Dyes and Pigments 3 (1982) 133–160

HETEROCYCLIC AZO COUPLING COMPONENTS

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(Received: 7 October, 1981)

SUMMARY

Progress in azo dye chemistry during the last twenty years has been determined to a large extent by the development of new heterocyclic coupling compounds, which have become most important in disperse dyes. From a vast amount of available information, a selection had to be made for the following review, and preference was given to topics with technical importance or with a special interest from the point of view of the chemistry involved. Among the subjects discussed are pyrazolones, iminopyrazoles, pyridones, aminopyrimidines, aminopyridines, hydrochinolines, aminothiazoles and some special aspects of the chemistry of cationic dyes are mentioned.

1. INTRODUCTION

Azo compounds represent the greatest production volume in dyestuff chemistry today, and their relative importance may even be growing in the future. Due to competition among producers, industry has had to optimize its dyestuff ranges for economic reasons and one way to do so is, for instance, partly to replace anthraquinone-based dyes by azo compounds. This can be observed in recent years with the appearance of blue disperse dyes, and even with some brilliant bluish-reds. Since it has become possible to imitate the brilliance of shade of the anthraquinones, these can hardly compete with the tinctorially much stronger and, in consequence, much cheaper azo dyes.

The great success of azo dyes is due to several factors: the simplicity of the coupling reaction, the immense possibilities for structural variations and adaptation to the needs of the most diverse applications for these dyes, and the often very high molar extinction of azo compounds.

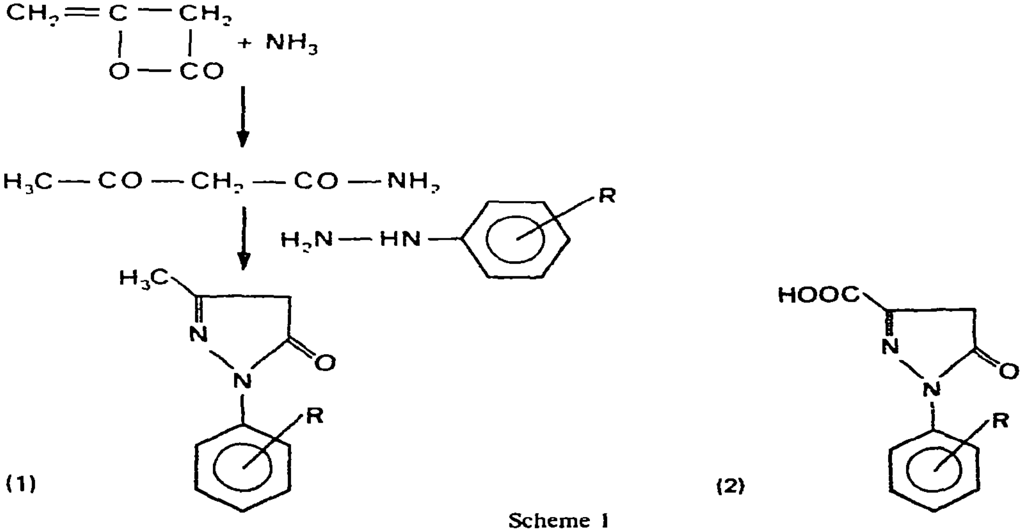
Dyes and Pigments 0143-7208/82/0003-0133/$02·75

As the great majority of azo dyes are prepared by the coupling reaction, progress in azo dye chemistry has been largely determined by technological progress in coupling, for instance by continuous coupling and coupling in organic solvents, and by the development of new diazo and coupling components. The success of new diazo components has been especially remarkable with disperse dyes, as it has become possible to cover the whole shade range with monoazo compounds. The new monoazo blues which can replace anthraquinones are part of this development. However, new azo coupling components, and in particular new heterocyclic coupling components, are no less important.

2. COUPLING COMPONENTS OF THE ENOL TYPE

2.1. Pyrazolones

The pyrazolones were discovered by Knorr in 1886 and introduced into azo dye chemistry at the beginning of this century. The synthesis first used, namely condensation of arylhydrazines with acetoacetic esters, leads in many cases to low yields of relatively impure products. A better method of synthesis of great technical importance today starts from acetoacetic acid amides, which can be prepared from diketene (Scheme 1). The aryl residue of the hydrazine may be substituted, of particular importance being the pyrazolonesulphonic acids which find use in direct and reactive dyes for cellulose, and in acid dyes for wool and polyamide. The hydroxyl groups of the pyrazolone azo dyes may take part in metal complex formation. Most widespread are methylpyrazolones (1) but, especially in reactive



(1)

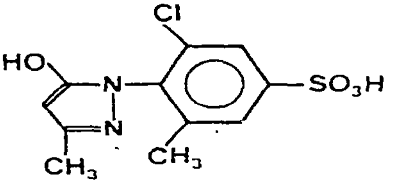
(2)

Scheme 1

dyes, pyrazolonecarboxylic acids (2) are often used. Their synthesis is based on oxaloacetic acid ester. Pyrazolone dyes in general are most important in the yellow to orange shade and some typical pyrazolone coupling components include compounds (3) to (9).

The pyrazolone (3) is a typical component for brilliant greenish-yellow wool and polyamide dyes, whereas compound (5) is to be found in reactive dyes. Compound (6) is an intermediate for copper-complex direct dyes and imparts good substantivity due to the stilbene system. All these pyrazolones are well established intermediates. Compounds (7) and (8) are newer developments designed for use as couplers in yellow disperse dyes. The substituents on the ring nitrogen, an aliphatic sulphone in one case and a triazine system in the other, serve to impart good build-up on polyester combined with good sublimation fastness. Compound (9), whose

(3)



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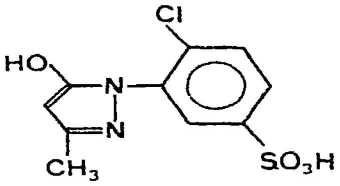

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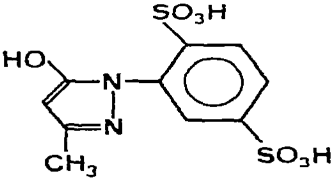

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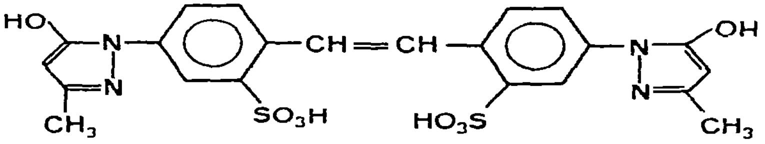

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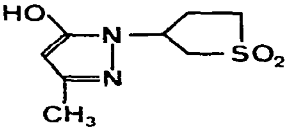

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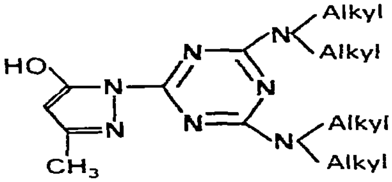
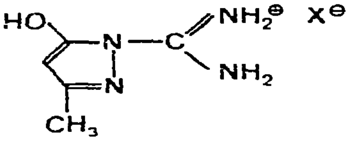


(9)



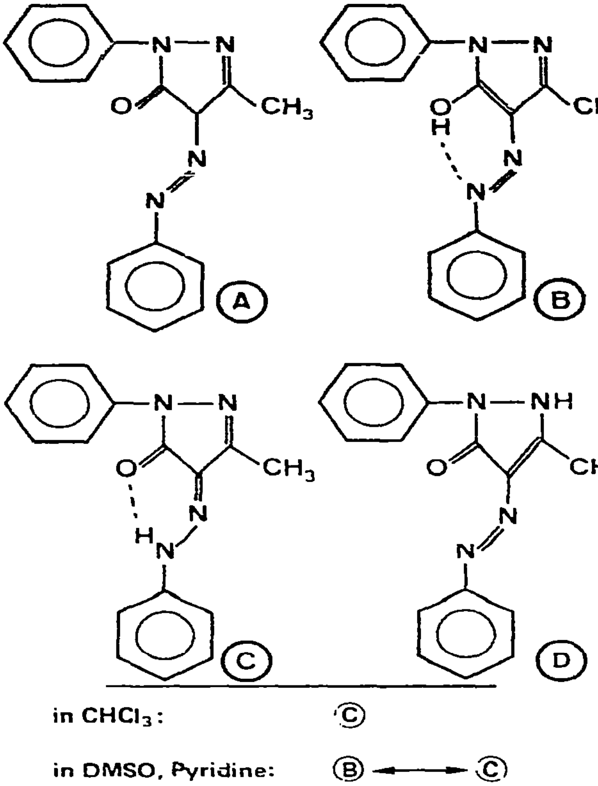


Fig. 1.

