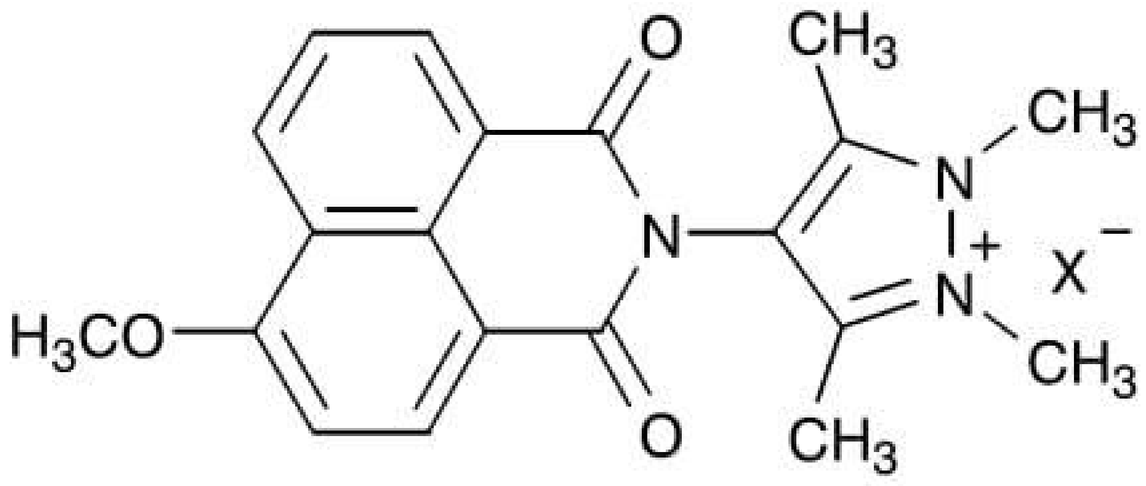
11.56



11.57



11.58



11.59

coumarin 11.58, which has been well-established for some years. Naphthalimide derivatives such as compound 11.59 can be used to obtain greenish shades of white on acrylic fibres in combination with a sodium chlorite bleach, but the effects are generally inferior to those produced by the preferred benzimidazoles 11.55 and 11.56.

Acrylic fibres can also be brightened during manufacture by gel application during the wet spinning process. Special FBAs have not been developed for this purpose. Products such as the pyrazoline sulphone 11.50 and the benzofuranyl-benzimidazole 11.55 are suitable for this application.

Some interesting organic chemistry is involved in the synthesis of chlorite-resistant brighteners for acrylic fibres. None of these compounds is easy to make and methods for preparation of the starting materials can be complex. Much manufacturing know-how is involved. One route for introduction of the benzimidazole nucleus into structure 11.55 is shown in Scheme 11.22. Preparation of the chemically rather simpler benzoxazole grouping in product 11.56 is shown in Scheme 11.23.

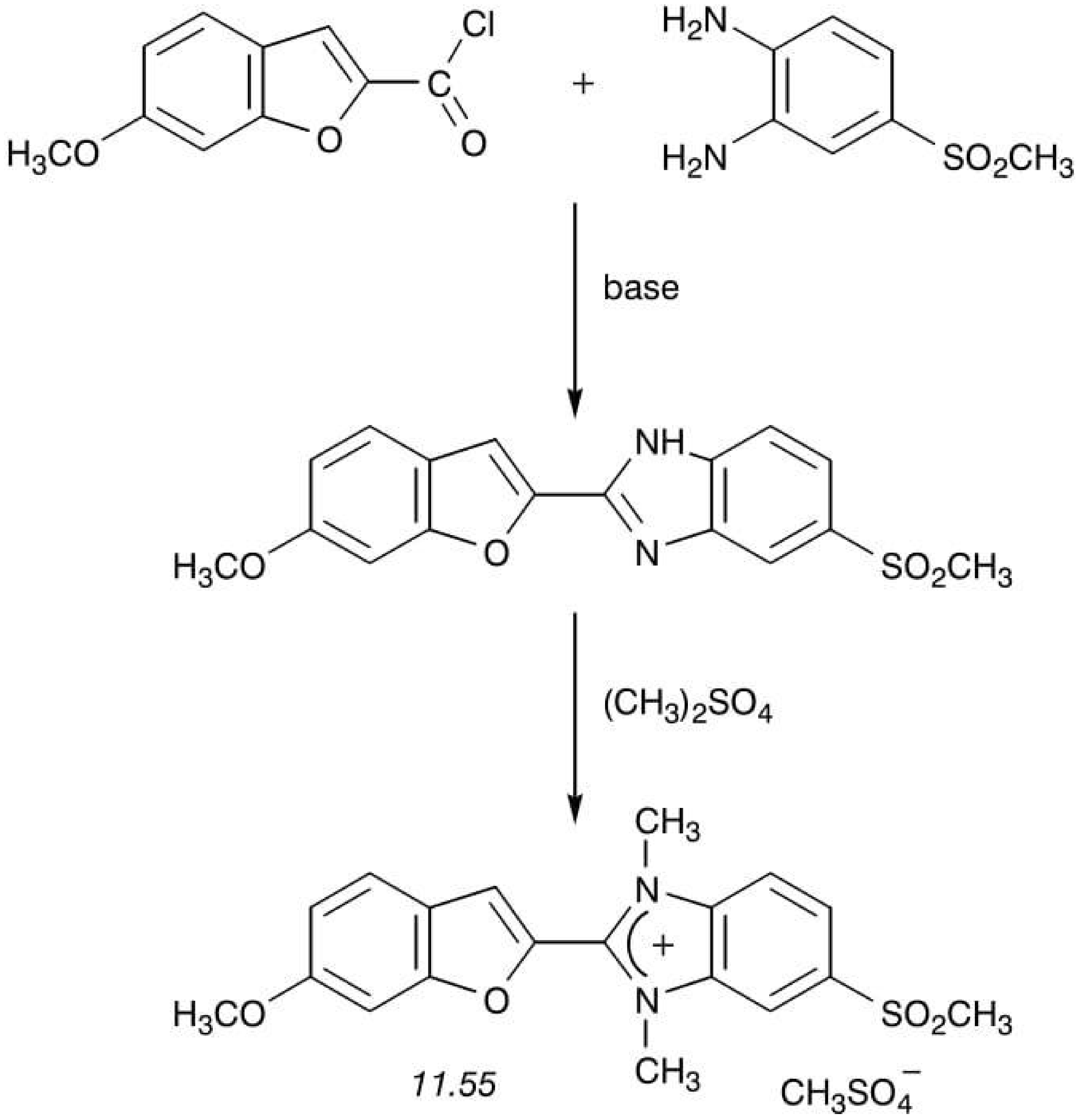
Synthesis of the coumarin derivative 11.58 containing two isomeric triazolyl rings is indicated in Scheme 11.24. The substituted pyrazolyl derivative of naphthalimide 11.59 is prepared by a reaction sequence somewhat similar in principle to that already shown in Scheme 11.14, using 4-amino-1,3,5-trimethylpyrazole in the penultimate step followed by quaternisation.

