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HETEROCYCLIC DIAZO COMPONENTS

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SUMMARY

Dyes with heterocyclic diazo components have received much attention because of their high tinctorial power and excellent brightness. Historically, dyes prepared from 2-aminobenzothiazoles and 2-aminothiazoles have played a significant role in disperse dye technology. More recently, dyes prepared from various heterocyclic amines including 2-amino-1,3,4-thiadiazoles, 5-amino-1,2,4-thiadiazoles, 5-aminoisothiazoles, 2-aminoimidazoles, 2-aminothiophenes, 3-amino-2,1-benzisothiazoles, and 5-aminopyrazoles have been evaluated as disperse dyes. Some of these dyes offer excellent brightness of shade and are commercially competitive with more expensive anthraquinone dyes. Heterocyclic diazo components have now been used to prepare acid dyes for polyamide carpet fibres, and some of these acid dyes have been shown to have excellent levelling properties. In some cases, new preparative chemistry has been developed for synthesis of the older as well as the newer heterocyclic diazo components.

1. INTRODUCTION

Heterocyclic amines have been used extensively in the preparation of disperse dyes with outstanding dischargeability on cellulose acetate. These dyes are characterized also by having generally excellent brightness and high extinction coefficients, relative to azo dyes derived from substituted anilines. These properties encouraged work on dyes prepared from heterocyclic amines suitable for dyeing polyester and polyamide fibres. Heterocyclic amines also proved useful for preparing cationic and metallized dyes, but the chemistry of these dyes is beyond the scope of this review. Some recent attention to the use of heterocyclic amines in preparing acid dyes will be

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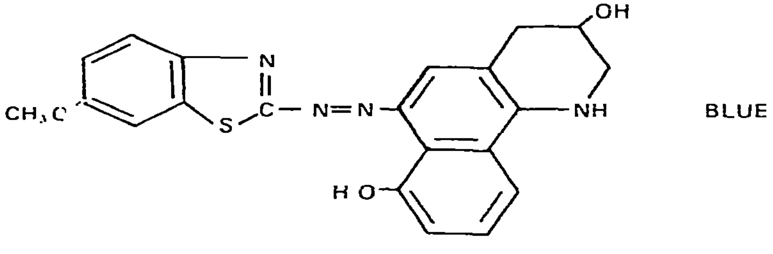
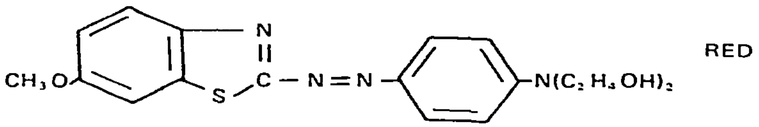
noted. Popular preparative routes to the most important heterocyclic amines are given. The scope of this review then is limited to disperse dyes and to a few comments on acid dyes.

2. EARLY HISTORY

Early interest in heterocyclic diazo components was stimulated by the need for blue disperse dyes with improved dischargeability and gas fastness (oxides of nitrogen) for cellulose acetate. Before 1950, almost all the disperse blue dyes used were prepared from the anthraquinone class and had the limitations of poor dischargeability and sensitivity to oxides of nitrogen. Red and blue azo dyes with good dischargeability for use in printing were developed and commercialized earlier from 2-amino-6-methoxybenzothiazole[1] (Fig. 1), but these dyes had relatively poor fastness properties, particularly lightfastness. Investigation of the use of heterocyclic diazo components was stimulated by the discovery by J. Dickey[2] that 2-amino-5-nitrothiazole could be used to produce bright blue dyes (Fig. 2) with adequate lightfastness combined with excellent dischargeability, gas fastness and dyeability on cellulose acetate. Greenish blue dyes can be prepared by choosing a coupler containing electron donating groups such as 5-acetamido-2-methoxyaniline derivatives. Additional early work on the 2-thiazolylazo dyes resulted in violet dyes from 2-amino-4-trifluoromethyl-5-carbalkoxythiazole,[3] 2-amino-5-alkysulphonylthiazole,[4] 2-amino-4-methyl-5-cyanothiazole[5] and even more bathochromic dyes from 2-amino-4-alkylsulphonyl-5-nitrothiazole[6] (Fig. 3). The pronounced



C.I. DISPERSE BLUE 15; C.I. 11435



C.I. DISPERSE RED 58; C.I. 11135

Fig. 1.

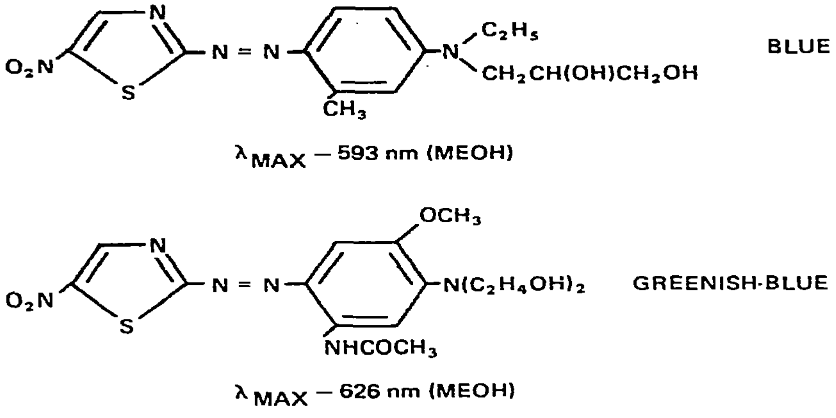


Fig. 2.

bathochromic shift[7] of the 5-nitro-2-thiazolylazo dyes, compared with the red azo dyes derived from the corresponding nitroaniline, was of great interest and may be illustrated by comparing the dyes in Fig. 4. The bathochromic shift was explained[7] as probably being due to the sulphur atom imparting greater polarizability to the 2-thiazolylazo system than the phenylazo structure, although recently it has been stated that the origin of the large shifts cannot be explained convincingly by

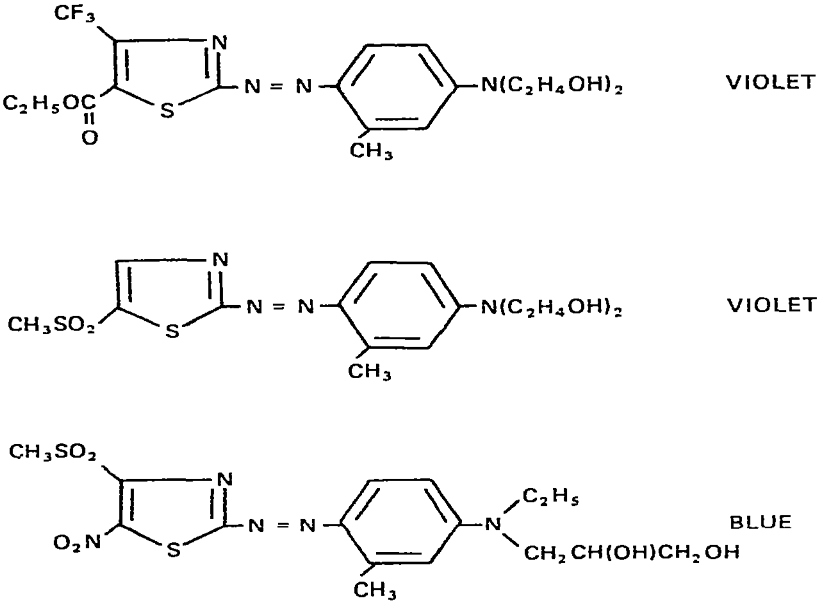


Fig. 3.

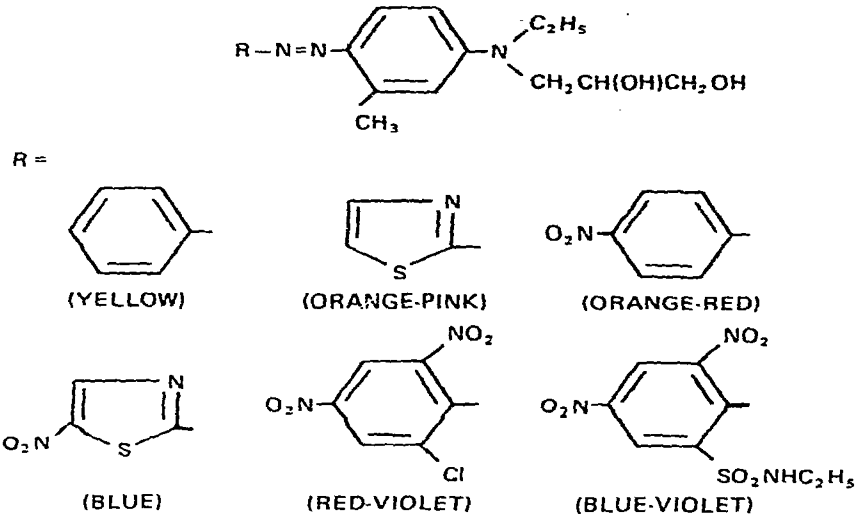

R—N=N—
C₂H₅
N
CH₂CH(OH)CH₂OH
CH₃
R =
(YELLOW)
N
S
(ORANGE-PINK)
O₂N
(ORANGE-RED)
N
O₂N
S
(BLUE)
NO₂
O₂N
Cl
(RED-VIOLET)
NO₂
O₂N
SO₂NHC₂H₅
(BLUE-VIOLET)

Fig. 4.