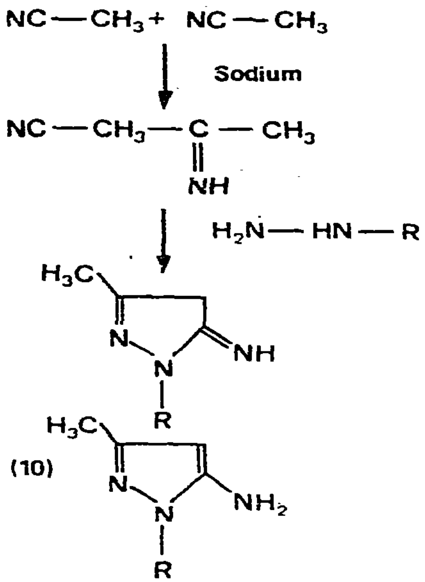
synthesis starts from aminoguanidine, has been proposed for the preparation of cationic yellow dyes with good migrating properties on polyacrylonitrile.

Pyrazolone disperse dyes have lost much of their importance on polyester, since dyes with much higher extinctions, such as the pyridones, have been developed during the past few years.

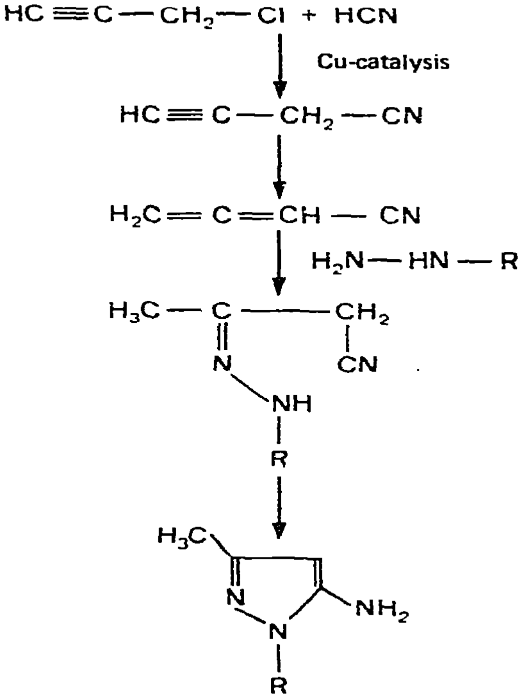
Pyrazolone dyes can exist in different tautomeric forms. The results of an investigation[1] of the dye obtained by coupling aniline on phenylmethylpyrazolone are illustrated in Fig. 1. In chloroform, this dye exists as the hydrazone C, whereas in polar solvents such as dimethylsulphoxide or pyridine an equilibrium mixture of the hydrazone C with the enol form B is present.

2.2. *Iminopyrazoles*

The iminopyrazoles may be considered as the imino analogues of the pyrazolones and their classical synthesis starts from diacetonitrile, obtained from acetonitrile and sodium, which then reacts (Scheme 2) with a hydrazine derivative to give the



Scheme 2

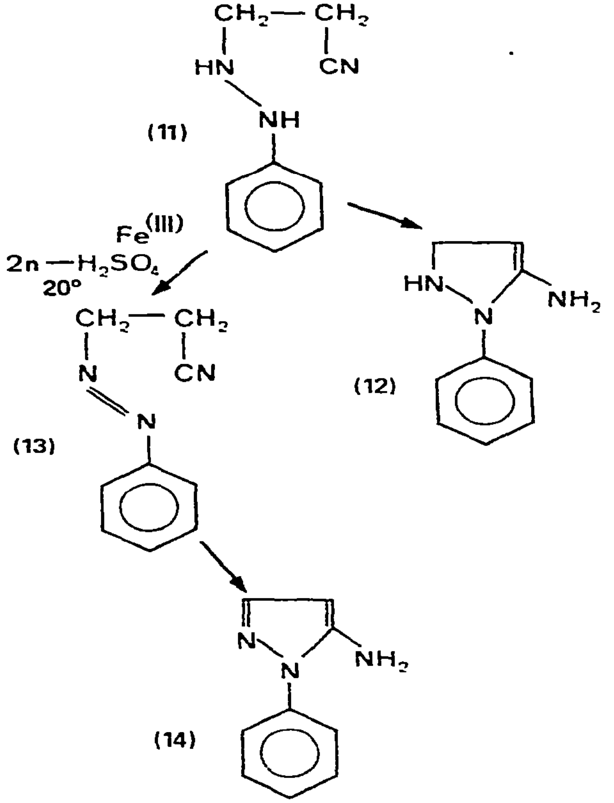


Scheme 3

iminopyrazole, which behaves in many reactions as the tautomeric aminopyrazole (**10**).

Many new syntheses for this type of intermediate have been conceived in recent years avoiding the use of the relatively expensive diacetonitrile and at the same time avoiding the necessity for the introduction of a methyl group in the 3-position of the heterocycle. Kurtz and Gold[2] have described a synthesis from propargyl chloride, which is reacted with hydrogen cyanide to form the propargyl cyanide. The latter isomerizes to the cyanoallene, which then reacts with a hydrazine derivative to form the hydrazone of cyanoacetone. Subsequent ring closure yields a 3-methyl-5-aminopyrazole (Scheme 3).

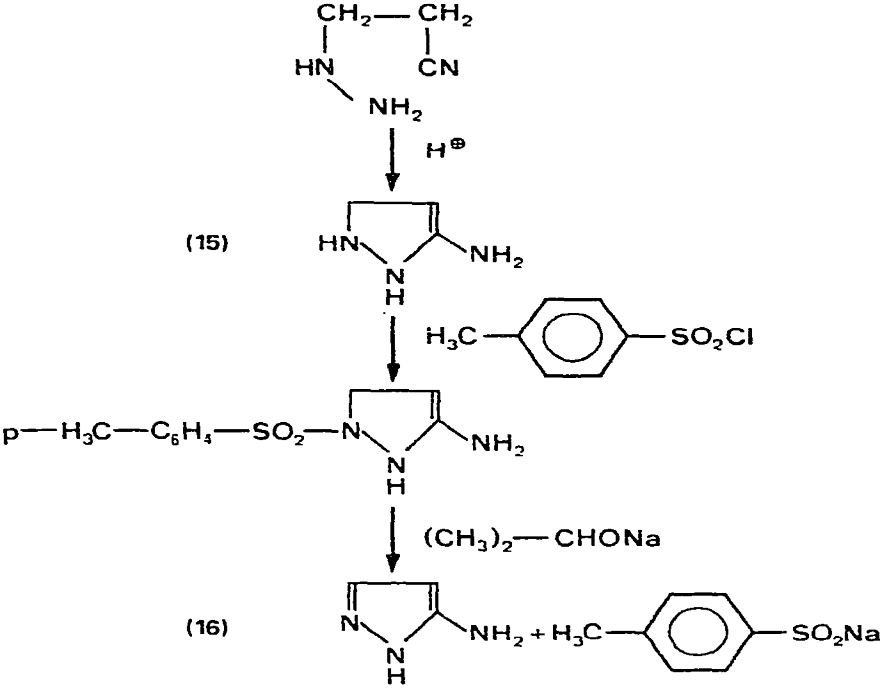
Another synthesis,[3] which leads to an aminopyrazole unsubstituted in the 3-position, is shown in Scheme 4. From cyanoethylphenylhydrazine (**11**) under acid conditions (**12**) is obtained but could not be dehydrogenated in a satisfactory manner. However, in the presence of oxidising agents, ring closure to the



Scheme 4

aminopyrazole (14) could be obtained in good yield. As the pyrazoline (12) cannot be dehydrogenated under these conditions, oxidation must take place prior to ring closure, and the reaction probably proceeds by way of the azo intermediate (13).

Another approach[4] makes use of the pyrazoline intermediate (15) of the type already mentioned. Dehydrogenation of the latter is accomplished in an unusual way by treating the tosyl derivative with alkali, whereby a sulphinate ion acts as the leaving group (Scheme 5). Yields in all stages are good.