11.12 BRIGHTENERS IN DETERGENT FORMULATIONS

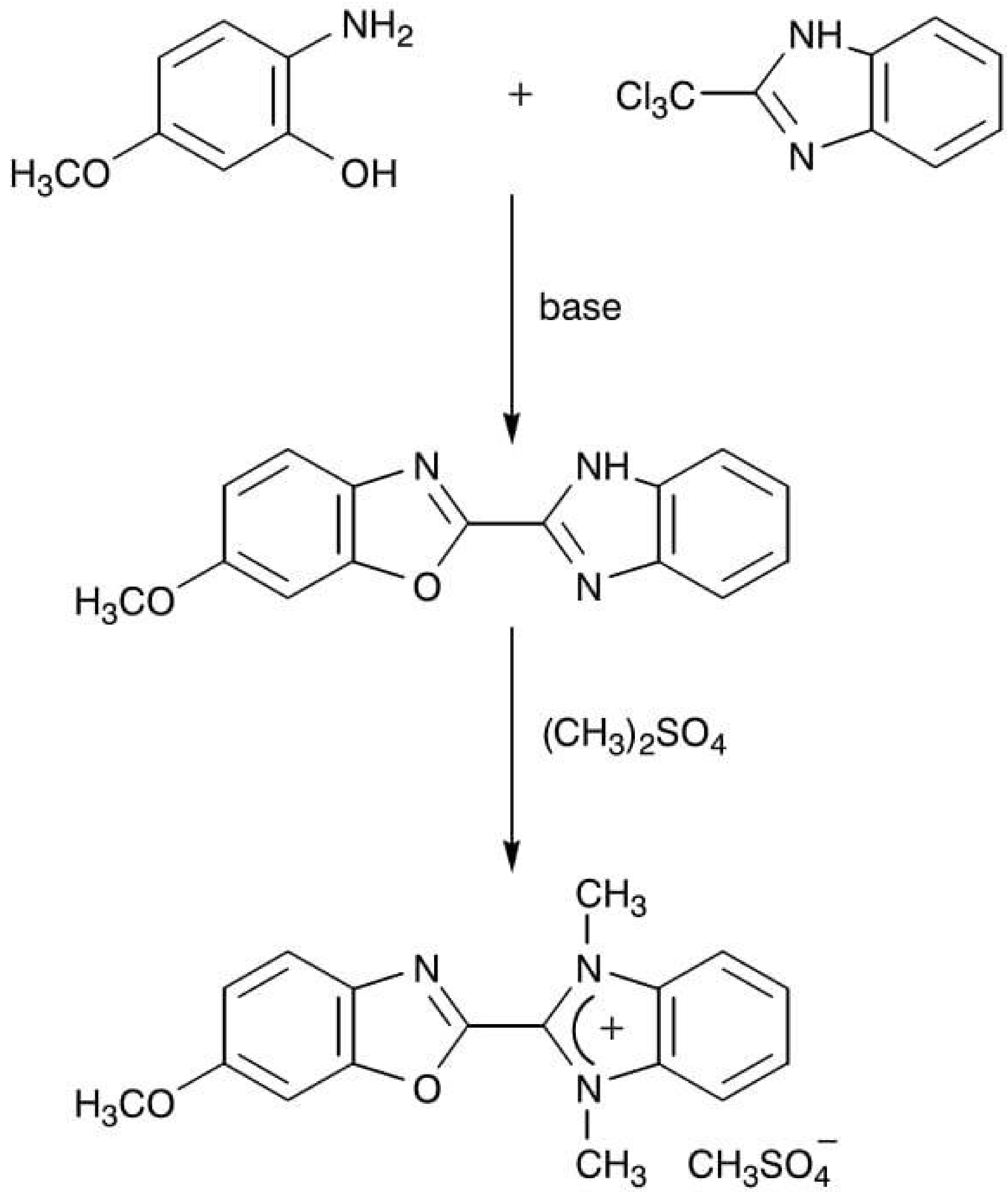
The largest single commercial use of FBAs is in domestic detergents. Detergent technology is continually changing; modified, improved or even chemically new FBAs are still appearing on the market. The combination of large-volume sales by a limited number of detergent manufacturers with several suppliers of FBAs competing for the available business ensures that prices remain low.

In the 1960s, FBAs for both cotton and nylon were incorporated into household detergents. Today FBAs for nylon are of negligible significance for the detergent industry. FBAs that are capable of effectively brightening polyester from a household wash at an acceptable laundering temperature (≤60 °C) remain undiscovered. Fibre types other than the cellulosics are essentially ignored from the viewpoint of FBA selection in the context of household detergents.

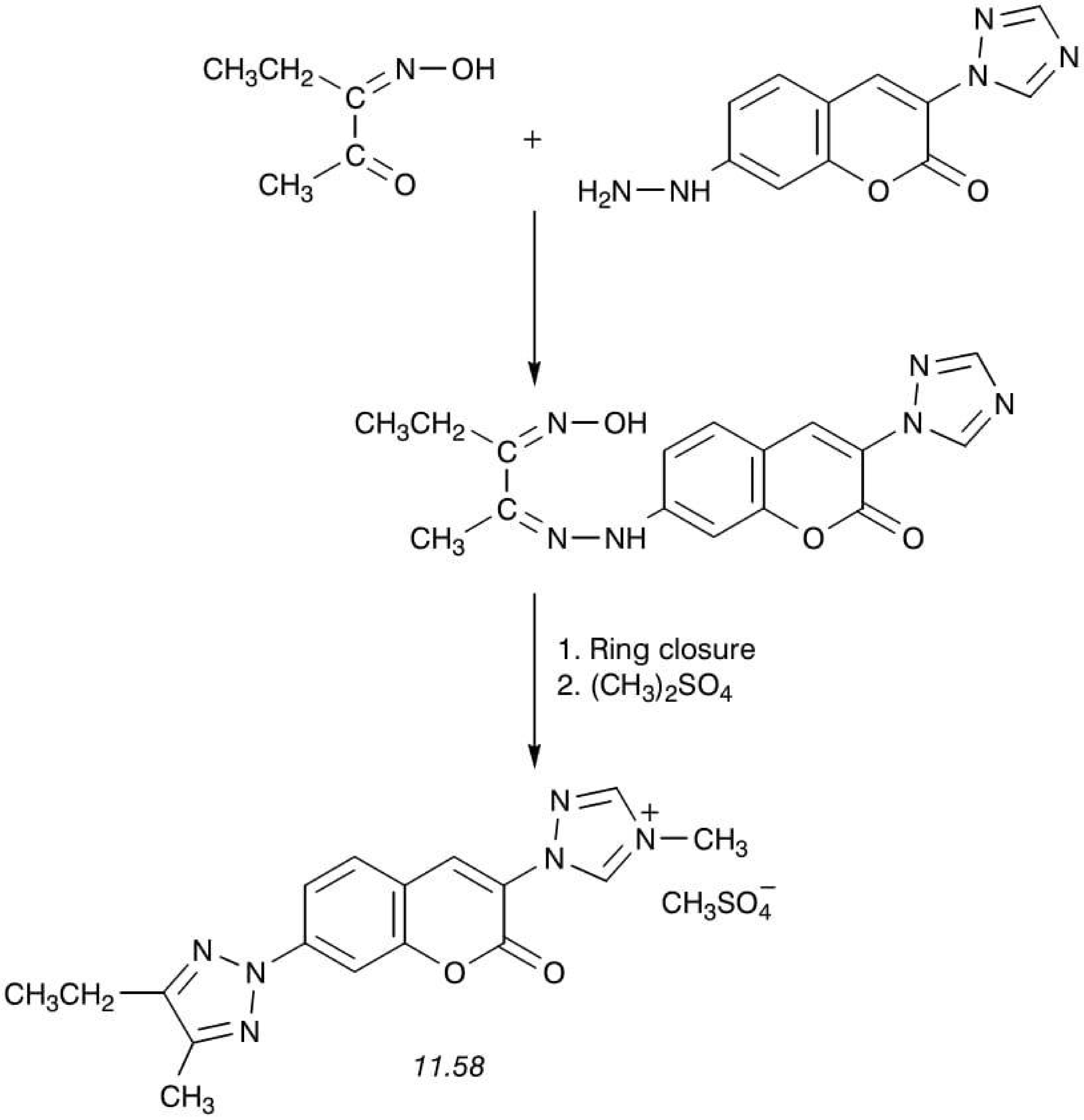
There are fundamental differences in approach to the selection of FBAs for either household detergents or textile finishing. Brighteners in detergent formulations are intended to preserve the whiteness of fabrics that already contain FBAs during many successive wash and



