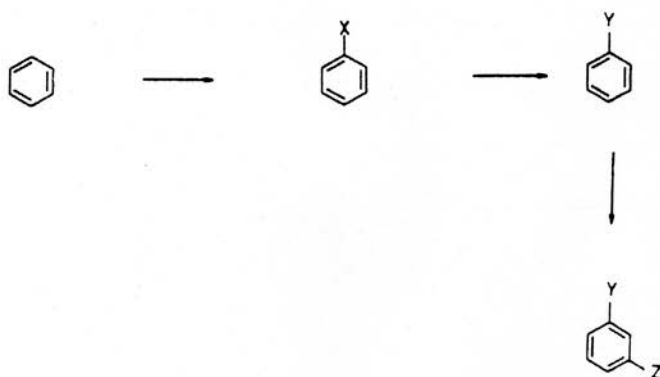


carbonate, ammonia and lime), salts (sodium chloride, sodium nitrite and sodium sulphide) and other substances such as chlorine, bromine, phosphorus chlorides and sulphur chlorides. The important point is that there is a significant usage of at least one inorganic material in every process and the overall tonnage used by, and therefore the cost to, the dye industry is high.

5.5.2.2 The chemistry of intermediates. The chemistry of intermediates may be conveniently divided into two parts: the chemistry of carbocycles, such as benzene and naphthalene, and the chemistry of heterocycles, such as pyridones and thiophenes. The chemistry of carbocyclic intermediates involves the sequential introduction of groups into the aromatic rings by a variety of steps known as unit processes (Scheme 5.1). The unit processes employed in dye chemistry are listed in Table 5.8.



Scheme 5.1.

The substituents are introduced into the aromatic ring by one of two routes, either by electrophilic substitution or by nucleophilic substitution. In general, aromatic rings, because of their inherently high electron density, are much more susceptible to electrophilic attack than to nucleophilic attack. Nucleophilic attack only occurs under forcing conditions unless the aromatic ring already contains a powerful electron-withdrawing group, e.g. NO_2 . In this case, nucleophilic attack is greatly facilitated because of the reduced electron density at the ring carbon atoms.

In contrast to carbocyclic chemistry, aromatic heterocycles are built up from acyclic precursors and the ring is functionalised if necessary (equation 5.3).

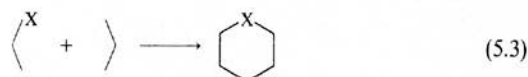


Table 5.8 Unit processes in dyes manufacture

Process	Primaries (no. of occurrences within 30 identified product manufactures)	Intermediates (common usage)	Colourants (common usage)
Nitration	6	✓	
Reduction	8	✓	
Sulphonation	4	✓ (Incl. chlorosulphonation)	
Oxidation	5	✓	
Fusion/hydroxylation	3	✓	
Amination	3	✓ (Incl. Bucherer reaction)	
Alkylation	2	✓	
Halogenation	2	✓	
Hydrolysis	2	✓	✓
Condensation	1	✓	✓
Alkoxylation		✓	
Esterification		✓	
Carboxylation		✓	
Acylation		✓	
Phosgenation		✓	✓
Diazotisation		✓	✓
Coupling (azo)		✓	✓

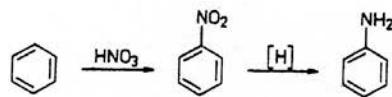
5.5.2.3 Primary intermediates. Primary intermediates are chemicals that are manufactured on a very large scale because they are used in several industries, of which the dyes industry is just one. Some of the more important primary intermediates are shown in Table 5.9.

Aniline. This is prepared by nitration of benzene with nitric acid–sulphuric acid to give nitrobenzene, which is reduced to aniline, usually by catalytic hydrogenation (Scheme 5.2).

Table 5.9 Production (tonnes) of primary intermediates

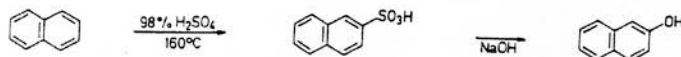
Product	USA	Japan
Phenol	1 167 050	212 173
Phthalic anhydride	371 930	219 943
Aniline	299 737	84 661
Nitrobenzene	278 012	50 961
Salicylic acid	17 749	2 338
<i>p</i> -Nitroaniline	6 558	
<i>p</i> -Chloronitrobenzene	*(2)	20 262
β -Naphthol	*(1)	4 485
Dimethylaniline	*(3)	1 504

*Manufactured (number of producers in parentheses) but quantities not disclosed.