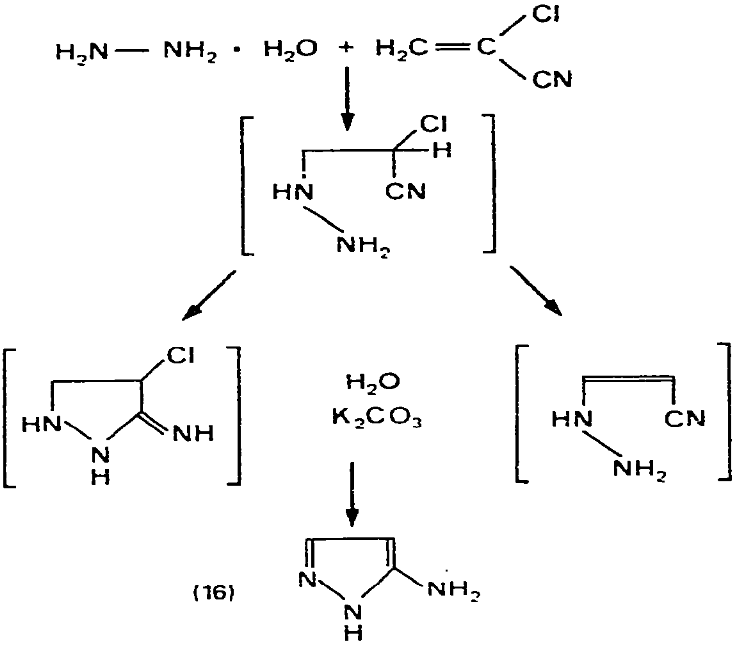
(15)

(16)

Scheme 5

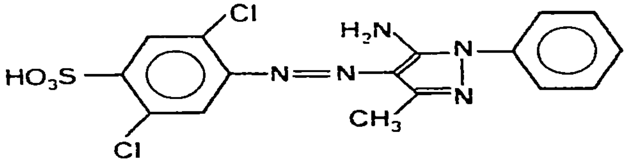
A very interesting one-pot synthesis of the same unsubstituted aminopyrazole (16) has been described by Ege and Arnold[5] (Scheme 6). The synthesis starts from α-chloroacrylonitrile, which is condensed in water under slightly alkaline conditions with hydrazine hydrate. No intermediate stage of the condensation reaction was isolated, and the exact course of the reaction is unknown. It is quite interesting that ring closure in this case takes place under alkaline conditions. The product is finally extracted and distilled, the yield being about 70 %. This type of synthesis appears to be limited to the pyrazole (16).

Iminopyrazoles can be coupled under acidic conditions to give yellow azo dyes. They are important for the production of very bright, greenish-yellow shades of



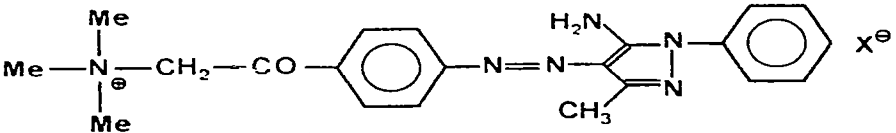
Scheme 6

(17)



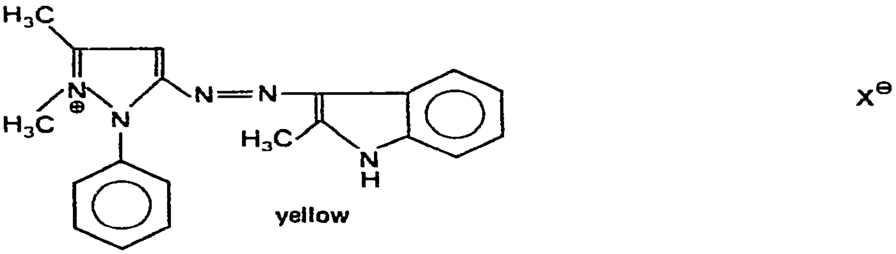
yellow

(18)



yellow

(19)

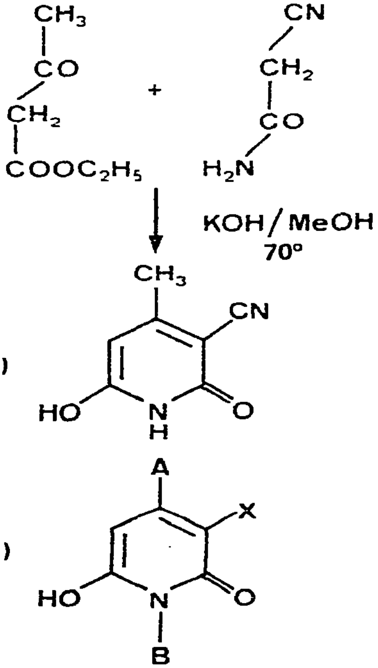


yellow

good lightfastness, especially on wool, polyamide and acrylics. They are outstanding among heterocycles insofar as they can be used as coupling and as diazo components. The amino group can be diazotized, resulting in diazos of strong coupling power. Some typical examples of azo dyes based on these intermediates are shown (**17**–**19**): (**17**) corresponds to a bright greenish-yellow dye for polyamide, with good lightfastness and good migration; (**18**) represents a so-called pending cationic yellow for acrylic fibres; (**19**) is a cationic dye where the iminopyrazole functions as a diazo component and is a diaza-hemicyanine-yellow of good lightfastness.

2.3. *Pyridones*

Other enol-type coupling components of great importance are to be found in the pyridone class, the prototype of pyridone couplers, (**20**), being reported in the last century (Scheme 7).[6] The great value of this type of coupler was, however, recognized only in the mid sixties, and since then there has been tremendous research activity in this field, resulting in more than 200 published patents. Structural variations are easily possible, as all three substituents in (**21**) can be varied. Group A is in most cases the methyl group, due to the cheapness of acetoacetic acid ester. Group B can be varied in many ways, starting from readily accessible *N*-substituted cyanoacetamides. Group X has to be an electron-attracting



(20)

(21)

Scheme 7

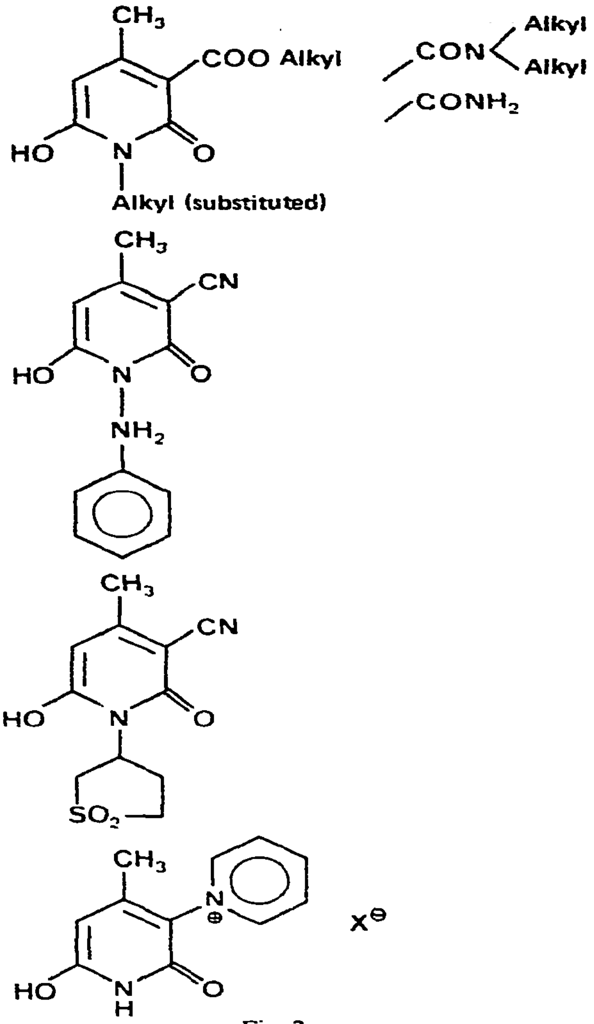
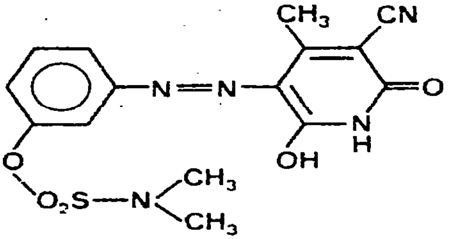


Fig. 2.

group to ensure sufficient activation of the adjacent methylene group; the cyano group seems to be the most satisfactory as its transformation after synthesis is also possible. Pyridone dyes have very good fastness and dyeing properties, and can replace the more expensive styryl dyes on polyester for very greenish-yellow shades.