Scheme 11.22



Scheme 11.23



11.58

Scheme 11.24

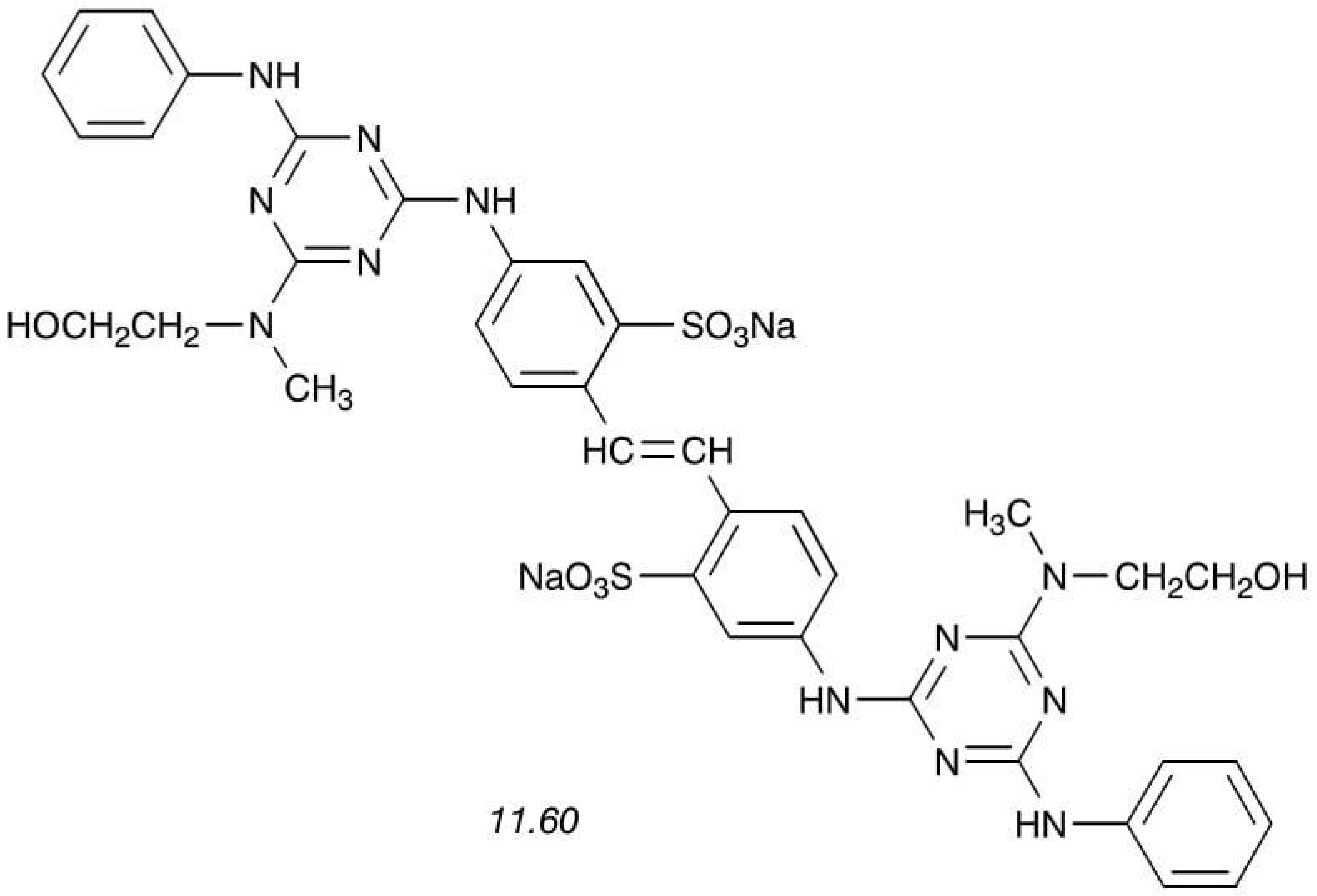
wear cycles, whereas textile finishers apply FBAs to unbrightened material. If too much FBA is present during household washing then most of it is wasted. Using excessive amounts could even lead to deterioration in whiteness, as an excess of FBA builds up after several washes. If too little FBA is used, the goods will gradually suffer a loss in whiteness although it could be several months before this is noticed by the detergent user. Typically a household detergent powder contains 0.02–0.05% FBA, although the trend is towards the use of less FBA with activated oxidative bleaching agents that are effective at lower washing temperatures.

The washing conditions and the type of surfactant present in household detergents vary from one part of the world to another. In some countries washing temperatures can be as low as 30 °C, whereas in others they can be as high as 90 °C. Chlorine-containing bleaches are routinely added to the wash in some countries but in others very rarely, if at all. The intensity of sunlight to which the washed goods are exposed during drying greatly influences the rate of fading of the FBA and this obviously varies considerably throughout the world. Since household detergents are marketed directly to the public, much attention has been given to packaging, physical appearance and handling of the various formulations available. Discoloration or development of odour on storage of the product, for example, would inhibit sales whatever the actual performance of the product in the wash. All these considerations influence the choice of type and quantity of FBA to be incorporated into a formulation. Furthermore, wash loads normally contain a variety of textile articles and an FBA designed to brighten cellulosic fibres must not adversely affect other fibre types present under the conditions of use of the detergent into which it has been incorporated.