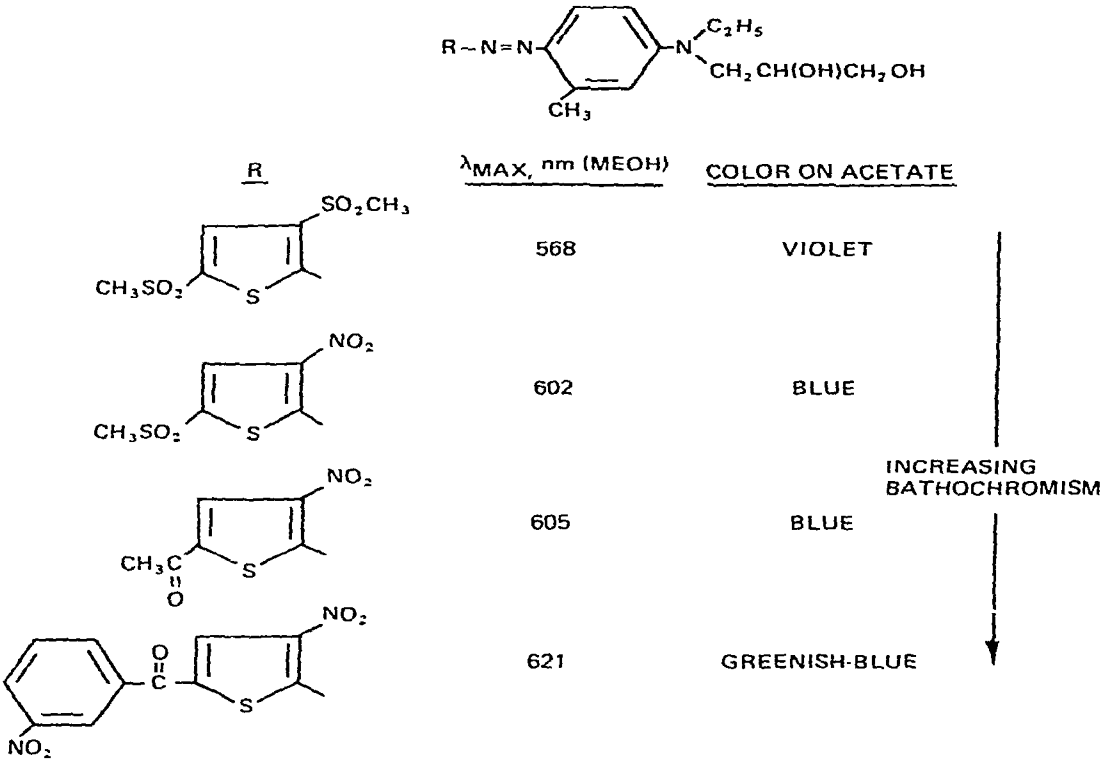

R—N=N—
C₂H₅
N
CH₂CH(OH)CH₂OH
CH₃
R
λMAX, nm (MEOH)
COLOR ON ACETATE
SO₂CH₃
CH₃SO₂
S
568
VIOLET
NO₂
CH₃SO₂
S
602
BLUE
NO₂
CH₃C
O
S
605
BLUE
NO₂
O
C
S
NO₂
621
GREENISH-BLUE
INCREASING
BATHOCHROMISM

Fig. 5.

resonance and that molecular orbital calculations indicate that the role of the sulphur atom may not be particularly relevant. It may be the increased diene character of the ring that is responsible for the shift.[8]

The observed bathochromism, dischargeability and tinctorial power of azo dyes from 2-amino-5-nitrothiazole encouraged further work which led to the discovery of dyes from 2-amino-3-nitro-5-acyl(or aroyl)thiophenes.[9] These dyes are even more bathochromic[10] than the 5-nitro-2-thiazolylazo dyes and may have been of commercial interest if economical synthetic routes had existed. Other negatively substituted thiophene dyes developed in early work were derived from 2-amino-3-nitro-5-alkylsulphonylthiophenes and 2-amino-3,5-dialkylsulphonylthiophenes;[11] however, these dyes were hypsochromic in shade to the dyes from 2-amino-3-nitro-5-acylthiophenes[7] (Fig. 5).

As indicated previously, the dischargeability of dyes from 2-aminobenzothiazoles was recognized early, with dyes from 2-amino-6-methoxybenzothiazole[12-14] being of considerable interest. Negative groups in the 6-position of the benzothiazole ring were found to improve the lightfastness and give bathochromic shifts,[15,16] and red dyes containing 6-nitro,[15,17] 6-alkylsulphonyl,[18] 6-sulphonamido,[19] 6-cyano[20] and 6-thiocyano[20] groups were patented. Negative groups in the 4-position of the

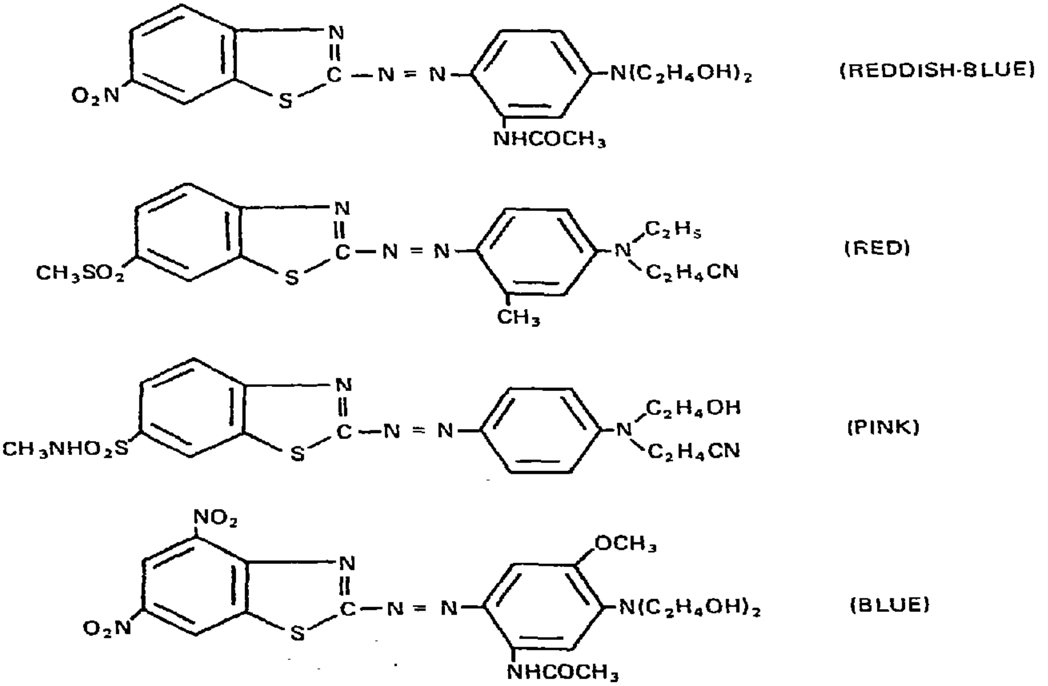


Fig. 6.

benzothiazole ring gave additional bathochromic shifts in colour, and dyes from 2-aminobenzothiazoles containing 4,6-dinitro,[21] 4-nitro-6-alkylsulphonyl[22] and 4-halo-6-alkylsulphonyl[22] groups were prepared. Typical dyes from this early work are shown in Fig. 6. Although initially developed chiefly for cellulose acetate, some of these early 2-benzothiazolyl dyes were found to have utility as dyes for polyester and polyamide fibres; however, lightfastness on these substrates is usually poorer than on cellulose acetate.[16]

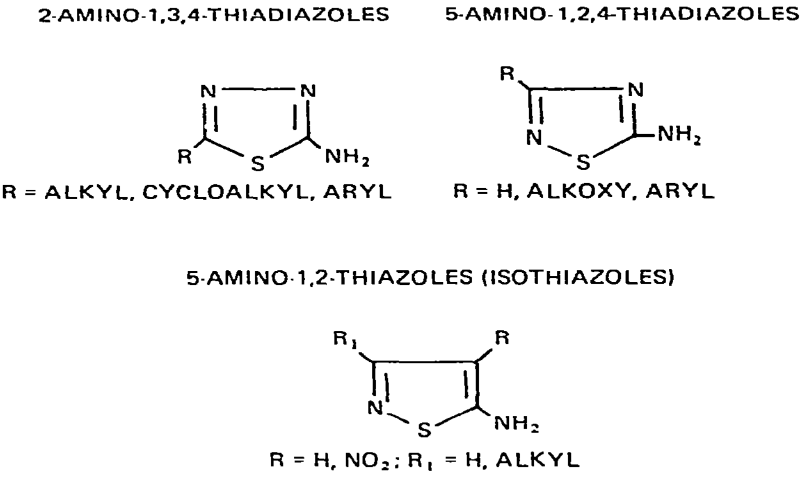


Fig. 7.

Concurrently, dye researchers investigated other diazotizable heterocyclic amines (Fig. 7), and dyes from 2-amino-1,3,4-thiadiazoles[23] and 5-amino-1,2,4-thiadiazoles[24] were shown to have outstanding brightness. Early interest was also shown in 5-aminoisothiazoles[25] as diazo components.

3. PREPARATION OF HETEROCYCLIC AMINES

3.1. 2(4)-Aminothiazoles

The 2-aminothiazoles are generally prepared by reacting α-haloaldehydes or their functional derivatives, such as acetals, with thiourea[7] (Fig. 8). Thiazoles substituted in the 4-position are prepared by reacting the appropriate α-haloketone with thiourea. For example, α-chloroacetone, α-bromoacetophenone, and 3-bromo-1,1,1-trifluoroacetone yield 2-amino-4-methyl-,[7,26] 2-amino-4-phenyl-,[26] and 2-amino-4-trifluoromethylthiazole.[27] The 2-aminothiazoles, their acyl derivatives, or both, undergo electrophilic substitution in the 5-position (Fig. 9) and can be nitrated,[27] brominated,[7,28] chlorosulphonated,[28] thiocyanated,[29] formylated[30]

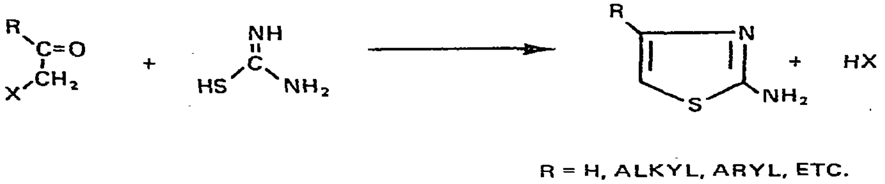


Fig. 8.

and nitrosated.[31] Nitration[27] of the 2-aminothiazole is effected in concentrated sulphuric acid below 15°C. An intermediate 2-nitroamino compound is formed, which rearranges under reaction conditions to give the 2-amino-5-nitrothiazole (Fig. 10). The 2-amino-4-alkyl-, 2-amino-4-phenyl-, and 2-amino-4-trifluoromethylthiazoles nitrate similarly.[7,27] The nitration of 2-aminothiazole can present hazards when carried out on a commercial scale.[32] The 2-amino-5-alkylsulphonylthiazoles (Fig. 10) are prepared by reacting 2-amino-5-bromothiazoles with mercaptans,[7] followed by acylation, oxidation and hydrolysis, or by treating 2-acetamido-5-thiocyanothiazole with alkali, followed by alkylation, acylation, oxidation[7,33] and hydrolysis.