In addition, they have often very high molar extinction, and consequently, high tinctorial strength. Their shade range goes from greenish-yellow to orange. They are to be found among cellulose-reactive dyes. They have also been introduced in cationic dye ranges, and are becoming more and more important as disperse

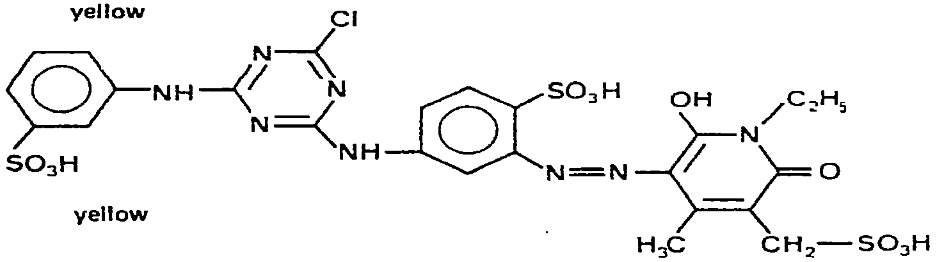
(22)



λmax 425 nm
Σ = 41000

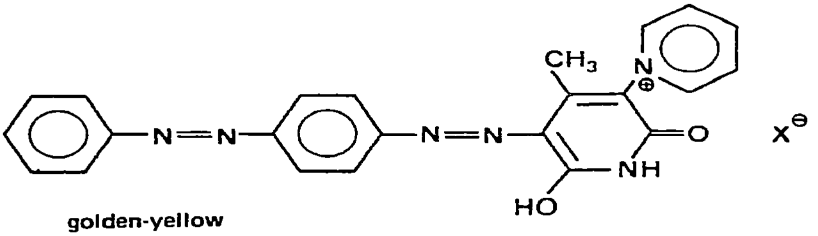
yellow

(23)



yellow

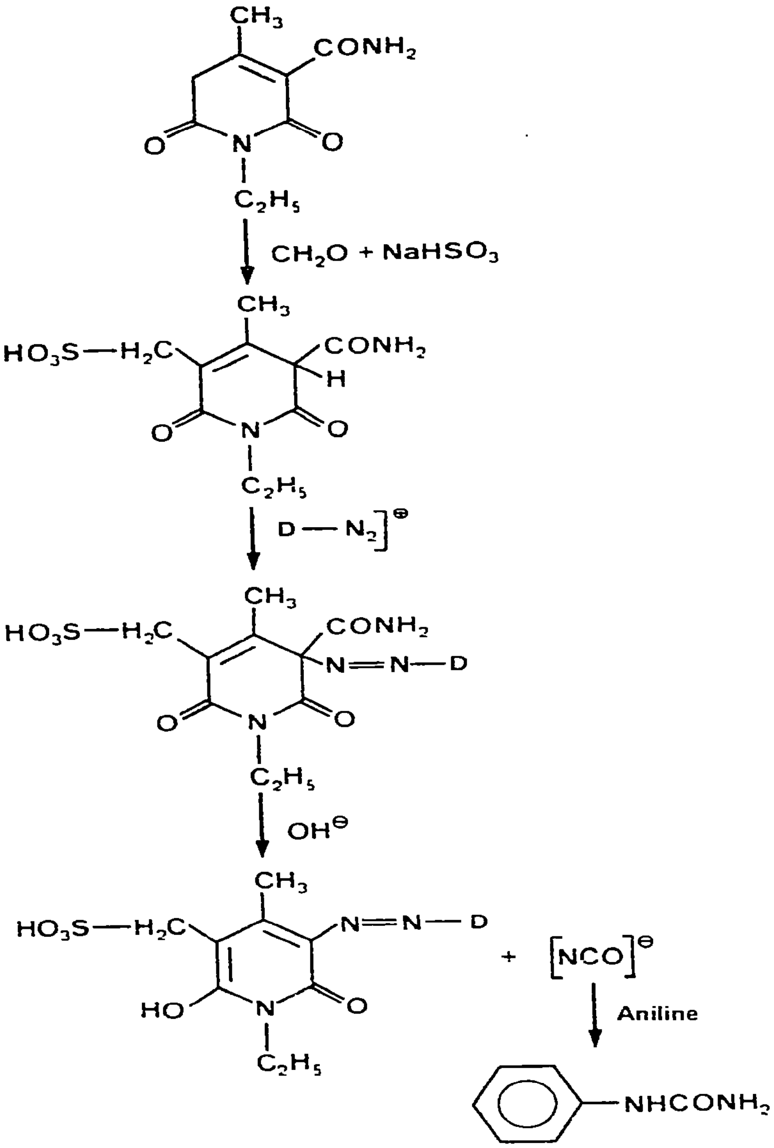
(24)



golden-yellow

yellows. It is probable that pyridones will dominate the yellow shade range in disperse dyes in the near future. They have been less successful in wool and polyamide dye ranges up to now, due to only marginal lightfastness on these fibres. Overall, the introduction of pyridone coupling components may be considered as one of the most important achievements in dye chemistry over the last 20 years.

Typical examples of pyridone coupling components are shown in Fig. 2. The component containing the pyridinium group can be prepared from pyridinium acetamide, the pyridinium group activating the adjacent methylene group for the pyridone condensation. Some typical pyridone dyes are illustrated (**22**–**24**): (**22**) is a very greenish-yellow disperse dye which contains an unusual diazo component. The high molar extinction is quite remarkable, being about twice that of pyrazolone yellow, and makes such types of dye highly competitive from the point of view of price. Compound (**23**) is an example of a greenish-yellow cellulose reactive dye. Compound (**24**) is a cationic dye for acrylic fibres prepared from a pyridinium-substituted pyridone. In (**23**) the pyridone moiety is substituted by a sulphomethylene group. The way such a group can be introduced has been described by Hegar[7] (Scheme 8).

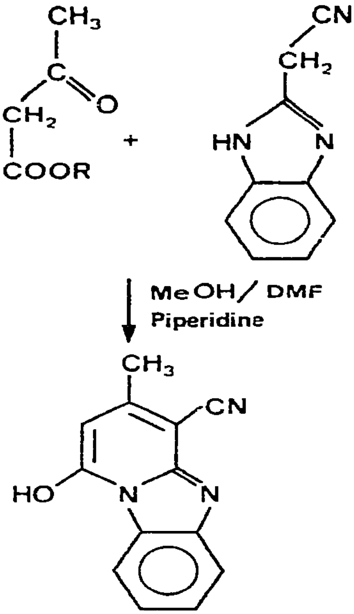

CH3
CONH2
O
N
O
C2H5
CH2O + NaHSO3
HO3S—H2C
H
D—N2 ⊕
N=N—D
OH⊖
HO
+ [NCO]⊖
Aniline
NHCONH2

Scheme 8

A pyridone carbonamide is reacted with formaldehyde bisulphite and a methylene sulphonic acid derivative is obtained with no free coupling position. Nevertheless, this intermediate can be coupled with a diazonium compound, whereby the carbonamide group is eliminated, cyanate ion functioning as the leaving group.

The last reaction step can be verified by capturing the cyanate ion with aniline to form phenylurea.

Some other coupling components should be mentioned which can also be considered as pyridone derivatives in the widest sense.

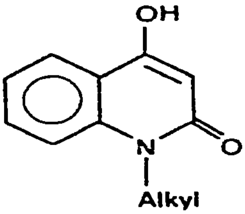


Scheme 9

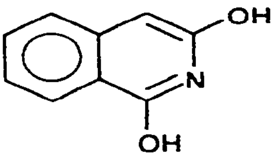
Benzimidazolylacetonitrile may be condensed with acetoacetic acid ester in the presence of a basic catalyst (Scheme 9) to form a new heterocyclic compound (25), which may be considered as a pyridone derivative.[8] This new coupling component has been proposed as a coupler in azo pigments.

Compounds (26)–(28) may also be considered as pyridone derivatives; (26) has been used as a coupler for yellow disperse dyes,[9] which are mostly obsolete nowadays, and the non-alkylated compound is a coupler for yellow metal complex pigments; (27) has also been proposed as a coupler for azoic pigments, its *N*-alkyl derivative having been used for acid yellows for polyamide;[10] (28), prepared from homophthalic acid and *o*-phenylenediamine,[11] is a coupler which is more bathochromic compared with the compounds of type (27).