Safety in use and environmental impact are increasingly important factors for the selection of FBAs used in household detergents. The waste water from a household wash is discharged directly into the municipal drainage system. There is no opportunity for treatment of this effluent before disposal, in contrast to washing processes operated under factory conditions. The total quantity of waste waters from domestic washing is a major contribution to the effluent load on municipal effluent treatment facilities. Accordingly, the FBA and other components in a household detergent must be innocuous in the environment and free from toxic hazard.

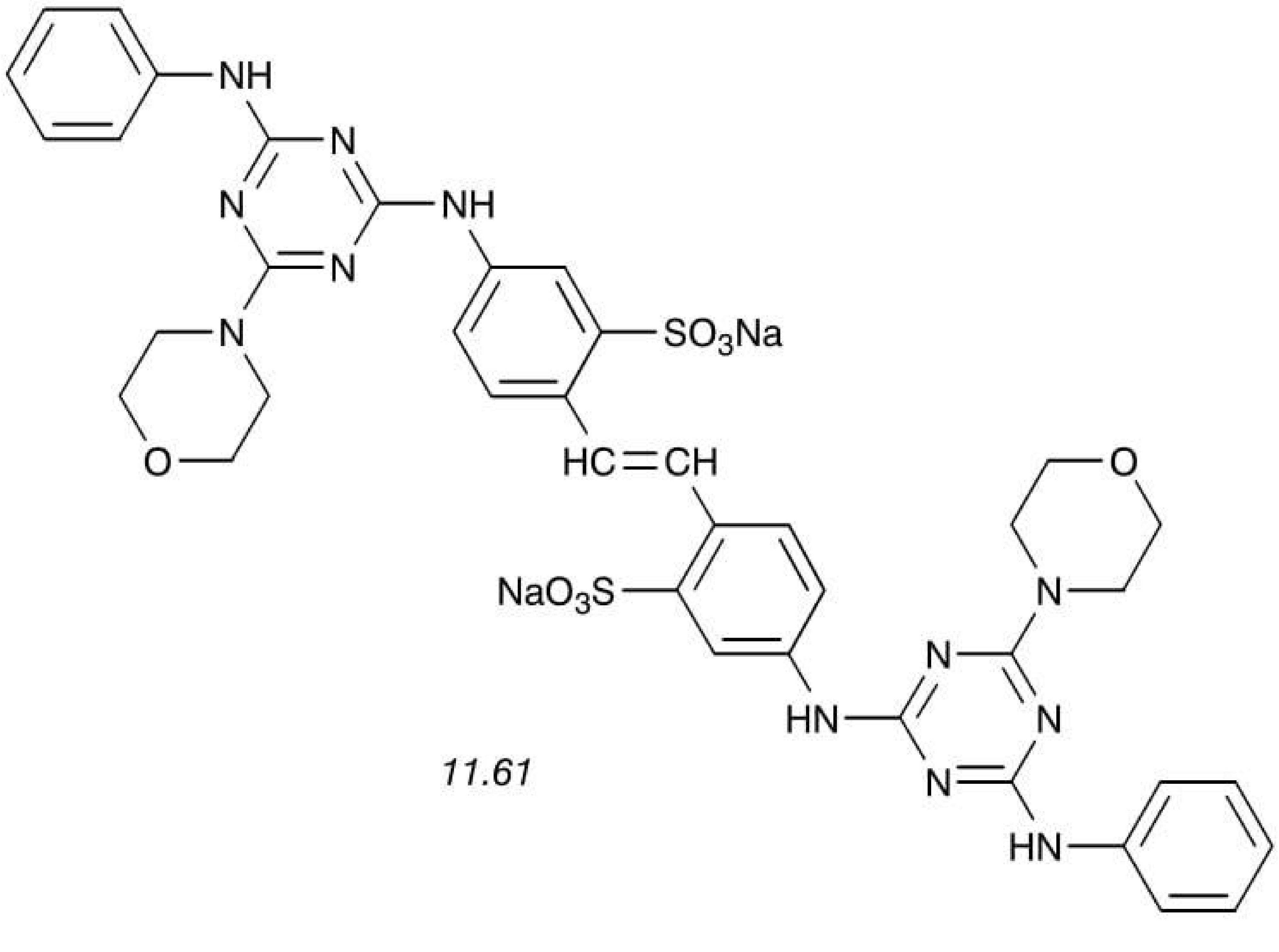
Evaluation of an FBA for use in household detergents is a lengthy and costly procedure. The information obtained from a standard washing test on unbrightened cotton is valuable but does not go far enough. Products must also be screened by measuring the build-up of whiteness during a series of successive washes using a detergent formulation containing the small proportion of FBA usually present in practice. Further tests continue on pre-brightened textiles in machine washing cycles and in field trials. Extensive toxicity and environmental test protocols must also be followed. Although many different FBAs have been found acceptable for use in household detergent formulations, only a few products remain important today.

The structures of typical examples have been mentioned already, such as the substantive DAST-type product 11.60, the distyryldiphenyl 11.15 and the *vic*-triazole 11.17. Certain FBAs, including these three compounds, can exist in relatively purer, near-colourless β-crystal modifications or in less pure yellowish crystalline forms. They are most easily prepared in the yellower form but incorporation of this material into a detergent formulation leads to unacceptable discoloration of the powder. Today, these products are supplied in a near-colourless form that may be prepared, for example, by heating an aqueous alkaline suspension of the yellowish material together with a co-solvent.



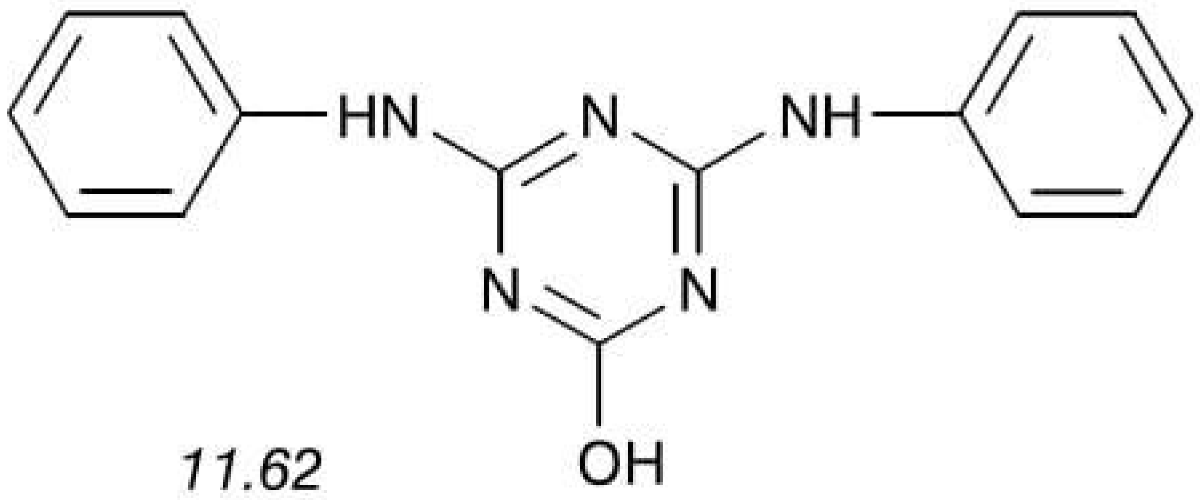
11.60

The DAST brightener 11.61 is the most important FBA used in detergent formulations and is probably the cheapest to manufacture. It shows excellent performance at temperatures of 60 °C and above but relatively poor solubility in cold water compared with the alternatives specified above. If it is to perform satisfactorily in low-temperature washing, it must be supplied in a finely divided form so that it will dissolve adequately during a typical household washing treatment. The necessary particle size can be achieved in various ways, one of which is wet milling in the presence of excess salt.