Substituted 4-aminothiazoles have been prepared by first reacting cyanamide with carbon disulphide in the presence of potassium hydroxide.[34,35] Further reaction with, for instance, haloacetonitriles gives 4-amino-2-cyanomethylthio-5-cyanothiazole (Fig. 11). This concept has been extended to include the 5-nitro and the 3- or 5-alkylsulphonyl derivatives.[36]

2-Aminothieno[2,3-*d*]thiazoles have been described as diazonium components.

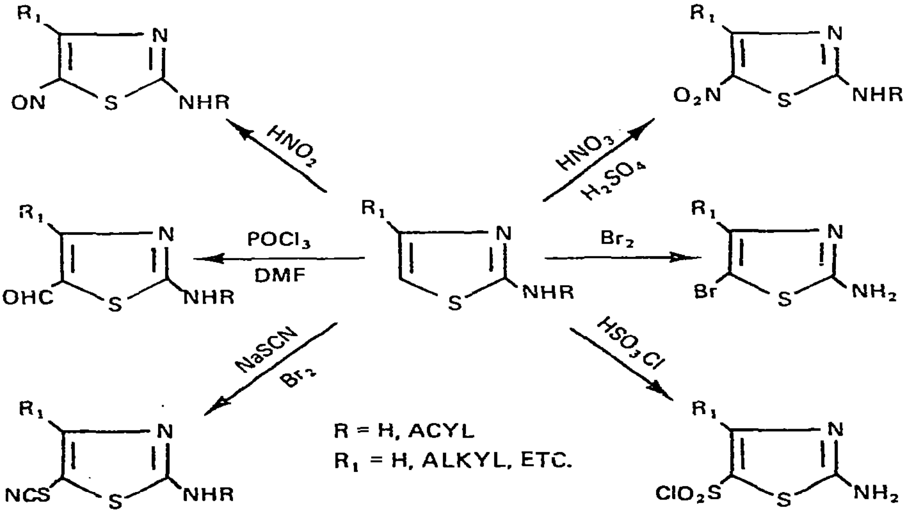
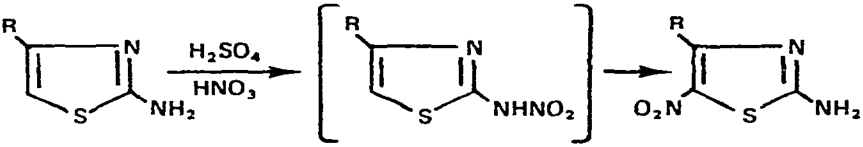
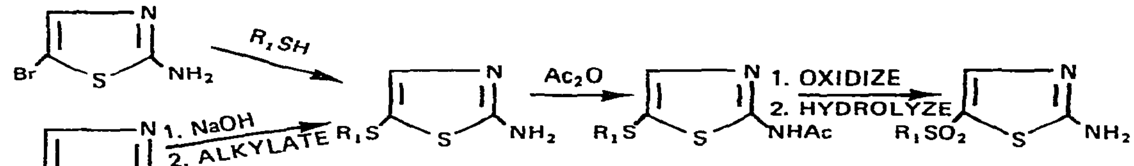


Fig. 9.

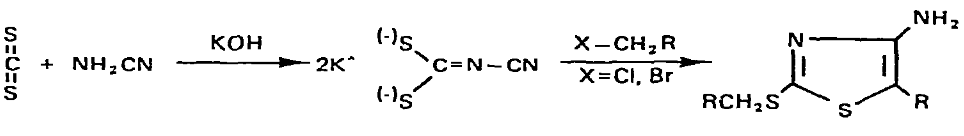


R = H, ALKYL, ARYL, CF₃, ETC.



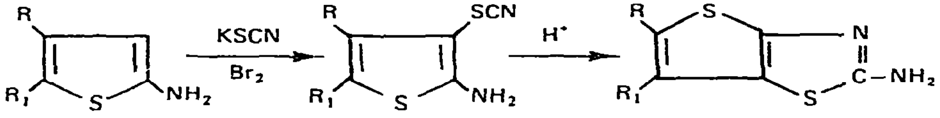
R₁ = ALKYL

Fig. 10.



R = CN, COO ALKYL
CONH₂, ETC.

Fig. 11.



R = H, ALKYL; R₁ = CO₂ ALKYL

Fig. 12.

They are prepared from 2-aminothiophenes by thiocyanation and ring closure of the 2-amino-3-thiocyanothiophenes[37] (Fig. 12).

3.2. 2-Aminobenzothiazoles

The preparation of 2-aminobenzothiazole was first carried out by Hoffmann in 1879 by the reaction of 2-chlorobenzothiazole with ammonia.[38] Later methods proved more versatile (Fig. 13). Nearly quantitative yields of 2-aminobenzothiazoles can be obtained by treating phenylthioureas with halogen compounds.

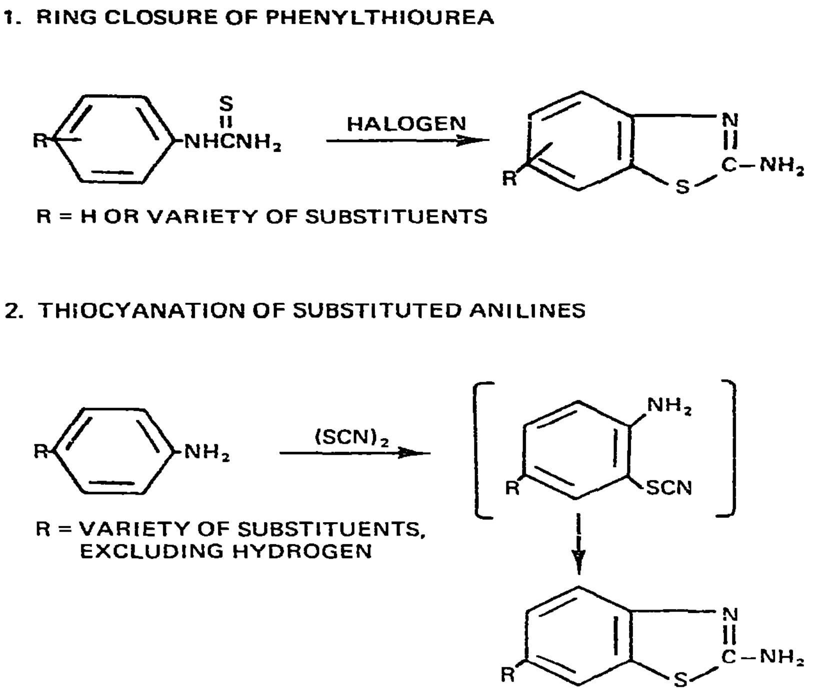


Fig. 13.

Although bromine[39] was used, other halogen compounds including chlorine,[40-42] sulphur monochloride,[43,44] sulphur dichloride,[43] and sulphuryl chloride[41-43,45] have been utilized successfully. Somewhat lower yields are obtained when the phenyl ring of the phenylthiourea is negatively substituted.[46] Another versatile synthetic route to 2-aminobenzothiazoles which are substituted in the 6-position is the reaction of thiocyanogen with a *para*-substituted aniline compound.[47,48] This reaction is usually run by treating the aniline compound in acetic acid with ammonium or sodium thiocyanate and bromine or chlorine to generate 'nascent' thiocyanogen, which reacts readily to produce an intermediate *o*-thiocyanoaniline. Ring closure usually proceeds under the acidic reaction conditions to produce 2-aminobenzothiazoles. When aniline itself is thiocyanated both the *ortho*- and *para*-positions are reactive, and 2-amino-6-thiocyanobenzothiazole (Fig. 14) is produced. This product is useful as an intermediate for preparing dyes or other intermediates such as 2-amino-6-methylsulphonylbenzothiazole.[49]

2-Aminobenzothiazoles also undergo electrophilic substitution in the 4- and 6-positions (Fig. 15). For example, 2-aminobenzothiazole can be nitrated directly to yield 2-amino-4,6-dinitrobenzothiazole[21] and 2-amino-6-alkylsulphonylbenzothiazole can be halogenated, nitrated and sulphonated in the 4-position.[22]

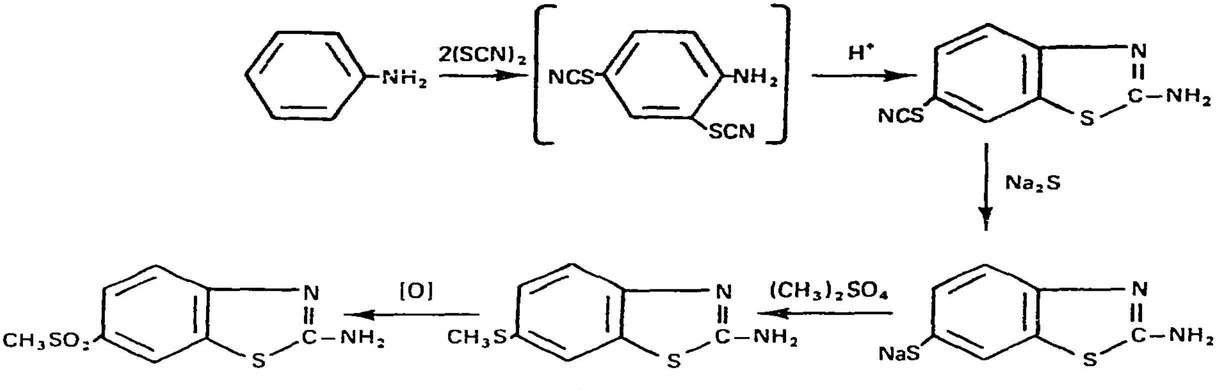


Fig. 14.

Electrophilic substitution reactions also occur in 2-alkylthiobenzothiazoles. For example, 2-aminobenzothiazoles with a 6-sulphonic acid ester group have been prepared by alkylating 2-mercaptobenzothiazole, followed by chlorosulphonation in the 6-position. Esterification with a phenol, followed by amination in the 2-position, gives the desired amine.[50,51]

3.3. *5-Aminoisothiazoles*

Isomeric with the 1,3-thiazoles are the 1,2-thiazoles or isothiazoles. 5-Aminoisothiazoles are prepared in general by oxidative cyclization of a β-aminothioamide.