(26)



(27)



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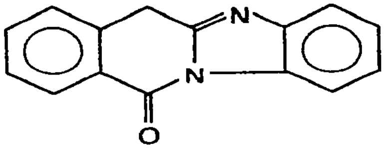
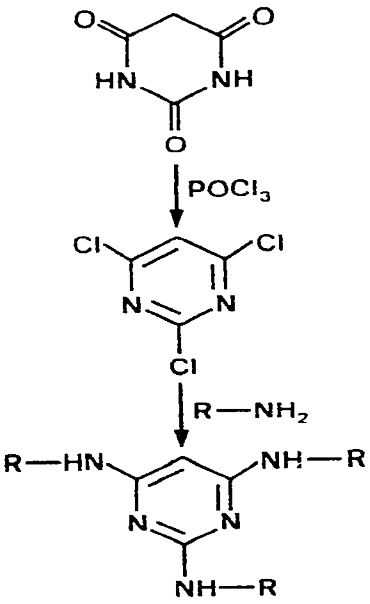




Scheme 10

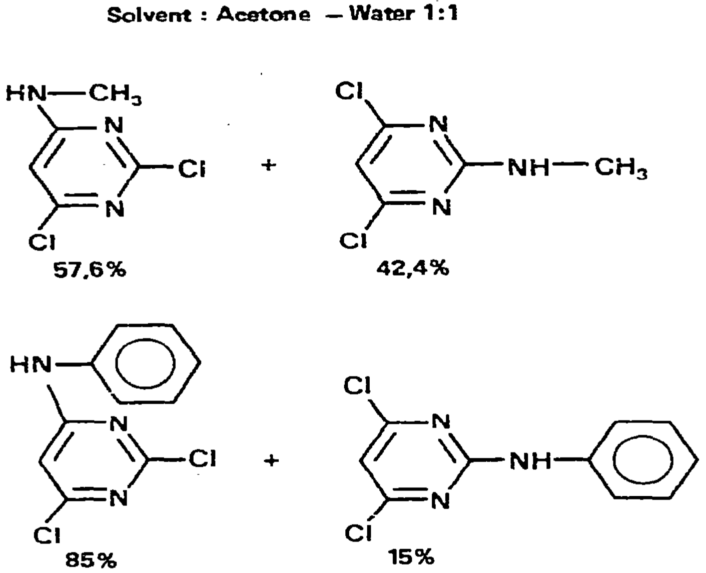


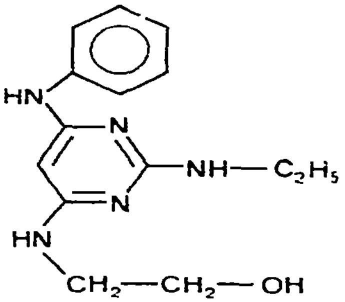
Fig. 3.

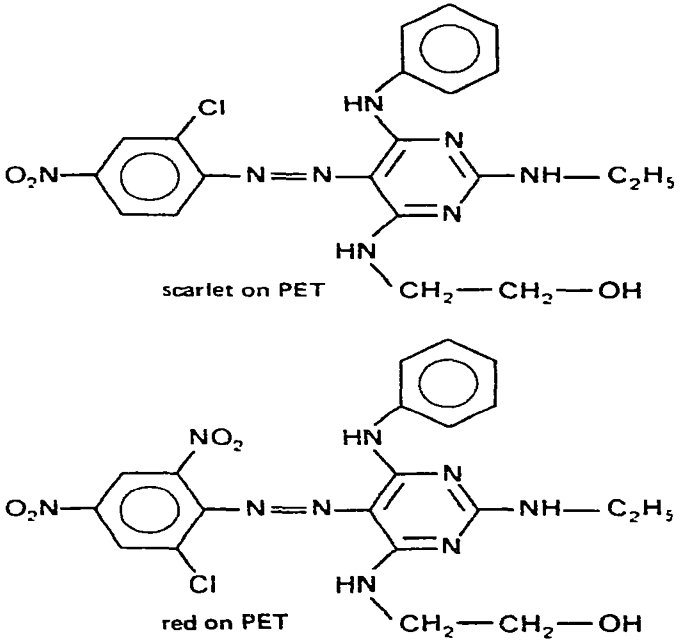
3. HETEROCYCLIC COUPLING COMPONENTS BEARING AMINO GROUPS

It has been known for some time in pharmaceutical chemistry that some aminopyridines and pyrimidines may be coupled with diazonium compounds, but only in the late sixties did such components find attention in dyestuffs chemistry.

Couplers of the aminopyrimidine-type may be considered first. Reaction of trichloropyrimidine with suitably substituted amines is the simplest way to obtain these compounds (Scheme 10). The problem arises as to how it may be possible to introduce different amine substituents in the three positions of the pyrimidine ring in a stepwise manner. The isomer distribution resulting from the reaction of chloropyrimidines with amines has been studied,[12,13] and some of the results are illustrated in Fig. 3. The investigation revealed that the solvent system has a great influence on the isomer distribution, and that aliphatic amines show a greater tendency to random distribution than the less basic aromatic amines where substitution at the 4-position predominates. When reacting trichloropyrimidine with different amines, mixtures are always obtained, but by using amines with differing reactivity in stepwise reaction a product can be obtained in which one of the possible isomers largely predominates. Such a coupling component, (**29**), is shown in Fig. 4 together with two disperse dyes prepared from it.[14] It is obvious that these pyrimidine couplers are hypsochromic compared with couplers of the dialkylaminobenzene-type of classic disperse dye chemistry, especially when the red dye with the very

(29)





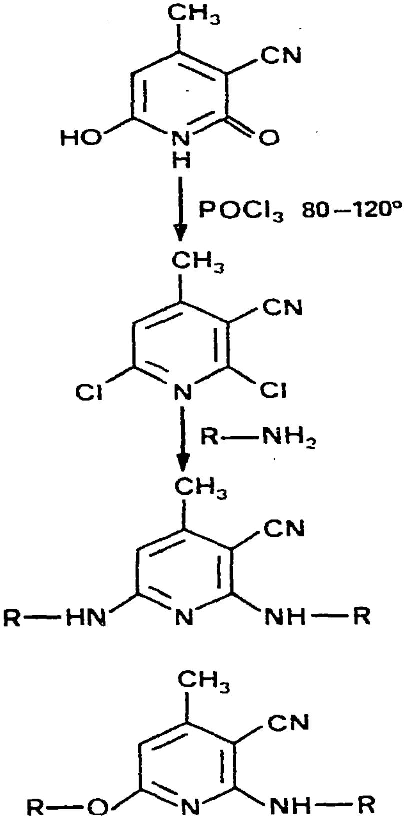
scarlet on PET

red on PET

Fig. 4.

bathochromic dinitro–chloroaniline–diazo is considered. The shade range of dyes based on aminopyrimidine couplers is for this reason limited to yellow and red.

Several advantages are offered by these coupling components. Firstly, the dyes are very brilliant and in this respect surpass those based on dialkylaminobenzene couplers. This holds especially for the reds on polyester, where no dyes with a comparable brilliance were previously available. Secondly, the dyes often have very high lightfastness and high molar extinction when employed in disperse dyes for polyester or acid dyes for polyamide. However dyes for cellulosic fibres from such components are of no interest, due to insufficient lightfastness.



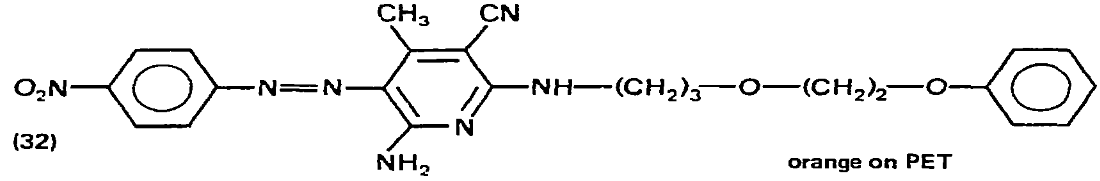
(30)

(31)

Scheme 11

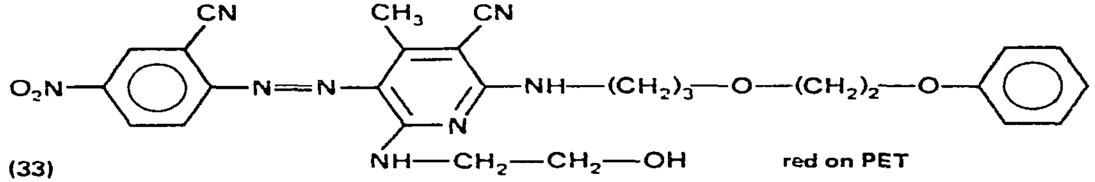
Related to the pyrimidine couplers are some coupling components derived from cyanopyridines. The synthesis of a key intermediate[15–17] for this type of compound is shown in Scheme 11. The cyanomethylpyridone is reacted in the usual way with phosphorus oxychloride to form a dichlorocyanomethylpyridine. By reaction of this compound with amines the coupling component (30) is obtained. As with the trichloropyrimidines, stepwise reaction with suitable amines is possible to introduce two different amine residues. By stepwise reaction of the dichlorocyanopyridine firstly with an amine, and then with an alcoholate, aminoalkoxy-substituted coupling components (31) can be obtained.[18] In all these cases, as with the triaminopyrimidines, mixtures of products are obtained, with one component more or less predominating, depending on the reaction conditions.