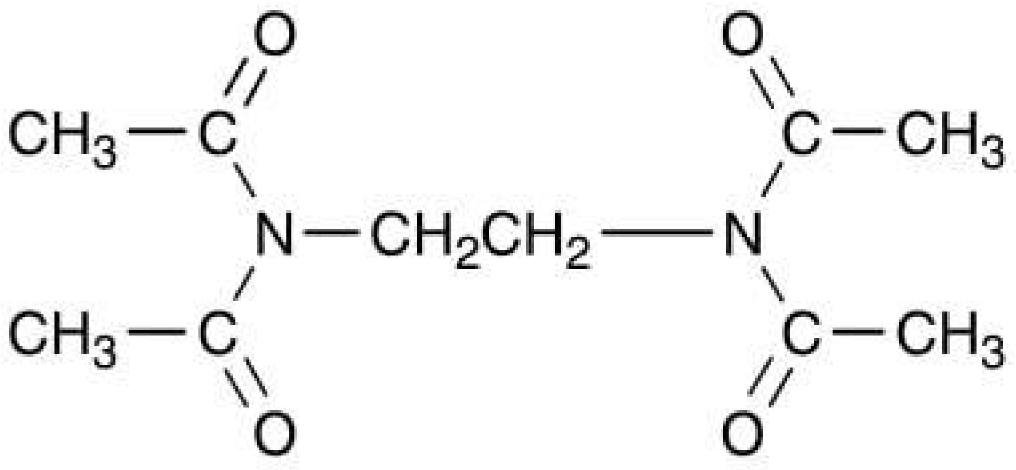
11.61

DAST-type FBAs may contain by-products (such as 11.13) derived from hydrolysis of one or more of the chloro substituents in cyanuric chloride (11.10). One such troublesome by-product is 2,4-bis(anilino)-6-hydroxy-*s*-triazine (11.62). Not only is this compound environmentally undesirable, it may also interact with certain bleaching agents and its presence can lead to the development of unpleasant odours on storage of a detergent powder. The proportion of this triazine present as an impurity in a brightener such as 11.61 can be kept to a minimum by careful control of the reaction conditions during manufacture. Alternatively, it can be extracted from the FBA using hot alkali.



11.62

The instability of DAST-type brighteners towards chlorine-containing bleaches has been mentioned already. They also show limited stability towards per-acids. As recommended washing temperatures have tended to fall in recent years, a bleach consisting of sodium perborate activated by addition of tetra-acetylethylenediamine (11.63) has become an important component of household detergent formulations. This system is effective at temperatures as low as 40–50 °C. Since the FBA may be sensitive to the activated oxidant, however, in some formulations it is necessary to protect compounds such as 11.60 or 11.61 by encapsulating either the brightener or the activator, if adequate shelf-life is to be maintained.



11.63

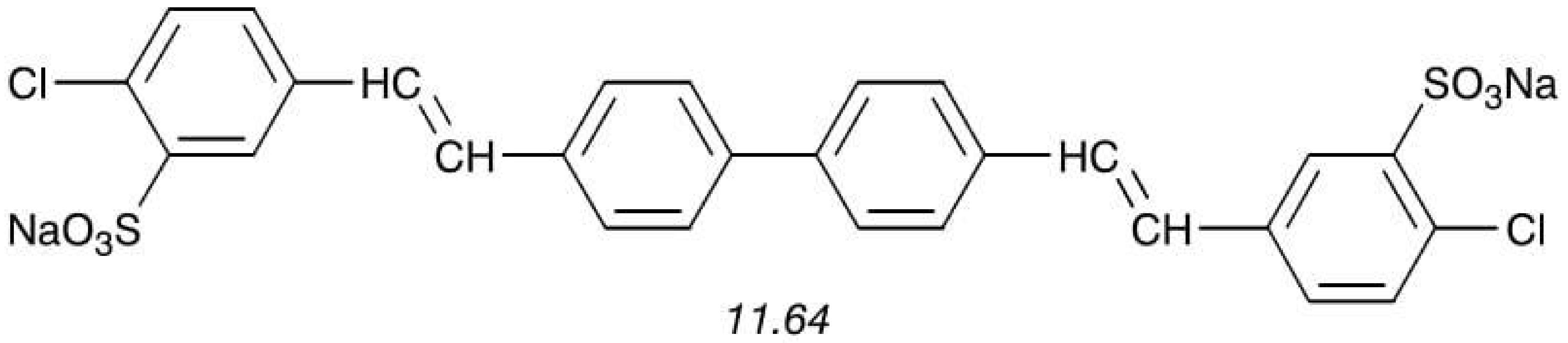
The so-called ‘super brighteners’ 11.15 and 11.17 are generally much more stable towards activated per-acid bleaching systems. Both products, and especially the *vic*-triazole 11.17, offer higher light fastness than the DAST brighteners. The distyryldiphenyl 11.15 is an effective FBA when applied from a wash liquor at a temperature below 50 °C, but shows poor performance at higher temperatures and poor washing fastness in soft water. The *vic*-triazole 11.17 is effective at all temperatures but is expensive. Nevertheless, it may prove cost-effective in tropical climates where washed textiles can fade severely during drying. Compound 11.15 is particularly effective in enhancing the brightness of the detergent powder itself, although this in no way indicates its performance in the wash. Table 11.5 summarises the advantages and drawbacks of the four major FBAs discussed above.

The poor performance of the distyryldiphenyl derivative 11.15 at higher washing temperatures is a serious drawback in some countries. In an attempt to overcome this disadvantage, product 11.15 has been marketed in admixture with an analogous FBA (11.64) derived from 4-chlorobenzaldehyde-3-sulphonic acid (see Scheme 11.5). This much less soluble variant is highly effective at high washing temperatures.