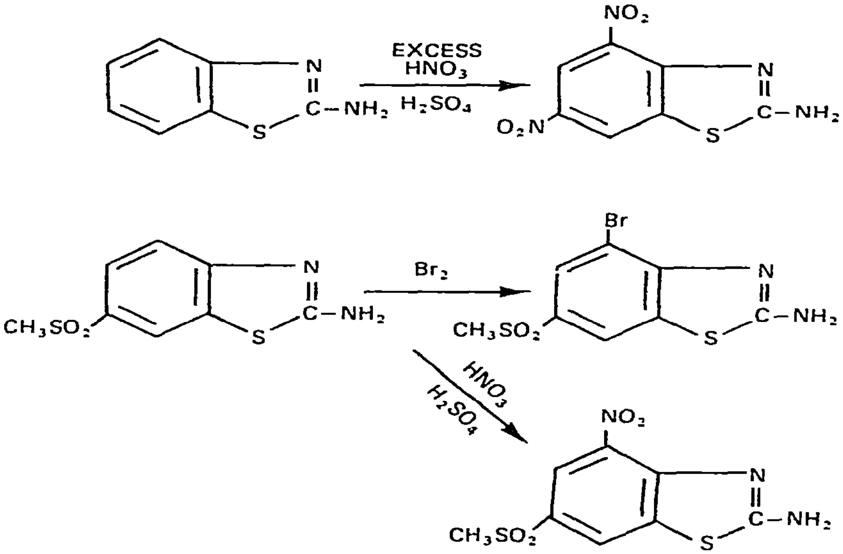


Fig. 15.

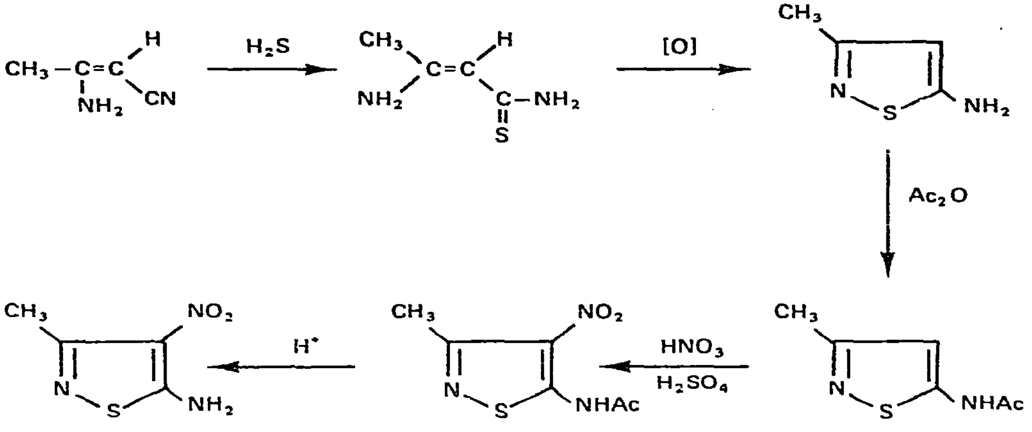


Fig. 16.

The thioamides are usually prepared from the nitrile by reaction with hydrogen sulphide (Fig. 16). For example, to prepare 5-amino-3-methylisothiazole, 3-iminobutyronitrile[52] (3-aminocrotononitrile) is treated with hydrogen sulphide to produce 3-iminothiobutyramide, which is ring closed to the product in 50–60% yield.[53,54] The 5-aminoisothiazoles (or acyl derivatives) undergo electrophilic reaction in the 4-position (Fig. 16). For example, nitration of 5-acetamido-3-methylisothiazole gives, in nearly quantitative yield, the 4-nitro derivative, which can be hydrolyzed in dilute hydrochloric acid to yield 5-amino-3-methyl-4-nitroisothiazole.[53] 5-amino-4-cyano-3-methylisothiazole[55] (Fig. 17) can be prepared in high yield by oxidative ring closure of 3-amino-2-cyanothiocrotonamide.[56] 3-Alkoxy-5-amino-4-cyanoisothiazoles[57] are prepared similarly from the appropriate alkoxy propenethioamide. Another synthetic route[58] to this ring system

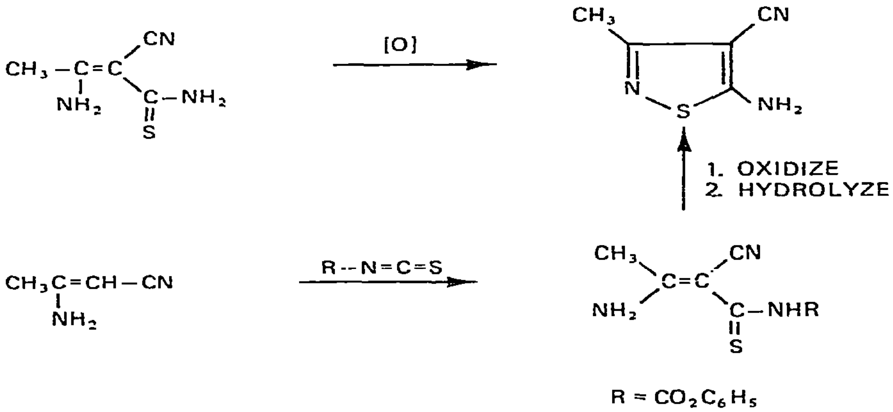


Fig. 17.

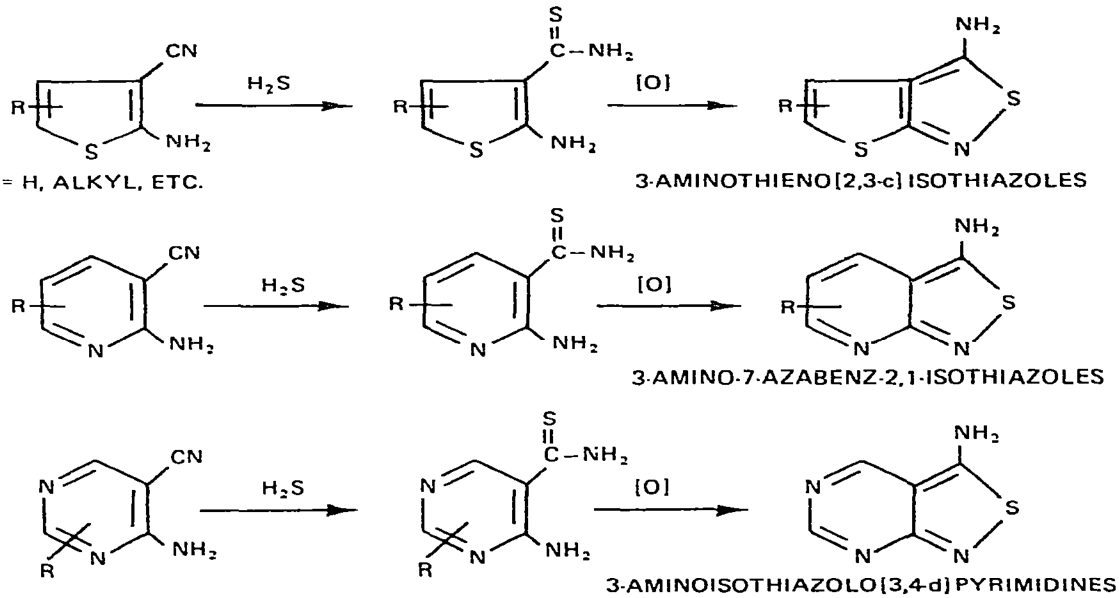


Fig. 18.

involves reacting β-aminocrotononitrile with an arylthiocyanate, followed by oxidation and hydrolysis to yield 2-amino-4-cyano-4-methylisothiazole (Fig. 17).

The isothiazole ring closure is also effective when the β-aminonitrile system forms a part of a heterocyclic ring (Fig. 18). 3-Aminothieno[2,3-*c*]isothiazoles,[37,59] 3-amino-7-aza-2,1-benzisothiazoles,[60] and 3-aminoisothiazolo[3,4-*d*]pyrimidines[61] have been prepared from the readily available thiophene, pyridine, and pyrimidine *o*-aminonitriles.

3.4. 3-Amino-2,1-benzisothiazoles

The 3-amino-2,1-benzisothiazoles (Fig. 19) are prepared by a similar method to that described above where the β-aminonitrile reactant is anthranilonitrile or a substituted anthranilonitrile. For instance, anthranilonitrile can be reacted with hydrogen sulphide to give *o*-aminothiobenzamide which can be oxidatively ring closed with hydrogen peroxide.[62,63] It has been shown recently that the ring closure also can be effected by heating the *o*-aminothiobenzamide in 85–110% sulphuric acid.[64] A further advantage of this method is that the resultant amine can be diazotized in the sulphuric acid solution without isolation. The 3-amino-2,1-benzisothiazole can be monosulphonated and disulphonated, depending on the reaction conditions, with oleum in the 5- and 7-position to produce intermediates for acid dyes[65] (Fig. 19).

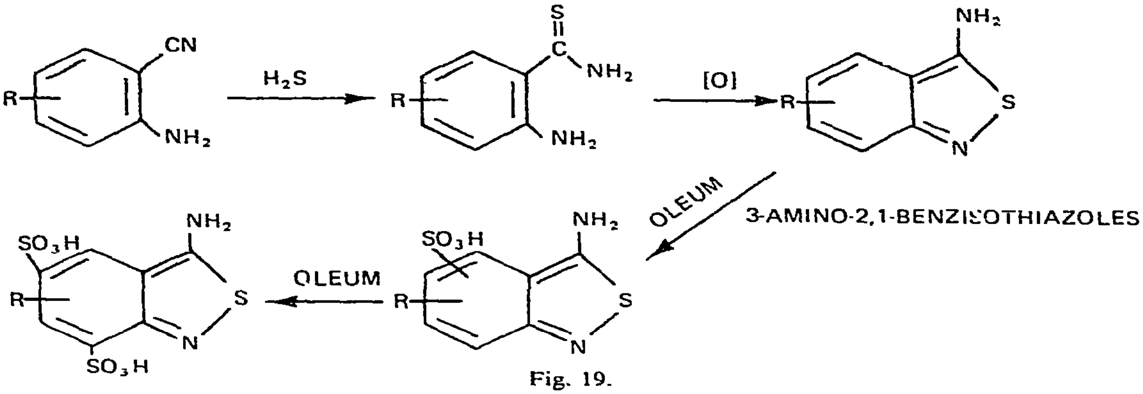


Fig. 19.