These cyanopyridine couplers have been proposed for the synthesis of disperse and acid dyes and some typical examples[19,20] are shown (32–35).



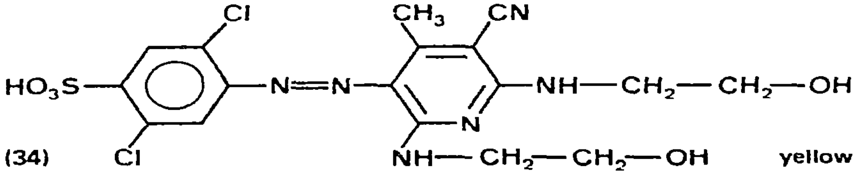
(32)

orange on PET



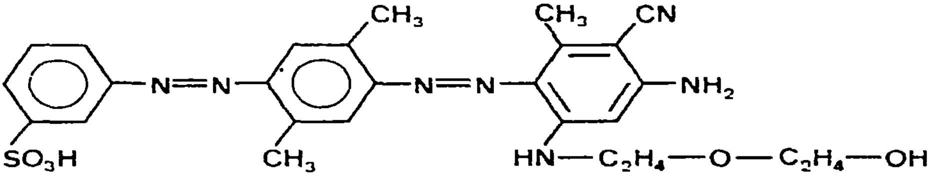
(33)

red on PET



(34)

yellow on PA

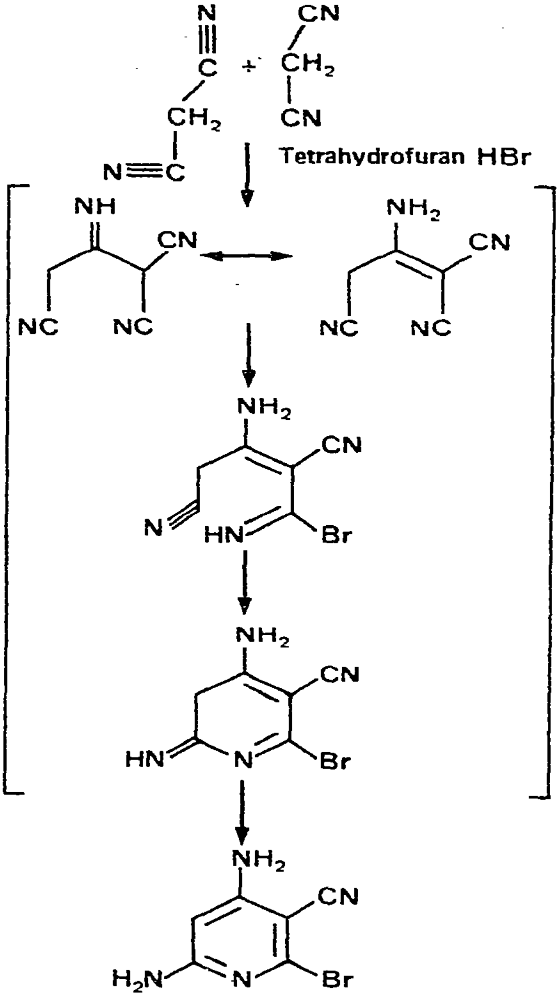


(35)

scarlet on PA

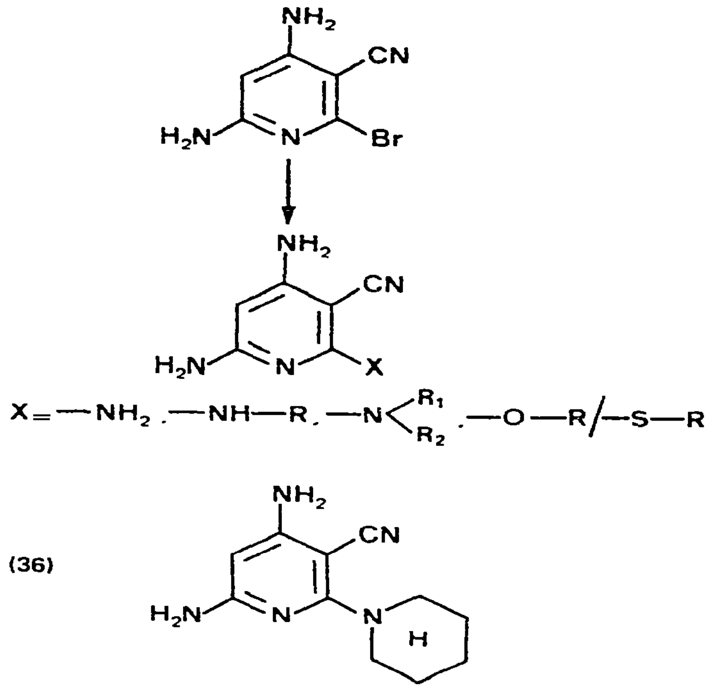
The dyes (32) and (33) are disperse dyes for polyester which they dye to extremely brilliant shades with good lightfastness. In (33) the hypsochromic nature of this type of coupler is again evident, since with the very bathochromic 2-cyano-4-nitroaniline diazo a neutral red is obtained. Compounds (34) and (35) are acid dyes for polyamide. To obtain a scarlet as in the case of (35) a disazo structure had to be chosen to ensure the necessary bathochromism.

A further possibility involves the preparation of triaminocyanopyridine coupling components making use of malononitrile dimer as starting material,[21,22] shown in Scheme 12. The course of the reaction of malononitrile dimer with hydrobromic acid is hypothetical, but may perhaps be interpreted as an addition of hydrobromic acid to a nitrile group, followed by a Thorpe–Ziegler ring closure and isomerization to an isomeric mixture of diaminocyanobromopyridines. The bromine atom can be



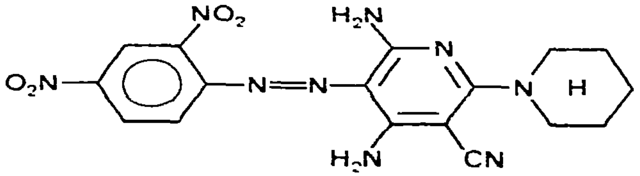
Scheme 12

exchanged by nucleophilic reaction with amines, alcohols, phenols or mercapto-compounds to produce potential coupling components (Scheme 13); (36) is a typical representative of this class of coupling component. A red dye for polyester with very good lightfastness and of high brilliancy,[23] prepared from (36) is shown in Fig. 5. The triaminopyrimidine dyes and the triaminocyanopyridine dyes of comparable structure have similar shades in accordance with Wizinger's statement that the groupings (37) and (38) are optically equivalent in dyestuffs.



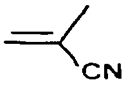
(36)

Scheme 13



red on PET

(37)



(38)

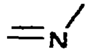
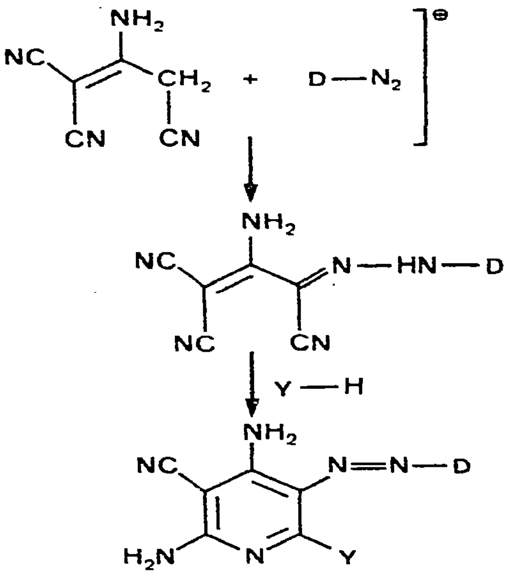


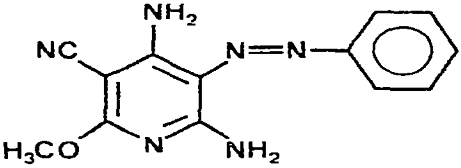
Fig. 5.