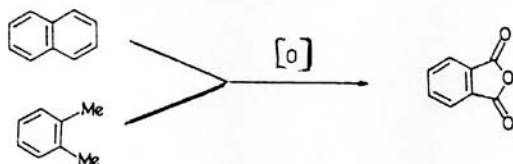
Scheme 5.2.

β -Naphthol. Naphthalene is sulphonated at high temperature to yield the thermodynamically more stable naphthalene-2-sulphonic acid. (Sulphonation at lower temperatures yields the kinetically controlled 1-isomer.) Caustic fusion causes a nucleophilic displacement of the sulphonic acid group by hydroxy to give β -naphthol (Scheme 5.3).



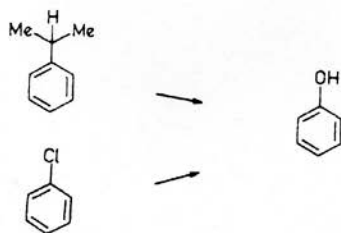
Scheme 5.3.

Phthalic anhydride. This is prepared by catalysed aerobic oxidation of either naphthalene or *o*-xylene (Scheme 5.4). It is used in large quantities for the production of phthalocyanine dyes and pigments, and for the synthesis of anthraquinone.



Scheme 5.4.

Phenol. Phenol is made both by the oxidation of cumene and by nucleophilic substitution of chlorobenzene under forcing conditions (high temperature and pressure) (Scheme 5.5).

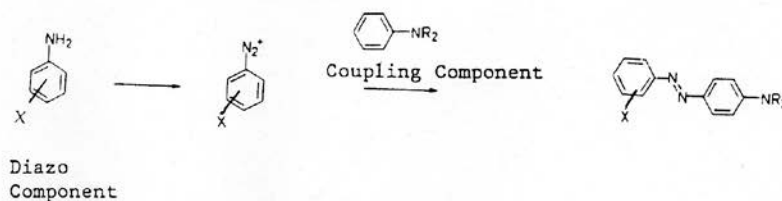


Scheme 5.5.

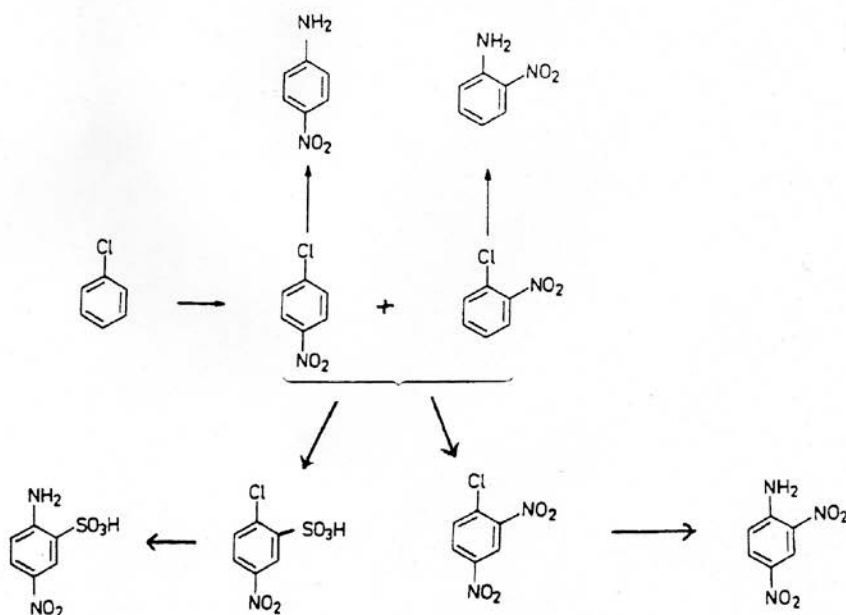
5.5.2.4 Dye intermediates. Products under this heading are of relatively small tonnage and are often made by dye manufacturers themselves for internal use and for sale to other dye manufacturers where competitive interests are compatible.

Carbocyclic.¹⁶ As mentioned earlier these are made by unit processes on benzene and naphthalene.

Benzene intermediates. Aniline is the principle benzene intermediate. The two major uses of aniline intermediates are diazo components and coupling components for azo dyes (Scheme 5.6).