3.5. 2-Amino-1,3,4-thiadiazoles

2-Amino-5-alkyl- and 5-phenyl-1,3,4-thiadiazoles are usually prepared by either of two methods, both involving thiosemicarbazide as the starting material (Fig. 20). Young and Eyre[66] found that benzalthiosemicarbazone could be oxidized with ferric chloride to yield 2-amino-5-phenyl-1,3,4-thiadiazole. This reaction is quite general and can be used to produce a variety of 5-substituted-2-amino-1,3,4-thiadiazoles. Aldehydes such as cinnamaldehyde and methyl-*p*-formyl benzoate

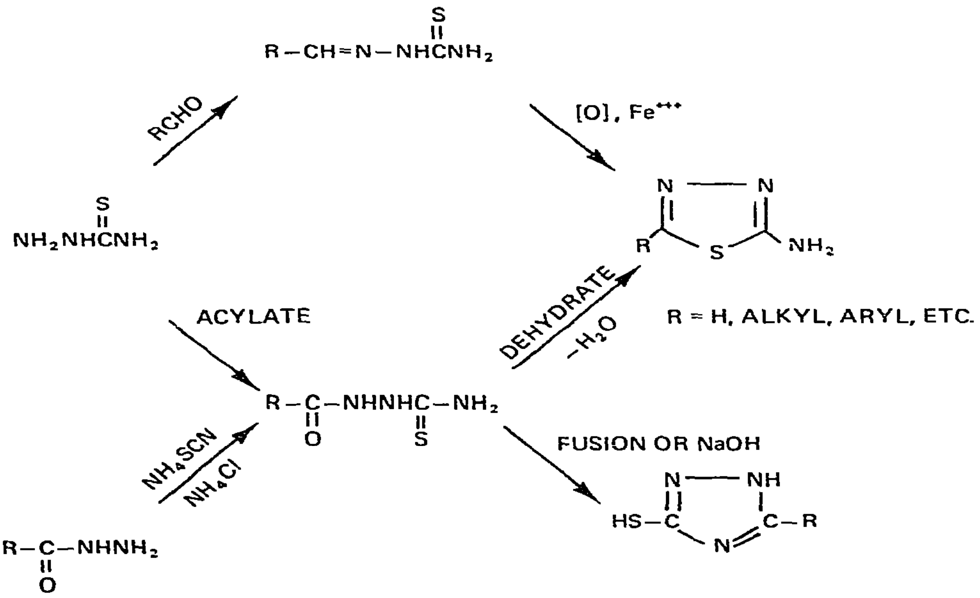


Fig. 20.

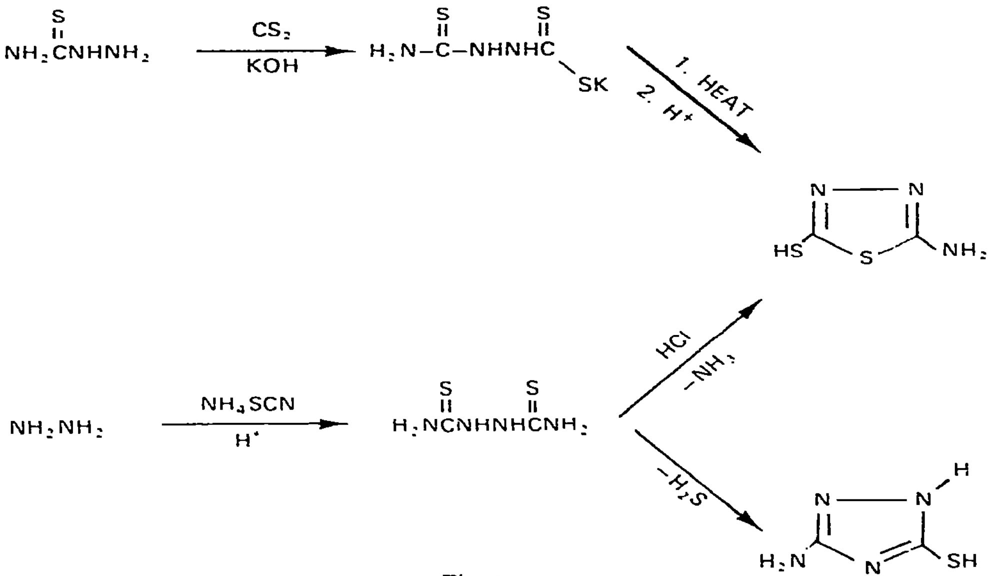


Fig. 21.

have been used to produce a 2-amino-5-styryl-1,3,4-thiadiazole[67] and 2-amino-5-(*p*-methoxycarbonyl)-phenyl-1,3,4-thiadiazole.[68] Thiosemicarbazide can also be acylated and the resultant acylthiosemicarbazide ring closed by dehydration to give 2-amino-1,3,4-thiadiazoles.[69,70] Dehydrating agents commonly used are acyl chlorides, anhydrides, sulphuric acid and polyphosphoric acid. Recently, methanesulphonic acid[71] has been shown to be a particularly useful reagent for this ring closure, requiring only a molecular equivalent. Ring closure of the acyl thiosemicarbazide by fusion[72] or by treatment with sodium hydroxide[70] results in 1,2,4-triazolethiols, instead of the 2-amino-1,3,4-thiadiazoles, in high yields. The intermediate acylthiosemicarbazide can also be conveniently prepared by reacting acyl hydrazide with thiocyanate.[70]

Thiosemicarbazide is also used as an intermediate for preparing 2-amino-5-mercapto-1,3,4-thiadiazole (Fig. 21) by reacting with carbon disulphide,[73,74] either with or without base present. The ring closure of the dithiocarboxylate salt occurs on heating under reaction conditions. Dithiobiurea can be ring closed by loss of ammonia to yield 2-amino-5-mercapto-1,3,4-thiadiazole,[75,76] but ring closure can also occur by loss of ammonia to yield 3-amino-5-mercapto-1H-1,2,4-triazole (tautomeric form is called iminothiourazole). The 2-amino-5-mercapto-1,3,4-thiadiazole can be alkylated[77] with a variety of alkylating agents, such as alkyl halides and alkyl sulphate, to yield the 5-alkylthio derivatives. Acetylated 2-amino-5-alkylthio-1,3,4-thiadiazoles are readily oxidized to the 2-acetamido-5-alkylsulphonyl[77] derivatives, which can be hydrolyzed to yield 2-amino-5-alkyl-

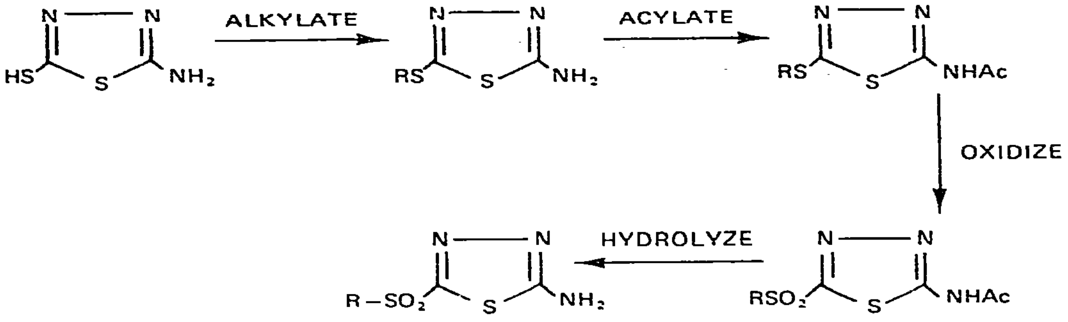


Fig. 22.

sulphonyl-1,3,4-thiadiazole (Fig. 22). Other 2-amino-1,3,4-thiadiazoles of interest include the 5-chloro-,[78,79] 5-sulphonamido-,[80] 5-alkoxy-,[81] and 5-thiocyano-[82] derivatives.

3.6. *5-Amino-1,2,4-thiadiazoles*

Fair yields of 5-amino-1,2,4-thiadiazoles (Fig. 23) are obtained by treating amidine hydrochlorides with halogen and thiocyanates.[83] For example, formamidine ·HCl, acetamidine ·HCl and benzamidine ·HCl yield 5-amino-1,2,4-thiadiazole, the 3-methyl and 3-phenyl compounds, respectively. Alkylisothiouronium salts under similar reaction conditions yield 5-amino-3-alkylthio-1,2,4-thiadiazoles,[84] which can be oxidized to the 3-alkylsulphonyl[84,85] derivatives.

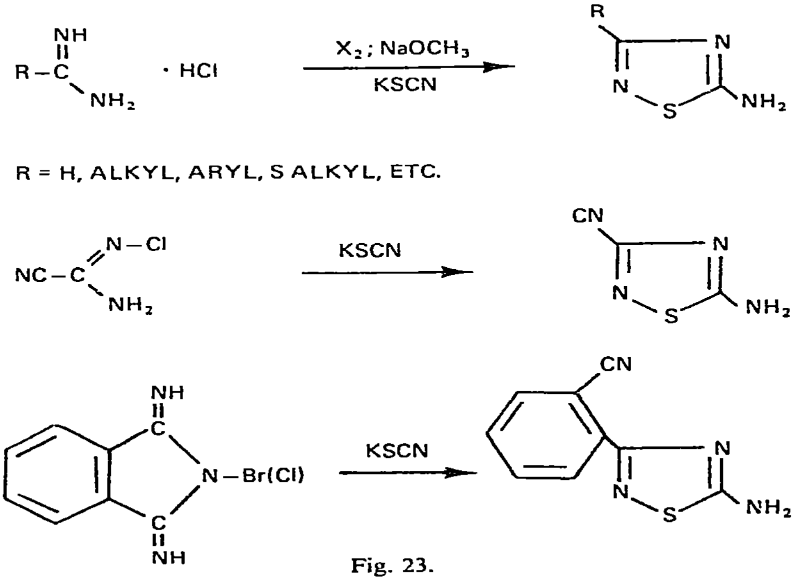


Fig. 23.