Another synthetic approach to dyestuffs containing these cyanopyridine components has been found,[24] which is illustrated in Scheme 14.



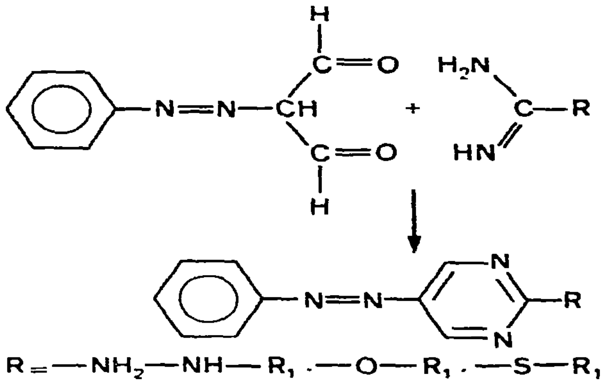
Scheme 14

This dyestuff synthesis is also based on the malononitrile dimer, which is coupled with a diazo compound to give a hydrazone. The hydrazone is then reacted with an alcohol, an amine or a mercapto-compound which results in ring closure to form the cyanopyridine, whereby two isomers may arise. When using methanol (Y═MeO—) for instance in the ring closing step, the yellow dyestuff shown in Fig. 6 will be formed. This method of dyestuff-synthesis is simpler than the former one, as the ring closure step using expensive hydrobromic acid to form the cyanopyridine is avoided. A similar synthesis of a dyestuff containing formally a pyrimidine coupling component[25] is shown in Scheme 15. A diazo component is coupled on malondialdehyde and the resulting azo compound then condensed with a urea or guanidine



yellow on PET

Fig. 6.



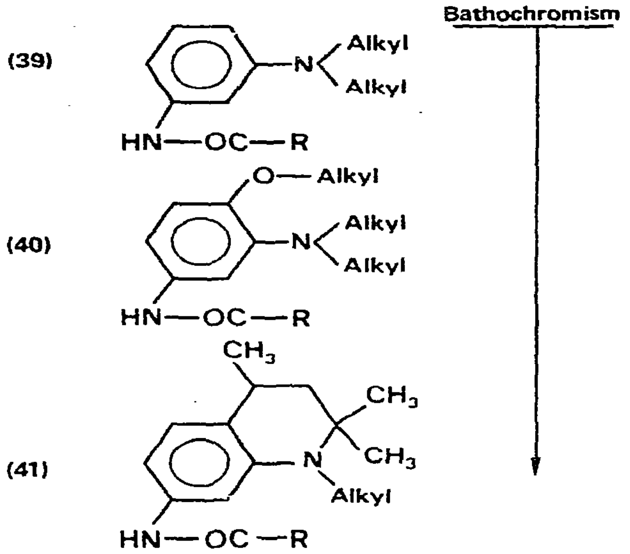
Scheme 15

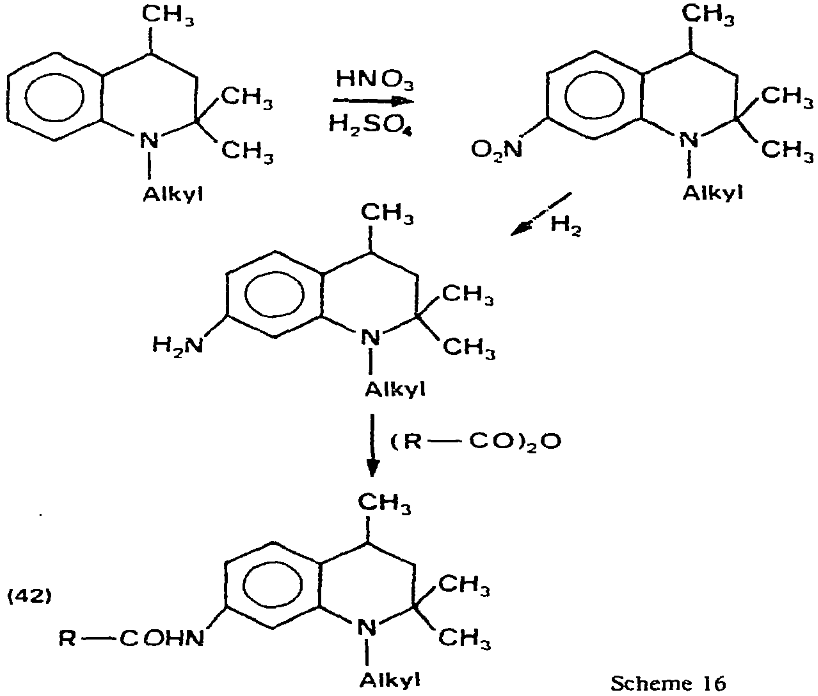
derivative to form the final dyestuff. This kind of dye is remarkable insofar as synthesis by azo coupling on the corresponding pyrimidine derivative would not be possible in view of insufficient nucleophilicity of such low-substituted pyrimidines.

It may be concluded that all these pyrimidine and pyridine coupling components have mainly contributed to the development of very brilliant disperse reds of a generally high standard of fastness. These coupling components have only one disadvantage, that is their relatively high price, due to the complicated chemistry involved. For that reason, it seems difficult to make predictions about their future commercial importance.

4. HETEROCYCLIC COUPLING COMPONENT FOR BLUE DISPERSE DYES

Heterocyclic coupling components have also made contributions to the development of new brilliant disperse blue dyes. The shade range of brilliant blues in disperse dyes has for a long time been dominated by anthraquinone dyes which are expensive, in great part due to their low molar extinction. A big effort has been made in recent years to introduce brilliant monoazo disperse blues. To obtain blue shades with monoazo dyes very bathochromic, strongly electron-attracting diazo compounds have to be combined with very bathochromic, strongly electron-donating coupling components. Some types of coupling components which may be used for this purpose are shown (**39**–**41**); (**39**) has long been known, as a very bathochromic component of the dialkylaminobenzene type and has also been much used in the red shade range, leading to brilliant shades of good lightfastness. By introducing an alkoxy group in the 6-position, as in (**40**), a still more bathochromic component is obtained. This type can be found in most disperse navy blues, although compared with (**39**) lightfastness of the resulting dyes is lower and the shades are duller. Finally, by connecting the 6-position with the tertiary amino group by a saturated chain as in


Bathochromism
(39)
Alkyl
Alkyl
HN—OC—R
(40)
O—Alkyl
Alkyl
Alkyl
HN—OC—R
(41)
CH3
CH3
CH3
N
Alkyl
HN—OC—R

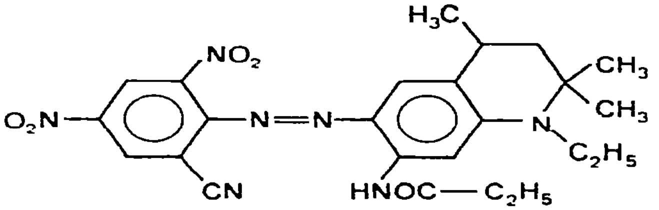

CH3
CH3
CH3
N
Alkyl
HNO3
H2SO4
O2N
H2
H2N
(R—CO)2O
(42)
R—COHN

Scheme 16

(**41**), a heterocyclic coupling component is obtained which can be used to produce relatively greenish brilliant blue shades.

The synthesis of components of this type is shown in Scheme 16. The *N*-alkylated trimethyltetrahydroquinoline starting material, prepared from aniline and acetone, is nitrated, the nitro-derivative hydrogenated to the amino compound and the latter acylated to the tetrahydroquinoline coupling component (**42**).[26] Compound (**43**) is