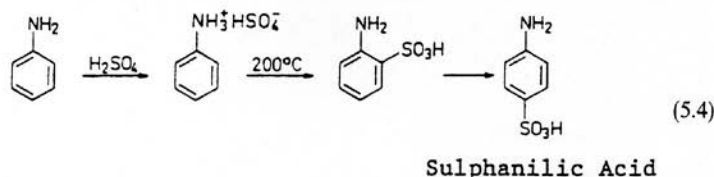


Scheme 5.6.



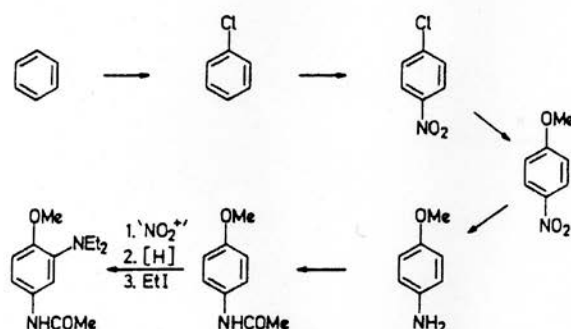
Scheme 5.7.

Aniline-based diazo components contain electron-withdrawing groups such as nitro, halogen, cyano and sulphonic acid. These are introduced by electrophilic attack (equation 5.4). As seen earlier the amino group is normally



introduced by nitration and reduction, but it may be introduced by nucleophilic substitution of an activated halogen (Scheme 5.7).

Aniline-based coupling components contain further electron-donating groups. Scheme 5.8 shows the synthesis of a fairly complex coupling component using a variety of the unit processes shown in Table 5.8.



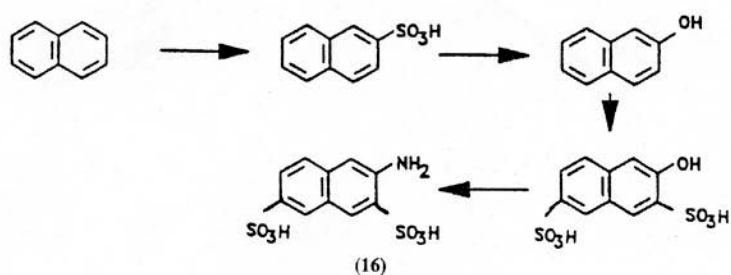
Scheme 5.8. Synthesis of a coupling component used in disperse dyes.

Naphthalene intermediates. As was the case with benzene, naphthalene intermediates can be split into diazo components and, in the case of naphthalene, the more important coupling components.

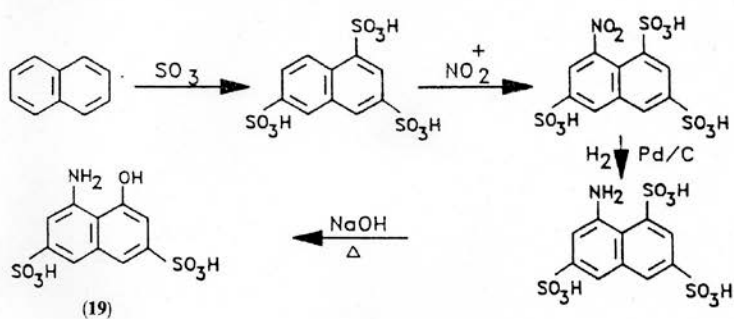
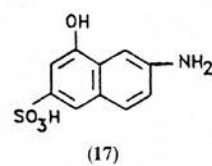
The most important naphthalene diazo components are 2-naphthylamine-sulphonic acids. These are generally prepared by sulphonation, caustic fusion and amination (Bucherer reaction). The synthesis of 2-naphthylamine-3,6-disulphonic acid (**16**) is typical (Scheme 5.9).

The most important naphthalene coupling components are the aminonaphtholsulphonic acids such as Gamma acid (**17**), J-acid (**18**) and especially H-acid (**19**). The syntheses of H-acid (Scheme 5.10) and of J-acid (Scheme 5.11) illustrate the principles involved.