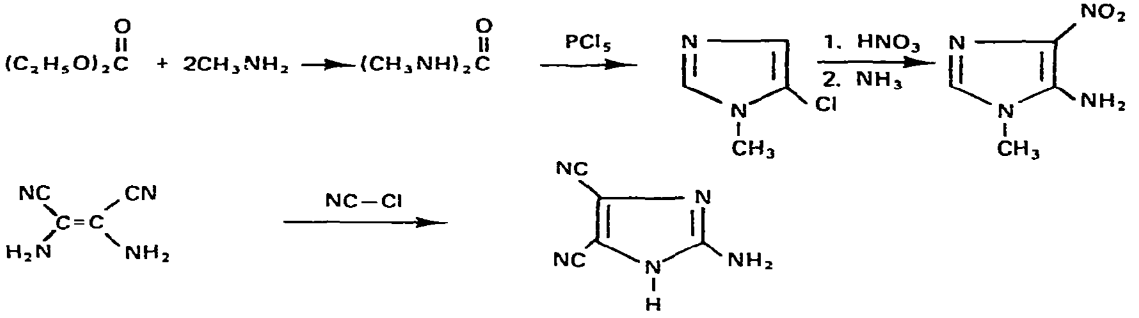


Fig. 24.

A similar reaction has been used to prepare 5-amino-3-cyano-1,2,4-thiadiazole.[86] A novel preparation of 5-amino-3-(2'-cyanophenyl)-1,2,4-thiadiazole[87] involves the reaction of *N*-bromo(chloro)di-iminophthalimide with ammonium or potassium thiocyanate. The reaction of 5-amino-3-benzylthio-1,2,4-thiadiazole with chlorine gas yields 5-amino-3-chloro-1,2,4-thiadiazole.[85]

3.7. 2(5)-*Aminoimidazoles*

Only a limited number of aminoimidazoles have been prepared and utilized as diazo components. A synthetic route to 5-amino-1-methyl-4-nitroimidazole[88] (Fig. 24) involves reacting diethyl oxalate with methylamine to produce *N*,*N*-dimethyloxamide, which is then reacted with phosphorus pentachloride to produce 5-chloro-1-methylimidazole.[89,90] This chloro compound can be nitrated[90] and reacted with ammonia[88] to produce the product. 2-Amino-4,5-dicyanoimidazole,[91,92] also of recent interest as a diazo component, is prepared by a novel reaction which involves treating diaminomaleonitrile[93] with chlorocyanogen (Fig. 24).

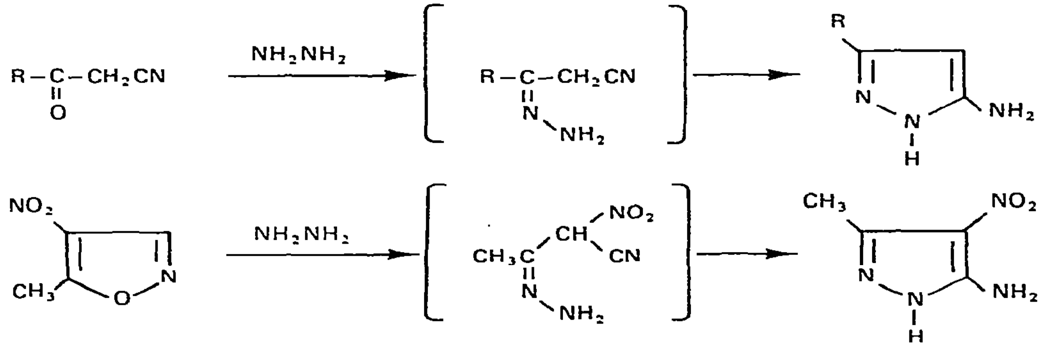


Fig. 25.

3.8. 5-Aminopyrazoles

An early preparation of 5-aminopyrazoles utilized the reaction of β-ketonitriles with hydrazine or its derivatives[94] (Fig. 25). The same reaction probably underlies the conversion of isoxazoles into pyrazoles by heating with hydrazine, since isoxazoles form cyanoketones with alkali.[94] For example, the reaction of methylnitroisoxazole with hydrazine produces 5-amino-3-methyl-4-nitropyrazole.[95]

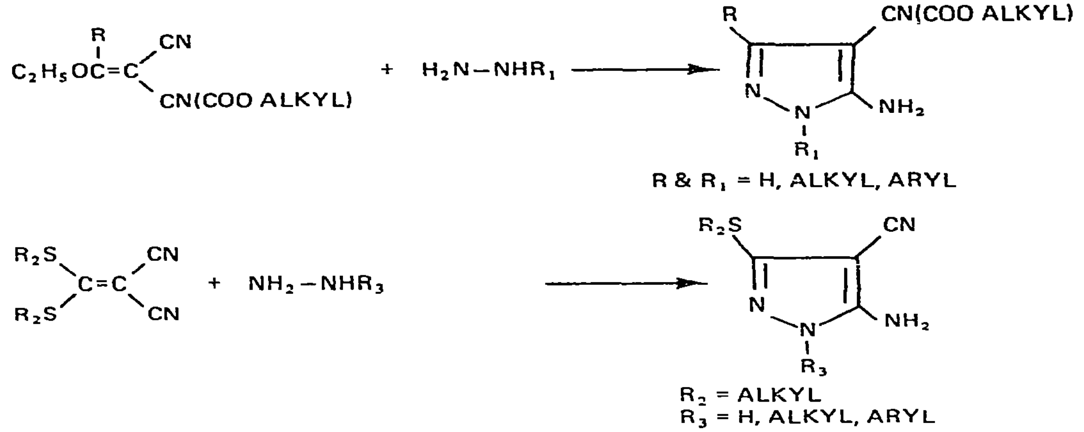


Fig. 26.

A convenient route to 5-amino-4-cyanopyrazoles[96,97] is available by the condensation of ethoxymethylenemalononitrile, or its *C*-alkyl or *C*-aryl derivatives, with hydrazine or substituted hydrazines (Fig. 26). The reaction is quite general, allowing the possibility of a variety of substituents at positions 1 and 3. Similarly, ethoxymethylene alkylcyanoacetates react with hydrazines to yield 5-amino-4-carboalkoxypyrazoles.[98,99] Overall, the yields in preparing 5-amino-4-carboalkoxy(or cyano)pyrazoles by these reactions are respectable, but a particular combination of reactants may give an unexpectedly low yield.

5-Aminopyrazoles with alkythio groups in the 3-position can be prepared by reacting dicyanoketene dithioacetals with hydrazine or its derivatives[100] (Fig. 26). 5-Amino-3,4-dicyanopyrazoles are available by reaction of tetracyanoethylene with hydrazine.[101] A process for the preparation of 4-aryl-5-amino-3-trifluoromethylpyrazoles from the appropriately substituted β-ketonitrile and substituted hydrazine has been discussed,[102] the ketonitrile being readily made from phenylacetonitrile and ethyl trifluoroacetate.[103] Aminopyrazoles with the alternative nitrogen atom substituted have been prepared[104] by reaction of phenylhydrazine with acrylonitrile and dehydrogenation of the pyrazoline formed.[105]

Aminobenzopyrazoles (or aminoindazoles) (Fig. 27) can be prepared by reacting an *ortho*-substituted benzonitrile, where the *ortho*-substituent is alkoxy or halogen,

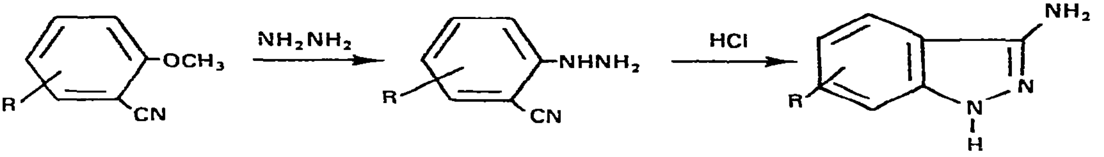


Fig. 27.

with hydrazine and cyclizing the resultant arylhydrazine with hydrochloric acid. Finally, alkylation can be carried out.[106,107]

3.9. 2(3)-Aminothiophenes

Before 1960, most 2-aminothiophenes were prepared by one of three routes: reduction of a 2-nitrothiophene,[108,109] electrophilic substitution of a 2-acetamidothiophene,[109,110] or amination of an activated 2-halothiophene compound.[9,10,111]

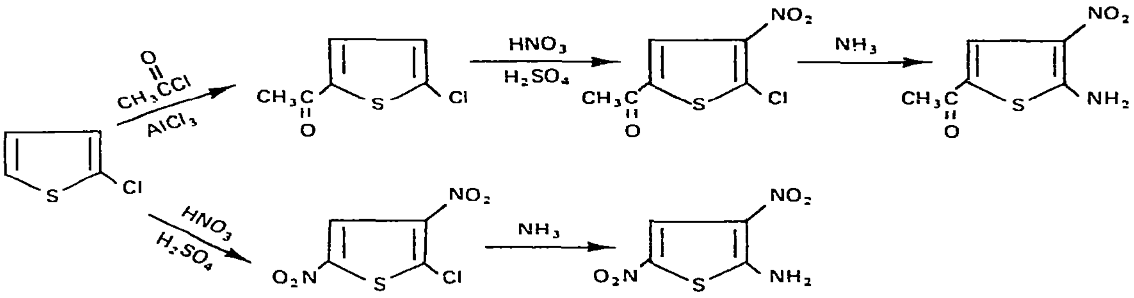
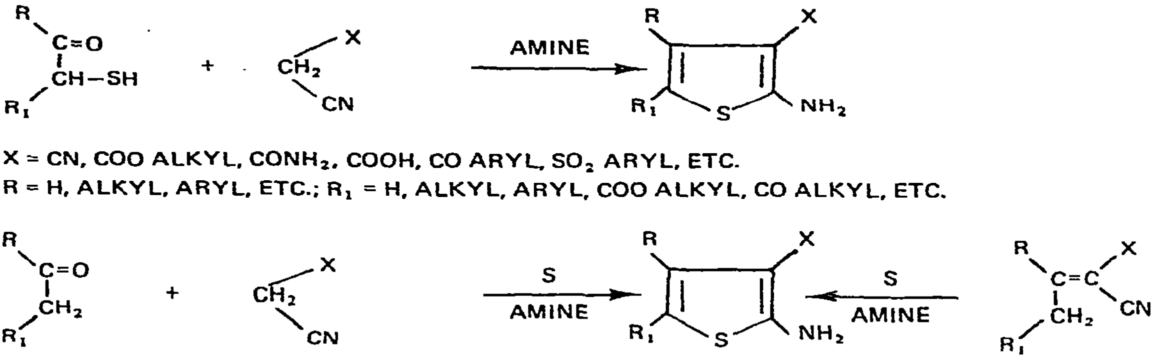


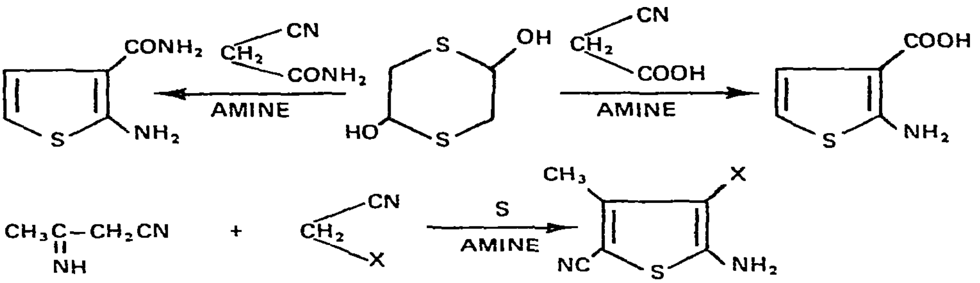
Fig. 28.