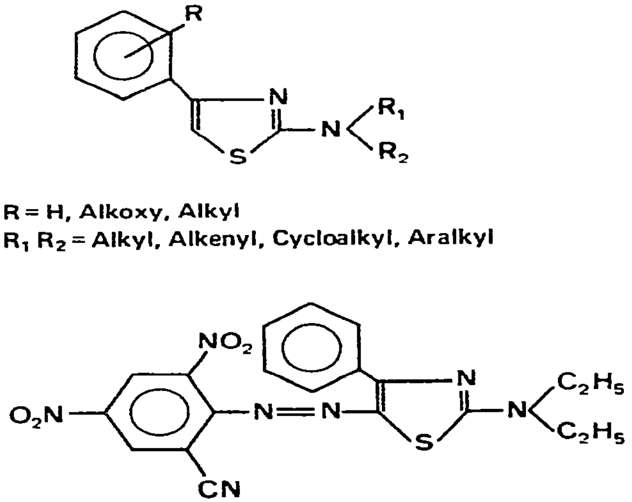
(43)



blue on PET

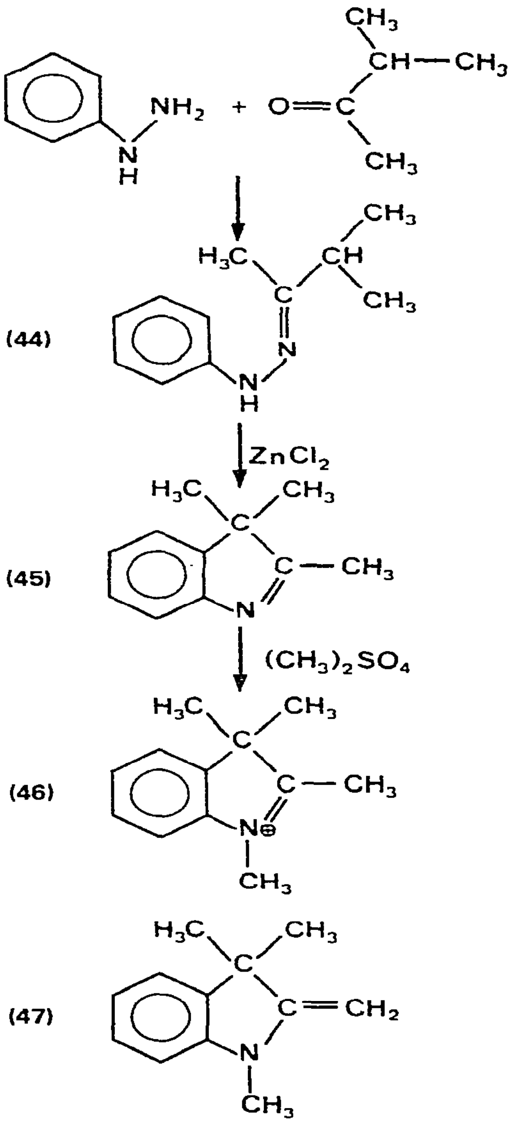
a greenish-blue disperse dye prepared from such a coupling component in combination with the very bathochromic diazo component dinitrocyanoaniline.[27,28]

Among other heterocyclic compounds which can be used as azo coupling components, some aminothiazoles may be mentioned. Numerous patents on this subject covering disperse and acid dyes have appeared in recent years. These components are relatively bathochromic compared with the more usual dialkylaminobenzene couplers and may be used for instance to produce monoazo disperse blues and even greens. Figure 7 shows some coupling components which can be



blue on PET

Fig. 7.

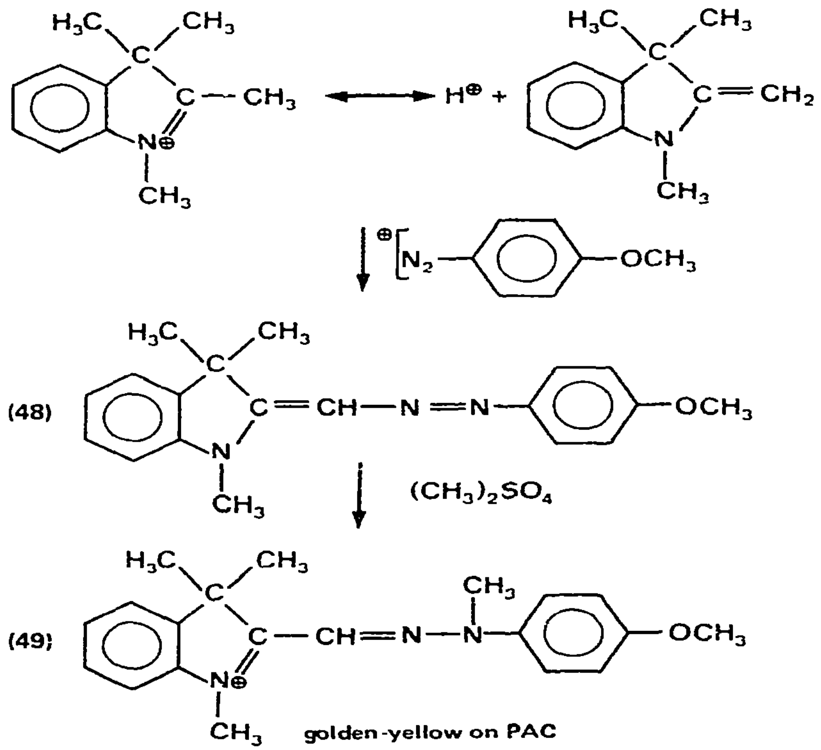


Scheme 17

prepared by known methods,[29,30] and a blue disperse dye for polyester made from one of them. This type of coupler is very bathochromic, but the lightfastness of the resulting dyes appears often to be marginal. As yet, no commercial dyes based on this chemistry have appeared.

5. HETEROCYCLIC COUPLING COMPONENTS FOR CATIONIC DYES

A very important coupling component for the synthesis of some azamethinecyanines is the so called 'Fischer Base', whose synthesis is shown in Scheme 17. Phenylhydrazine is condensed with methylisopropylketone to yield the corresponding phenylhydrazone (44), which by way of the Fischer indole synthesis gives the hydroindole (45). Methylation of the latter with dimethyl sulphate gives (46) which may be considered as the protonated form of 1,3,3-trimethyl-2-methyleneindoline (47), the so-called 'Fischer Base'.

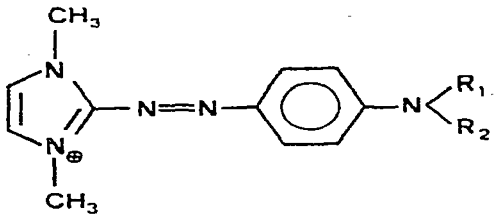


golden-yellow on PAC

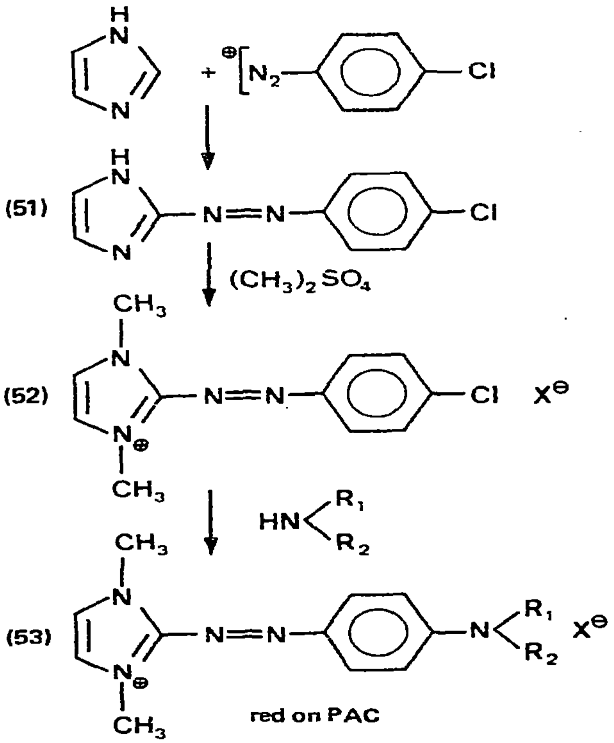
Scheme 18

This has the interesting property that it can function as a coupling component, whereby the azo-grouping attacks the activated methyl or methylene group respectively, as shown in Scheme 18.

(50)



With diazoanisidine for instance an azo dye, (**48**), is obtained which by methylation is transformed to the cationic dye (**49**). This is a golden yellow with high lightfastness and high tinctorial strength. Dyes of this type are among the most important dyestuffs for acrylics in the yellow shade range.



red on PAC

Scheme 19

The next topic concerns an unusual method of synthesis of an azo structure. Preparation of the dyestuff (**50**) using the dialkylaminobenzene as the coupling component cannot be realized, as the diazonium salts of aminoimidazole in the quaternized or non-quaternized form cannot be prepared. On the other hand, imidazole can be used as a coupling component, as shown in Scheme 19 to give (**51**), which is of an amphoteric character and of no interest as a dyestuff. Quaternisation of (**51**) leads to (**52**). In this intermediate the chlorine atom *para* to the azo group is highly activated and reaction with nucleophiles under very mild conditions is possible. The example given shows reaction with a secondary amine[32] which leads to azacyanine dyes, (**53**). In this way, dyestuffs are technically accessible which cannot be prepared by the azo coupling reaction. The dyestuffs (**53**) are brilliant red dyes for acrylics with good lightfastness and good migration.

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