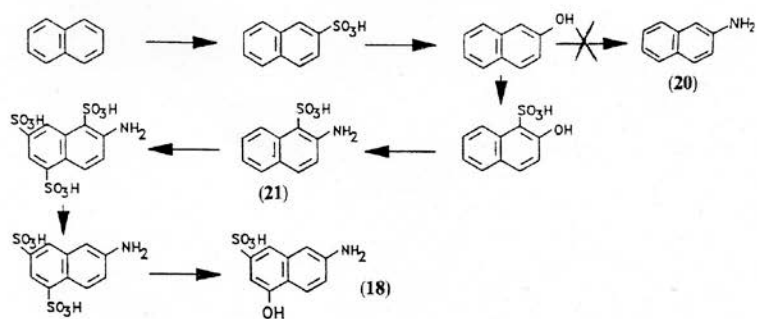
Noteworthy points are the selective replacement of a 1-sulphonic acid group rather than a 2-sulphonic acid group in the caustic fusion reaction and



Scheme 5.9.



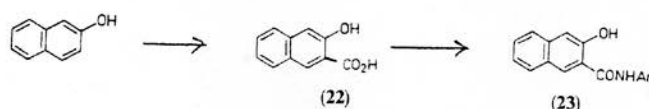
Scheme 5.10.



Scheme 5.11.

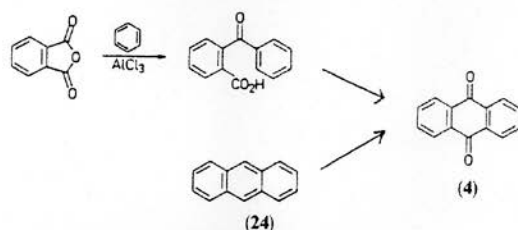
the use of the Bucherer reaction to convert a naphthol into a naphthylamine. Particularly important is the fact that β -naphthylamine (**20**) is a potent human carcinogen; it causes bladder cancer. Its use has been banned in dyes. It is circumvented in the synthesis of J-acid by introducing a sulphonic acid group prior to the Bucherer reaction. The sulphonic acid group, which is the best group for conferring water solubility on dyes and intermediates, is also the best detoxifying group. The presence of just one sulphonic acid group in β -naphthylamine, as in Tobias acid (**21**), renders it completely harmless.

The other important naphthalene coupling components are BON-acid (**22**) and its arylamides (**23**). These are important couplers for azo pigments. They are synthesised as shown in Scheme 5.12.



Scheme 5.12.

The only important intermediate from anthracene (**24**) is 9,10-anthraquinone (**4**). Anthraquinone is manufactured either by oxidation of anthracene or by the Friedel-Crafts acylation of benzene (Scheme 5.13).



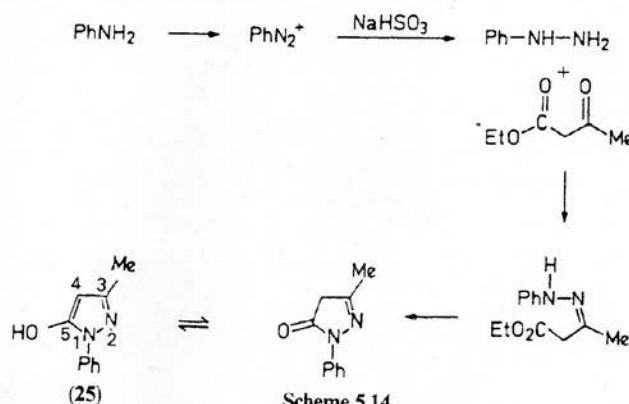
Scheme 5.13.

*Aromatic heterocyclic intermediates.*¹⁷ The most important heterocycles are those with five- or six-membered rings, and these rings may be fused to other rings, especially a benzene ring. Nitrogen, sulphur and to a lesser extent oxygen are the most frequently encountered hetero-atoms. They are conveniently divided into two groups: those containing only nitrogen, such as pyrazolones, indoles, pyridones and triazoles, which are used as coupling components in azo dyes except for triazoles, and those containing sulphur (and also optionally nitrogen), such as thiazoles, thiophenes and isothiazoles, which are used as diazo components in azo dyes. Oxygen is encountered as a hetero-atom in dyes, such as benzodifuranones and oxazines, rather than in intermediates.

Triazine is treated separately since it is used as the reactive system in many reactive dyes.

N-Heterocycles. Pyrazolones. Pyrazolones, e.g. (25), are used as coupling components since they couple readily at the 4-position under alkaline conditions to give important azo dyes in the yellow-orange shade area.