This last route (Fig. 28) has been used to prepare 2-amino-3,5-dinitrothiophene and 2-amino-5-acyl-3-nitrothiophene with 2-chlorothiophene as the starting material. The yield, however, at the amination step by using alcoholic ammonia is disappointingly low, and the starting 2-chlorothiophene is expensive. The discovery by Gewald[112,113] in 1961 (Fig. 29) that 2-aminothiophenes with electron acceptor groups in the 3-position could be prepared by reacting α-mercaptoketones and aldehydes with nitriles having an active methylene group in the α-position resulted in intense interest in these intermediates as disperse diazo components. Somewhat later it was found that thiophenes of this type could be obtained by an even simpler method by reacting carbonyl compounds containing a reactive methylene group in the α-position with the appropriate nitriles in the presence of sulphur and base[114] (Fig. 29). Sometimes it may be preferable to start with the preformed alkylidene derivative, which is subjected to sulphur and base.[114,115] In other variations of this reaction (Fig. 30) it has been shown that 2,5-dihydro-1,4-dithione (dimer of mercaptoacetaldehyde) reacts with active methylenes such as cyanoacetamide[116]



X = CN, COO ALKYL, CONH$_2$, COOH, CO ARYL, SO$_2$ ARYL, ETC.
R = H, ALKYL, ARYL, ETC.; R$_1$ = H, ALKYL, ARYL, COO ALKYL, CO ALKYL, ETC.

Fig. 29.



X = CN, COO ALKYL, CONH$_2$, CSNH$_2$, CO ARYL, ETC.

Fig. 30.

and cyanoacetic acid[117] sodium salt to yield 2-amino-3-carbamyl- and 2-amino-3-carboxy-thiophene, which can be reacted further to produce disperse dye intermediates. The synthesis of 2-amino-5-cyanothiophenes[118] is accomplished by reacting β-iminonitriles such as β-iminobutyronitrile with active methylenes containing a cyano group in the presence of sulphur and base (Fig. 30). The readily available 2-amino-3-carbalkoxythiophenes, or their acyl derivatives, undergo electrophilic substitution (Fig. 31) in the 5-position and can be nitrated, formylated, acylated and halogenated. They couple readily with diazonium salts[119] to produce intermediates for bis(azo) dyes. The 2-amino-3-cyano,[120,121] 2-amino-3-phenylsulphonyl[121] and 2-amino-3-carbamylthiophenes[116] (or their acyl derivatives) also undergo electrophilic substitution similar to the esters and can be readily nitrated or halogenated. An alternative method for preparing 2-amino-3-cyano-5-nitrothiophene has been suggested by dehydration of the 3-carboxamide compound.[122] The 2-amino-3-carboxythiophenes undergo transesterifications[120] and can be decarboxylated (Fig. 32) by first being saponified to 2-amino-3-thiophenecarboxylic

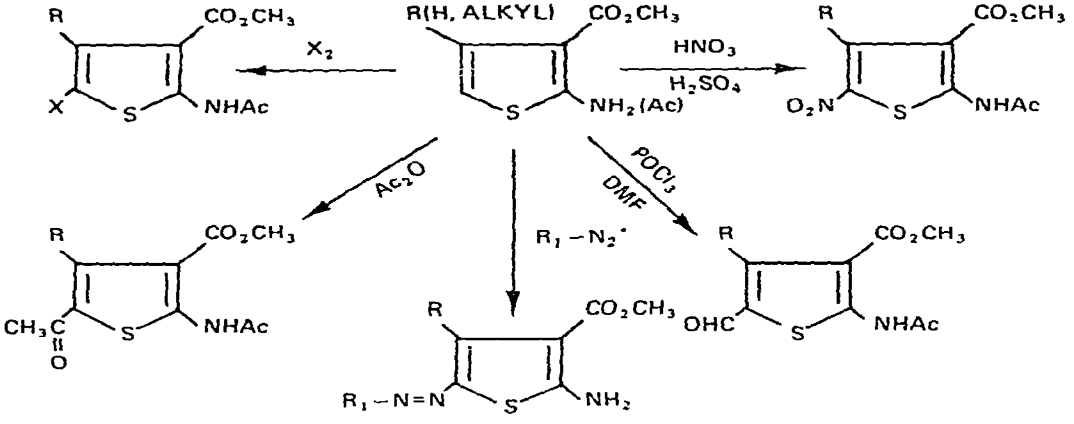
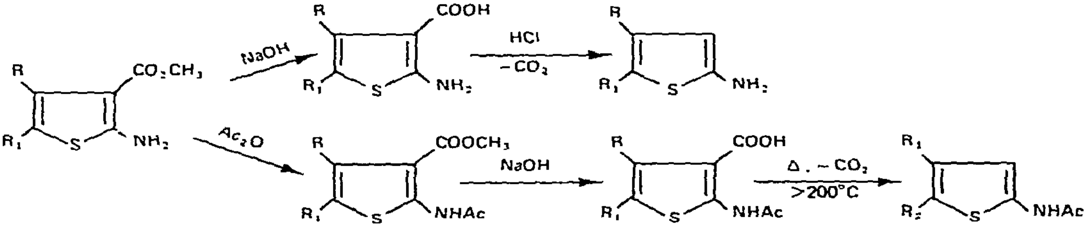


Fig. 31.



R AND R, = H, ALKYL, ARYL, ETC.

Fig. 32.

acids, which decarboxylate in the presence of oxalic or hydrochloric acid to give 2-aminothiophenes.[123] The ester grouping in 2-acetamido-3-carbalkoxy-carbalkoxythiophenes may be hydrolyzed to give 2-acetamido-3-thiophenecarboxylic acids. These acids undergo decarboxylation upon heating in such solvents as *N,N*-dimethylaniline at temperatures above 200°C.[117,123] 2-Acetamido-5-formylthiophene, prepared by Vilsmeier formylation of 2-acetamidothiophene, can be further nitrated in the 3-position,[124] thus leading to a useful diazo component. 2-Amino-5-formylthiophene can be converted to the 5-cyano derivatives by first reacting with hydroxylamine and then dehydrating the resultant oxime. Also, thiophenes having the nitrile group in the 3- or 5-position can be converted to the carboxamides by treating with 95% sulphuric acid.[121] The procedures mentioned above can be used to provide a wide variety of useful diazo components. For example, 2-amino-3,5-dinitrothiophene[125] results when 2-acetamidothiophene or 2-acetamido-3-thiophenecarboxylic acid is nitrated (Fig. 33), and the resultant product hydrolyzed, thus providing a more economical route to this compound than previously known.

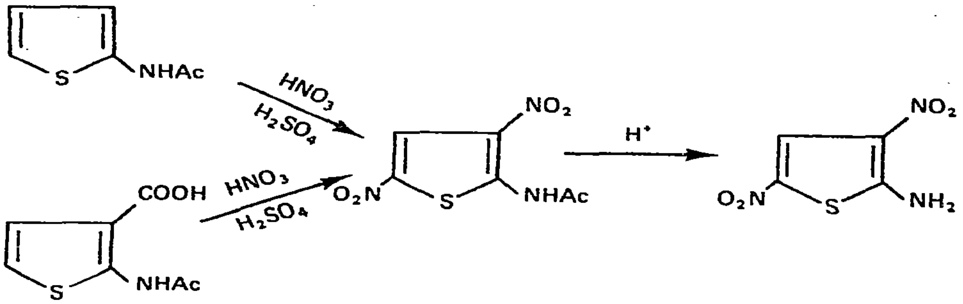
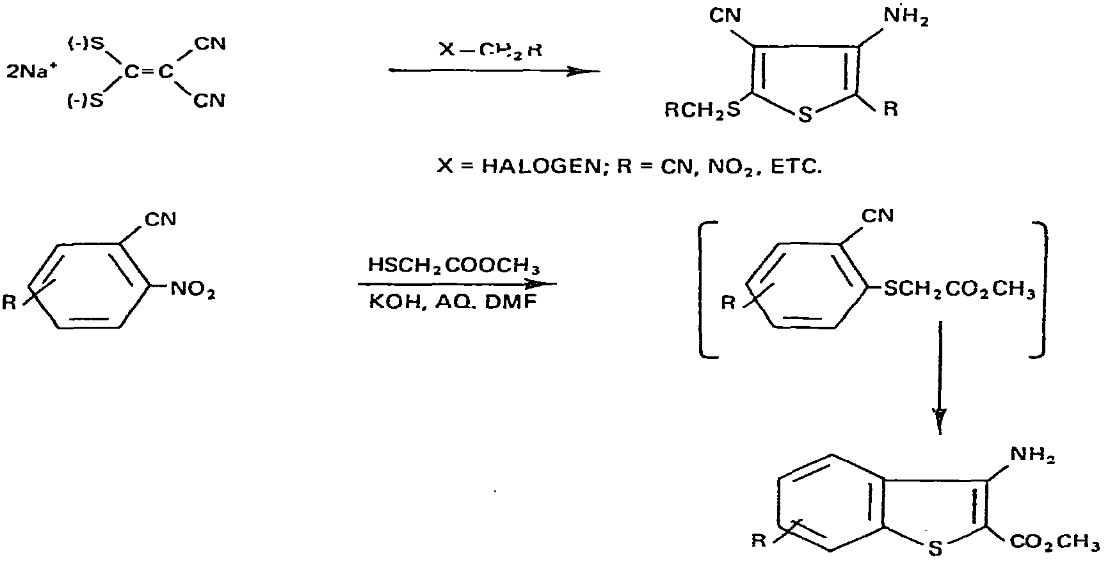


Fig. 33.