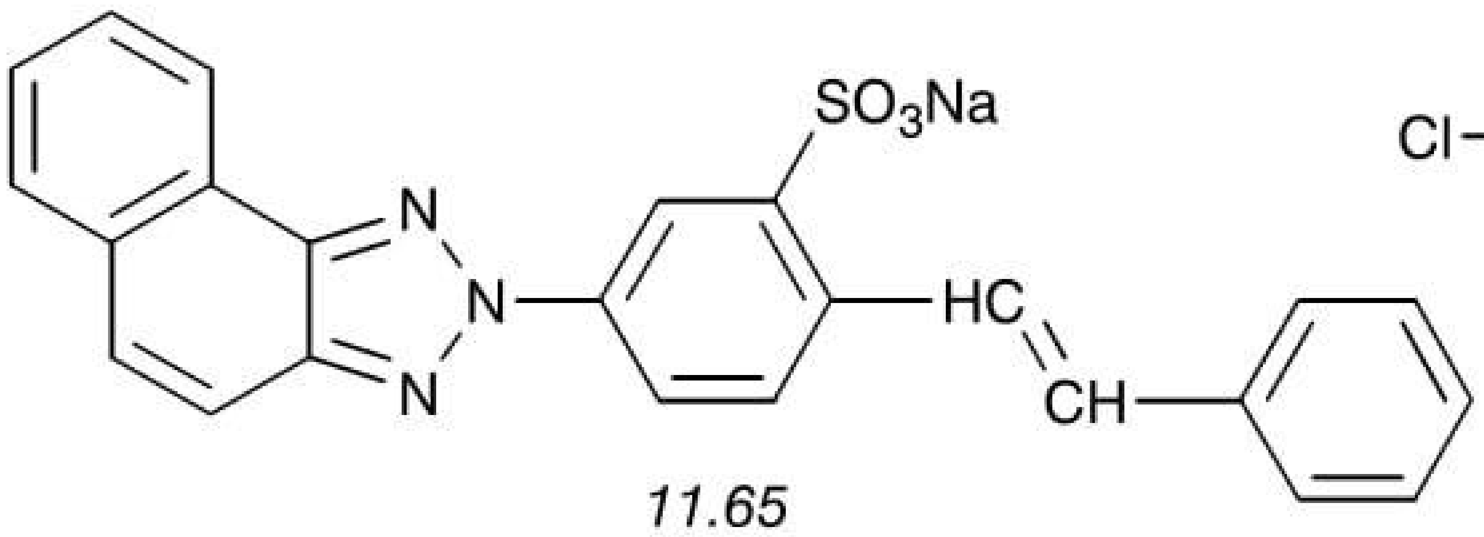
Where resistance to chlorine bleaches such as sodium hypochlorite is required, the naphthotriazole 11.65 can be used. Formerly, this FBA was extremely important for use in

Table 11.5 Advantages and disadvantages of FBAs in detergent formulations

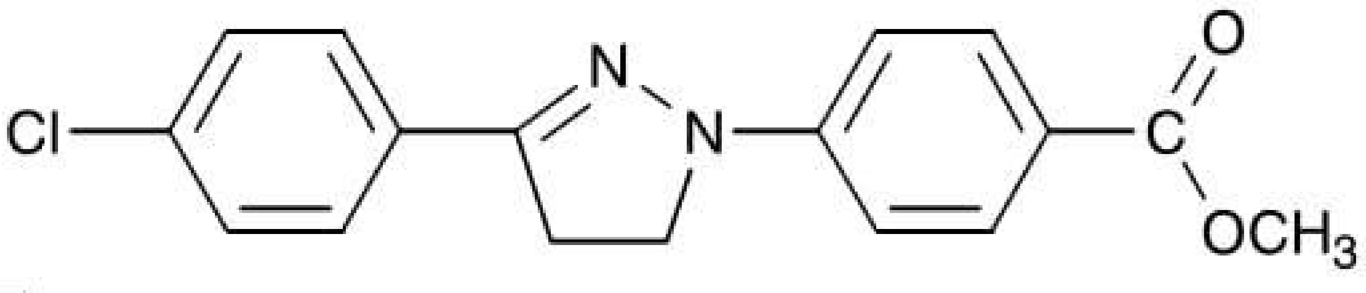
Product	Advantages	Disadvantages
11.61	Low price Effective at all temperatures	Unstable towards hypochlorite and activated perborate
11.60	Effective at all temperatures	Unstable towards hypochlorite and activated perborate
11.15	Stable in bleaching Good light fastness	Poor performance above 50 °C Poor wash fastness
11.17	Effective at all temperatures Stable in bleaching Excellent light fastness	High price



11.64



11.65

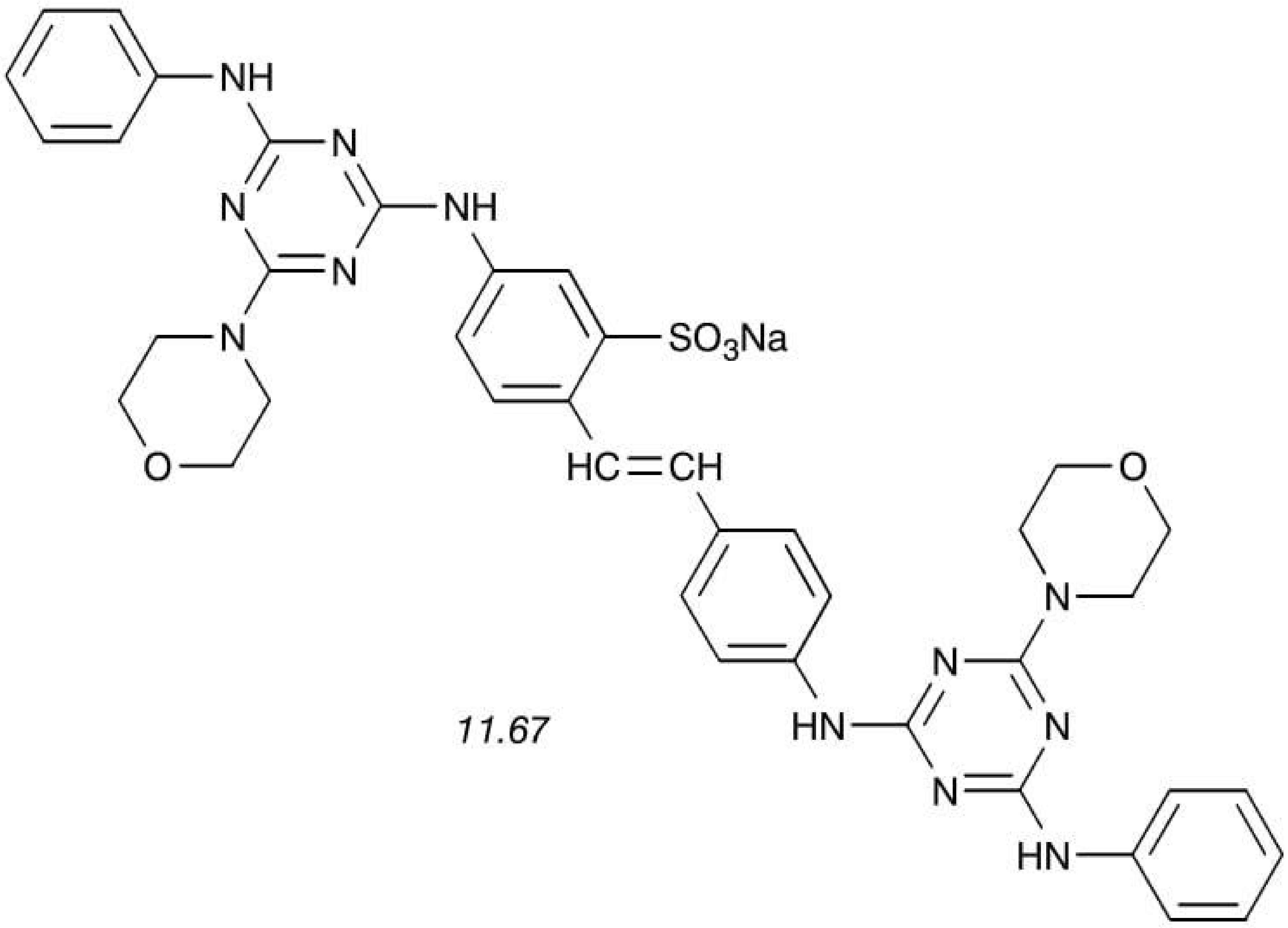


11.66

detergents but today it is much less so. It has the advantage of brightening both cotton and nylon from the wash bath.