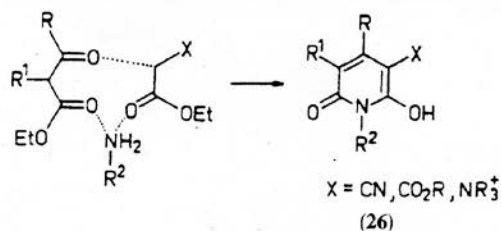
The most important synthesis of pyrazolones involves the condensation of a hydrazine with a β -ketoester. Commercially important pyrazolones carry an aryl substituent at the 1-position, mainly because the hydrazine precursors are prepared from readily available and comparatively inexpensive diazonium salts by reduction. In the first step of the synthesis the hydrazine is condensed with the β -ketoester to give a hydrazone; heating with sodium carbonate then effects cyclisation to the pyrazolone. In practice the condensation and cyclisation reactions are usually done in one pot without isolating the hydrazone intermediate. The example in Scheme 5.14 illustrates the condensation of phenylhydrazine with ethyl acetoacetate.



Scheme 5.14.

Pyridones. Pyridine itself has little importance as a dyestuff intermediate. However, its 2,6-dihydroxy derivatives have achieved prominence in recent years as coupling components for azo dyes, particularly in the yellow shade area.

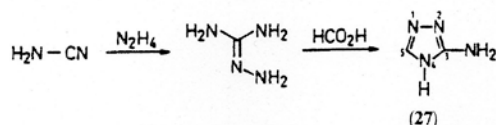
The most convenient synthesis of 6-hydroxy-2-pyridones (26) is by the condensation of a β -ketoester, e.g. ethyl acetoacetate, with an active methylene compound, e.g. malonic ester, cyanoacetic ester, and an amine (Scheme 5.15).



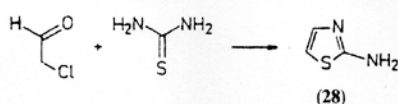
Scheme 5.15.

Triazoles. The triazoles are fairly representative of five-membered heterocycles containing three heteroatoms. Heterocycles containing more heteroatoms are not generally found in dyestuffs and even triazoles are not of widespread importance, although they do provide some useful red dyes for polyacrylonitrile fibres.

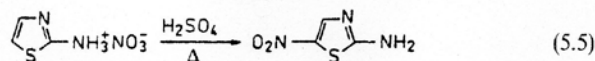
The most important triazole is 3-amino-1,2,4-triazole itself, used in the synthesis of diazahemicyanine dyes. The preparation of 3-amino-1,2,4-triazole (27) is simple, using readily available and quite inexpensive starting materials. Thus, cyanamide is reacted with hydrazine to give aminoguanidine which is then condensed with formic acid. Substituents in the 5-position are introduced merely by altering the carboxylic acid used.



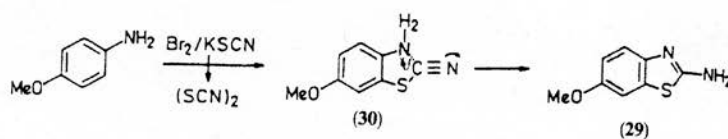
Sulphur and sulphur/nitrogen heterocycles. Aminothiazoles. In contrast to the pyrazolones and pyridones just described, aminothiazoles are used as diazo components. As such they provide dyes which are more bathochromic than their benzene analogues. Thus, aminothiazoles are used chiefly to provide dyes in the red-blue shade areas. The most convenient synthesis of 2-aminothiazoles is by the condensation of thiourea with an α -chlorocarbonyl compound; for instance, 2-aminothiazole (28) is prepared by condensing thiourea with α -chloroacetaldehyde—both readily available intermediates.



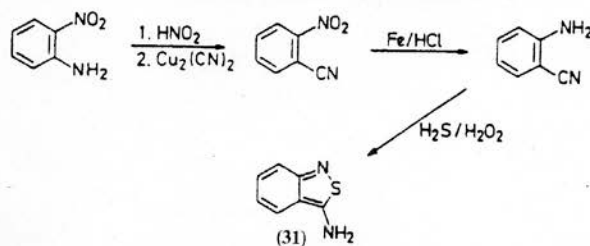
Substituents can be introduced into the thiazole ring either by using suitably substituted precursors or by direct introduction via electrophilic attack. An interesting example of the latter method is the preparation of 2-amino-5-nitrothiazole from the nitrate salt of 2-aminothiazole (equation (5.5)).