In the absence of hypochlorite bleach, pyrazolines such as the sulphonamide 11.20 and the ester 11.66 give brighter whites than the naphthotriazole 11.65 on nylon garments in the wash. Especially brilliant whites with a somewhat greenish tone are given by compound 11.66 but this FBA tends to stain polyester goods under wash bath conditions. The sulphonamide 11.20 gives less intense whites but stains polyester less. Neither pyrazoline derivative is effective on cotton, so they are not much used in detergent formulations nowadays.

Domestic detergents in liquid form have become increasingly popular in recent years. This trend has created problems in the choice of suitable FBAs, as it is more difficult to devise liquid formulations of adequate storage stability. Liquid detergents containing FBAs can cause yellow 'specking' faults on the washed goods, which can be a serious problem. It has been claimed [63] that the use of an FBA such as 11.65 or 11.67, which contain only one sulphonic acid group in their stilbene residue, ameliorates the 'specking' problem. Classical approaches to the preparation of stilbenes or their symmetrical disulphonates are not applicable to the synthesis of their unsymmetrical monosulphonated analogues. Several condensation routes provide viable opportunities to introduce a single sulphonic acid group into the stilbene nucleus but these procedures do add substantially to the cost of manufacture [64].



11.67

The disulphonated DAST derivative 11.25 containing four anilino groups per molecule is effective in liquid detergent formulations and much cheaper to manufacture than the monosulphonated DAST brightener 11.67, which was withdrawn from the market in the late 1980s. It has been necessary to purify compound 11.25 specially for use in detergents, in order to eliminate traces of residual unreacted aniline as far as possible, owing to the toxic properties of this impurity.

11.13 ANALYSIS OF FBAs

Qualitative analysis of FBAs is best carried out by thin-layer chromatography (TLC). Silica gel is the usual stationary phase for the TLC of FBAs. Various eluants are available and these can be chosen according to the chemical nature of the FBA under test. Suitable standards are required. The plethora of possible brighteners of the DAST type, together with the various impurities present in such products, can cause difficulties in their identification by TLC. The technique can be used quantitatively, although costly instrumentation is required and considerable care must be taken in preparing and handling chromatograms. Chapters by Theidel and Anders in the book edited by Anliker and Müller [7] contain valuable information on the analysis of FBAs by TLC. More recently, Lepri and Desideri have described methods for the TLC identification of FBAs in detergent formulations [65].

If suitable standards are unavailable (for example, if the FBA has not been encountered previously) the active agent must first be isolated and purified. The pure compound can be characterised by the usual techniques, including elemental analysis and infrared, n.m.r. and mass spectroscopy. Final proof of structure demands synthesis of the FBA indicated by the analytical data. Once again, difficulties may be encountered with compounds of the DAST class. Optical densitometry using a Shimadzu CS 9000 flying spot scanner has been evaluated for the analysis of anionic DAST-type brighteners [66].

Once the FBA has been identified, ultraviolet absorption spectroscopy affords a rapid and accurate method of quantitative analysis. Care must be taken when interpreting the spectra of stilbene-type compounds, since *trans* to *cis* isomerisation is promoted by ultraviolet radiation. Usually, however, a control spectrum of the *trans* isomer can be obtained before the compound undergoes any analytically significant isomerisation. FBAs are often marketed on the basis of strength comparisons determined by ultraviolet spectroscopy.

FBAs can also be estimated quantitatively by fluorescence spectroscopy, which is much more sensitive than the ultraviolet method but tends to be prone to error and is less convenient to use. Small quantities of impurities may lead to serious distortions of both emission and excitation spectra. Indeed, a comparison of ultraviolet absorption and fluorescence excitation spectra can yield useful information on the purity of an FBA. Different samples of an analytically pure FBA will show identical absorption and excitation spectra. Nevertheless, an on-line fluorescence spectroscopic method of analysis has been developed for the quantitative estimation of FBAs and other fluorescent additives present on a textile substrate. The procedure was demonstrated by measuring the fluorescence intensity at various excitation wavelengths of moving nylon woven fabrics treated with various concentrations of an FBA and an anionic sizing agent. It is possible to detect remarkably small differences in concentrations of the absorbed materials present [67].

High-performance liquid chromatography (HPLC) is being used increasingly to identify FBAs, to investigate product purity and for process control. HPLC has many attributes that TLC lacks, including greater sensitivity, better resolution and discriminatory power. Quantitative analysis can be carried out conveniently and rapidly using HPLC, providing the constitution of the FBA is known and a pure sample is available for calibration. Drawbacks of this approach, however, include the fact that samples have to be run sequentially rather than in parallel, substantially increasing the time for analysis. Care is needed to minimise the risk of cross-contamination caused by carry-over from one sample to the next.

Although HPLC quickly became established for the analysis of organic compounds in many fields, the development of test procedures for textile dyes and FBAs took place more slowly. This is attributable to the number and variety of chemical classes represented and the fact that these structures may be anionic, cationic or nonionic. Attempts to devise general eluant systems to cope with this diversity in solubility characteristics met with considerable difficulties. Gradient elution systems using mixed solvents in various proportions could be used but the techniques were complicated and time-consuming. Multichannel detection of peak wavelengths using a variable wavelength UV-Vis detector is effective in enabling simultaneous monitoring of different components in mixtures [68]. Chromatographic problems associated with the separation of anionic dyes and FBAs were attributed to undesirable properties of silica-based packing materials in the column and better results were found using a chemically inert copolymer of styrene and divinylbenzene [69]. The addition of di-t-butyl-*p*-cresol (11.42) as an antioxidant was useful in ensuring chemical stability of oxidation-sensitive dyes and FBAs during extraction and analysis [70]. Established techniques of HPLC analysis are available for estimation of the relatively few FBAs that are widely used in detergent formulations [71,72].