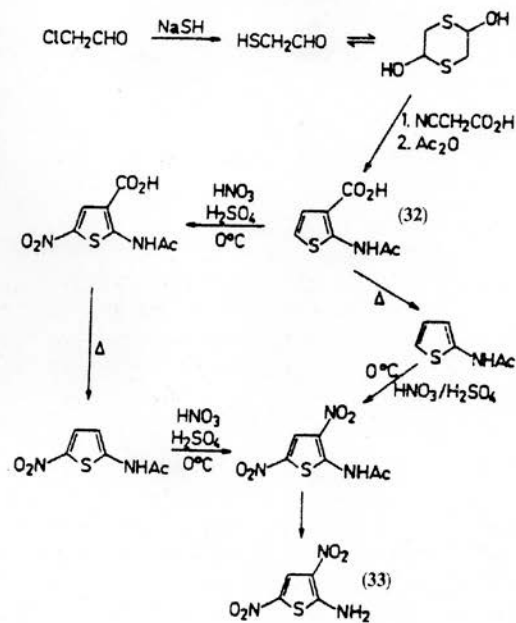
Aminobenzothiazoles. Aminobenzothiazoles are prepared somewhat differently to the thiazoles. Here the thiazole ring is annelated on to a benzene ring, usually via an aniline derivative. Thus, 2-amino-6-methoxybenzothiazole (29) is obtained from *p*-anisidine and thiocyanogen. The thiocyanogen, which is formed *in situ* from bromine and potassium thiocyanate (the Kaufman reaction), reacts immediately with *p*-anisidine to give the thiocyanate derivative (30); this spontaneously ring-closes to the aminobenzothiazole (29).



Benzoisothiazoles. 5-Aminoisothiazoles are relatively difficult to prepare cheaply but they are used as diazo components in magenta dyes for D2T2 (see later). However, the benzo homologues are easier to prepare and are important diazo components. Aminobenzoisothiazoles give dyes that are even more bathochromic than the corresponding dyes from aminobenzothiazoles. Aminobenzoisothiazoles (31) can be prepared from *o*-nitroanilines by the standard chemical transformation outlined in Scheme 5.16.



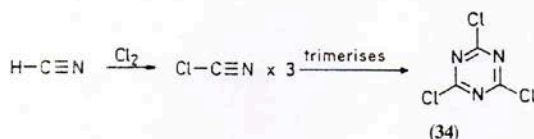
Scheme 5.16.



Scheme 5.17.

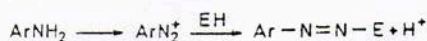
Thiophenes. The most important thiophenes, i.e. 2-aminothiophenes, are used as diazo components for azo dyes and are capable of producing very bathochromic dyes, e.g. greens, having excellent properties. Part of the reason for their later arrival on the commercial scene was the difficulty encountered in attaining a good synthetic route. However, this problem has been overcome by ICI. The synthetic route is very flexible so that a variety of protected 2-aminothiophenes can be obtained merely by altering the reaction conditions or alternatively by stopping the reaction at an intermediate stage. Thus, the initially formed thiophene (32) can be converted to the useful dinitrothiophene (33) by either of two routes (Scheme 5.17).

Triazines. The most commercially important triazine is 2,4,6-trichloro-s-triazine (cyanuric chloride, (34)). Cyanuric chloride has not achieved prominence because of its value as part of a chromogen but because of its use for attaching dyestuffs to cellulose, i.e. as a reactive group. This innovation was first introduced by ICI in 1956 and since then other active halogen compounds have been introduced.



5.5.3 Dyes

5.5.3.1 Azo dyes.¹⁸ Azo dyes are the most important class of dye, comprising over 50% of all commercial dyes. Almost without exception, azo dyes are made by diazotisation of a primary aromatic amine followed by coupling of the resultant diazonium salt with an electron-rich nucleophile (Scheme 5.18).



Scheme 5.18.

Formation of the azo dye constitutes the final step in the synthesis. Introduction of substituents is done on the precursor intermediates, the diazo component and the coupling component, normally by electrophilic substitution. This allows tremendous synthetic flexibility in azo dyes.

Azo dyes may be broadly divided into hydroxyazo dyes and aminoazo dyes. Hydroxyazo dyes can exhibit tautomerism⁹ (equation (5.6)) and many commercial hydroxyazo dyes exist in the more bathochromic and tinctorially stronger hydrazone form. Important dyes which exist in the hydrazone form are