REFERENCES

1. P Krais, *Melliand Textilber.*, **10** (1929) 468.
2. C Paine and J A Radley (ICI), BP 442 530 (1934).
3. A K Sarkar, *Fluorescent whitening agents* (Watford: Merrow, 1971).
4. H Gold in *The chemistry of synthetic dyes*, Vol. 5, Ed. K Venkataraman (New York: Academic Press, 1971).
5. D Barton and H Davidson, *Rev. Prog. Coloration*, **5** (1974) 3.
6. A Dorlars, C W Schellhammer and J Schroeder, Angew.Chem.Internat., **14**(1975)665.
7. *Fluorescent whitening agents*, Eds. R Anliker and G Müller (Stuttgart: Thieme, 1975).
8. R Zweidler and H Hefti, *Kirk-Othmer encyclopedia of chemical technology*, 3rd Edn., Vol. 4 (New York: Wiley-Interscience, 1978) 213.
9. R Williamson, *Fluorescent brightening agents* (Amsterdam: Elsevier, 1980).
10. I H Leaver and B Milligan, *Dyes and Pigments*, **5** (1984) 109.
11. A E Siegrist, H Hefti, H R Meyer and E Schmidt, *Rev. Prog. Coloration*, **17** (1987) 39.
12. T Martini, *Textilveredlung*, **23** (1988) 2.
13. B J Maier, *Text. Asia*, **21** (July 1990) 80.
14. W S Hickman in *Cellulosics dyeing*, Ed. J Shore (Bradford: SDC, 1995) 81.
15. *Luminescence spectroscopy*, Ed. M D Lumb (New York: Academic Press, 1978).
16. J R Lakowicz, *Principles of fluorescence spectroscopy* (London: Plenum Press, 1983).
17. M Pestemer, A Berger and A Wagner, *Textilveredlung*, **19** (1964) 420.
18. X Qian, Y Zhang, K Chen, Z Tao and Y Shen, *Dyes and Pigments*, **32** (1996) 229.
19. C Lubai, C Xing, H Yufen and J Griffiths, *Dyes and Pigments*, **10**, No 2 (1989) 123.
20. O Pitzurra, *Melliand Textilber.*, **77** (1996) 331.
21. R Griesser, *Col. Res. Appl.*, **19** (1994) 446.
22. J A Bristow, *Col. Res. Appl.*, **19** (1994) 475.
23. A Berger, *Die Farbe*, **8** (1959) 187.
24. P S Stensby, *Soap/Cosmetics/Chem. Specialities*, **43** (July 1967) 80.
25. R Griesser, *Rev. Prog. Coloration*, **11** (1981) 26.
26. J Rieker, R Griesser and C Puebla, *Textilveredlung*, **31** (1996) 64.
27. I Soljacic, A M Grancaric and K Weber, *Textilveredlung*, **10** (1975) 492.
28. A M Grancaric and I Soljacic, *Melliand Textilber.*, **62** (1981) 876.
29. J R Aspland, J S Davis and T A Waldrop, *Text. Chem. Colorist*, **23** (Sep 1991) 74.
30. I Soljacic and R Cenko, *Melliand Textilber.*, **60** (1979) 1032.
31. I Soljacic, D Kalovic and A M Grancaric, *Textil Praxis*, **46** (1991) 331.
32. I Soljacic and K Weber, *Textilveredlung*, **9** (1974) 220.
33. I Soljacic, A M Grancaric and B Luburic, *Textil Praxis*, **39** (1984) 775.
34. K Seguchi, Y Ebara and S Hirota, *Yukagaku*, **34** (1985) 17.
35. W Schürings, *Textilveredlung*, **29** (1994) 260, 291.
36. R S Davidson, G M Ismail and D M Lewis, *J.S.D.C.*, **104** (1988) 86.
37. R Zweidler, *Textilveredlung*, **4** (1969) 78.
38. R P Hurd and B M Reagan, *J.S.D.C.*, **106** (1990) 49.
39. H Ikuno, M Okuni, M Komaki and T Nakajima, *Text. Res. J.*, **66** (1996) 464.
40. Anon, Paper (June 1980) 33.
41. H Ikuno, M Komaki and T Nakajima, *J. Soc. Fibre Sci. Tech. Japan* (1994) 87.
42. I Grabtchev and T Philipova, *Dyes and Pigments*, **27** (1995) 321.
43. I Grabtchev, P Meallier, T Konstantinova and M Popova, *Dyes and Pigments*, **28** (1995) 41.
44. I Grabtchev and T Konstantinova, *Dyes and Pigments*, **33** (1997) 197.
45. B R Modi, N M Naik, D N Naik and K R Desai, *Dyes and Pigments*, **23** (1993) 65.
46. H Strahle, W Seitz and H Güsten, *Z. Naturforsch.*, **316** (1976) 1248.
47. H Güsten and G Heinrich, *Ber. Bunsen-Ges.*, **81** (1977) 810.
48. I H Leaver and G C Ramsay, *Text. Res. J.*, **39** (1969) 730.
49. R S Davidson, G M Ismail and D M Lewis, *J.S.D.C.*, **103** (1987) 308.
50. P Moechli, *Dyes and Pigments*, **1** (1980) 3.
51. R S Davidson, G M Ismail and D M Lewis, *J.S.D.C.*, **103** (1987) 261.
52. L A Holt and I W Stapleton, *J.S.D.C.*, **104** (1988) 387.
53. L E Aicolina, I H Leaver and I W Stapleton, *Dyes and Pigments*, **11**, No 3 (1989) 213.
54. K J Smit and K P Ghiggino, *Dyes and Pigments*, **13**, No 1 (1990) 45.
55. D Reinehr and E Schmidt, *J.S.D.C.*, **102** (1986) 258.
56. T Martini and H Probst, *Melliand Textilber.*, **65** (1984) 327.
57. S Yongjia and R Shengwu, *Dyes and Pigments*, **15**, No 3 (1991) 183.

58. Z Zhu, H Tian, X Zhang and S Ren, *Dyes and Pigments*, **21**, No 4 (1993) 235.
59. I N Bykova, *Tekstil. prom.*, **8** (Aug 1987) 55.
60. H Oda, N Kuramoto and T Kitao, *J.S.D.C.*, **97** (1981) 462.
61. D W Rangnekar and P V Tagdiwala, *Dyes and Pigments*, **7**, No 6 (1986) 445.
62. P L Moriarty, AATCC Internat. Conf. & Exhib. (Oct 1994) 297.
63. J Wevers, L A Halas and P R Peltre, USP 4 559 169 (1985).
64. R V Casciani *et al.*, AATCC Internat. Conf. & Exhib. (Oct 1991) 93.
65. L Lepri and P G Desideri, *J. Chromatog.*, **322** (1985) 363.
66. U Denter, K Tiroke, D Knittel and E Schollmeyer, *Melliand Textilber.*, **73** (1992) 834.
67. S Cleve and E Schollmeyer, *Textilveredlung*, **30** (1995) 18.
68. J C West, *J. Chromatog.*, **208** (1981) 47.
69. P C White and A M Harbin, *Analyst*, **114** (1989) 877.
70. B B Wheals, P C White and M D Paterson, *J. Chromatog.*, **350** (1985) 205.
71. B P McPherson and N Omelczenko, *J. Amer. Oil Chem. Soc.* (1980) 388.
72. G Micali, P Curro and G Calabro, *Analyst*, **109** (1984) 155.