Negatively substituted 3-aminothiophenes[126,127] are prepared by reacting 1,1-dicyano-2,2-dimercaptoethylenes (Fig. 34), or monoalkyl derivatives thereof, with alkylating agents such as bromonitromethane or chloroacetonitrile, thus yielding 3-amino-2-nitro- and 3-amino-2-cyanothiophene derivatives. 3-Aminothiophene diazo components have been prepared where the heterocycle has an additional fused ring. The fused ring may be a benzo ring[128] or another ring such as a thieno[126] or pyridino.[129] The compounds are prepared by cyclization of an *ortho*-cyanothioether when an activating group such as cyano or carbalkoxy is present on



METHYL 3-AMINOBENZO[b] THIOPHENCARBOXYLATES

Fig. 34.

the thioether (Fig. 34). The thioether can be prepared, for example, from *o*-nitrobenzonitrile by nucleophilic displacement of the nitro group with methyl mercaptoacetate. Cyclization in this case yields a 3-aminobenzo[*b*]thiophene compound.[128]

4. DYES FROM HETEROCYCLIC AMINES

4.1. Dyes from 2-aminothiazoles

The commercial success of dyes for cellulose acetate which were derived from 2-amino-5-nitrothiazole resulted in considerable interest in this class of dyes. Early dyes showed moderate lightfastness on cellulose acetate and polyesters, and lightfastness on polyamide was very poor. Also, on polyesters the dyes had poor sublimation fastness for the thermofixation method of drying and showed loss of colour under high temperature exhaust dyeing conditions, particularly at high pH values. Dyes with increased lightfastness and/or sublimation fastness (Fig. 35) were prepared from aniline-type coupling components containing one or more *N*-alkyl groups substituted with groups such as —CN,[130,131] CONH$_2$,[132] COO—alkyl,[133] $\overset{\text{O}}{\overset{\|}{\text{O}}}\text{C—alkyl}$,[134,135] $\text{NH}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—alkyl}$,[136] $\text{—}\overline{\text{N—COCH}_2\text{CH}_2\text{CH}_2}$,[137] and dicarboximide.[138-142] *N*-Alkylcarbazoles[143] and substituted *N*-alkyl-1,2,3,4-tetrahydroquinolines[144,145] were used as coupling components. These coupler types have the advantage of providing dyes which have a neutral or green cast when exposed to artificial light, whereas the corresponding dyes from *N*-alkylaniline-type couplers

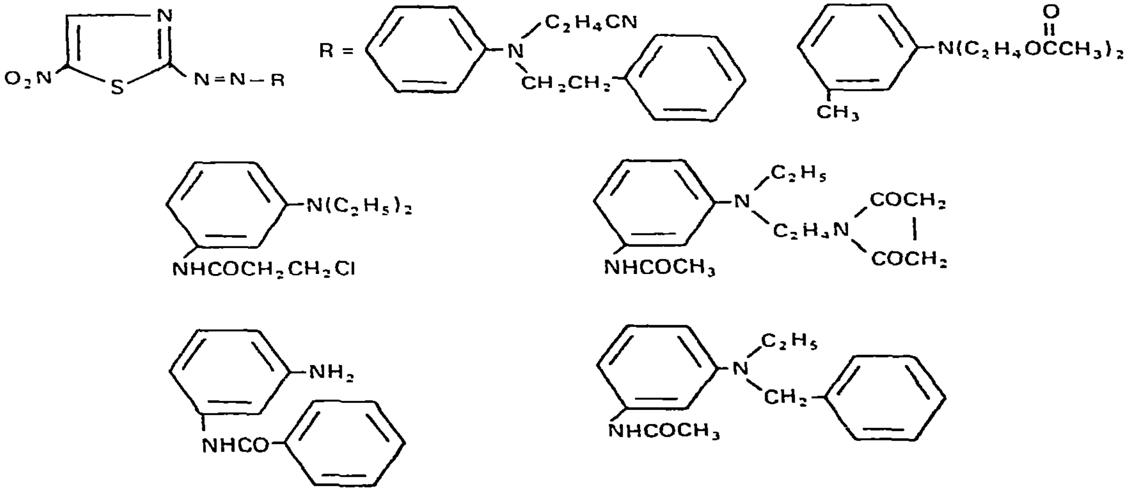
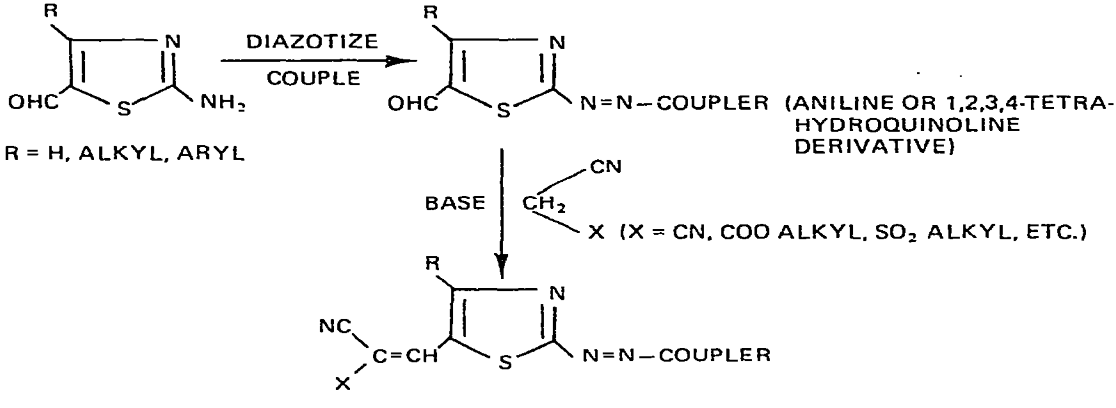


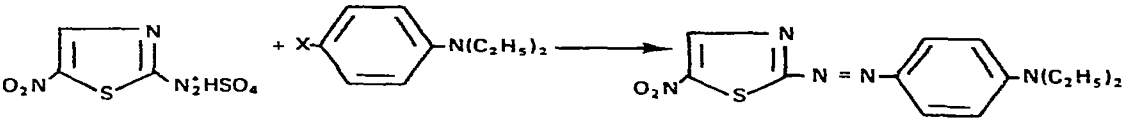
Fig. 35.

have an extremely red cast. The improved fastness to light and sublimation provided by 3-acylamidoaniline-type coupling components was not overlooked and dyes were patented from 3′-aminobenzanilide,[146] 3′-(*N*,*N*-dialkylamino)acylanilides,[147,148] 3′-(*N*-arylalkylamino)acylanilides,[149] and 3′-(*N*-cyclohexylamino)-acylanilides.[150] These dyes are reddish-blue in cast and flare red under artificial light. An attempt to make 2-thiazolylazo dyes more bathochromic (Fig. 36) than the known 5-nitro-2-thiazolylazo compounds involved the diazotization and coupling of 2-amino-5-formylthiazoles, followed by a condensation of the formyl group with active methylenes under basic conditions.[151] The dyes were indeed more bathochromic, particularly when malononitrile was the source of active methylene, and had better fastness to light and sublimation than the corresponding 5-nitro-2-thiazolylazo dyes; however, they suffered from the disadvantage of poor hydrolytic stability at high pH and high temperatures. The intermediate 5-formyl-2-thiazolylazo dyes show surprisingly good lightfastness on polyamides.[151] Finally, dyes from 2-amino-5-nitrothiazole and simple *N*,*N*-dialkylaniline couplers have shown utility for heat transfer printing application.[152]



BATHOCHROMIC 2-THIAZOLYLAZO DYES
Fig. 36.

The yields of dyes prepared from 2-amino-5-nitrothiazole are generally not high, usually of the order of 50 %. It has been found that the yields of azo dyes from this diazo component can be improved significantly by making use of displacement coupling. By blocking the coupling position of the coupler with certain displaceable groups (Fig. 37), such as formyl and carboxyl, higher yields of dyes can be produced with diazotized 2-amino-5-nitrothiazoles. Furthermore, the purity of the dyes so produced is higher than if no blocking group is present.[153] Oxidative coupling has been used to prepare 2-thiazolylazo dyes by reacting 2-hydrazinothiazoles with orthoquinones.[154]



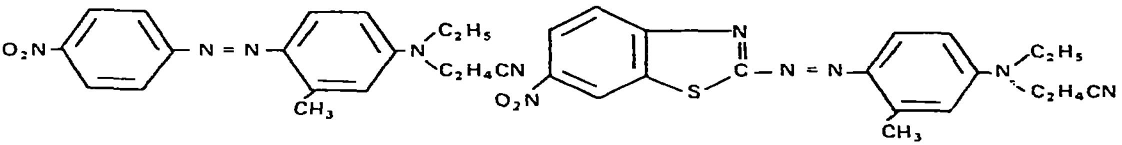
X = COOH, CHO, ETC.

Fig. 37.

2-Aminothiazoles having a fused hetero ring, such as 2-aminothienothiazoles,[155] have been widely studied as diazonium components and produce dyes considerably more bathochromic than 2-aminothiazole itself. Disazo dyes containing the thiazole ring as the middle component have been prepared.[156] Azo dyes from 4-aminothiazoles are known.[127,157]

4.2. Dyes from 2-aminobenzothiazoles

Sartori[158] gave a summary of the advantages of 2-benzothiazolylazo dyes compared with their phenylazo counterparts when applied to polyesters. These advantages include increased fastness to light and sublimation, increased absorptivities, and a bathochromic shift of 60–90 nm in the visible absorption maxima. The advantages are illustrated by comparing the dyes prepared from 4-nitroaniline and 2-amino-6-nitrobenzothiazole (Fig. 38), using *N*-(2-cyanoethyl)-*N*-ethyl-*m*-toluidine as a common coupler. The overall utility of red dyes from 2-amino-6-nitrobenzothiazole was emphasized by patents[159,160] and the commercialization of dyes such as that shown in Fig. 39. The early success of dyes from 2-amino-6-methyl-sulphonylbenzothiazoles resulted in further modification of this structure to produce certain desirable properties. Dyes from 2-amino-6-(hydroxyalkyl-sulphonyl) benzothiazoles[161] are reported to have excellent dyeability and



I

II

DYE	λ_{MAX} (nm), ACETONE	a_{MAX}	LIGHTFASTNESS (AATCC)	SUBLIMATION FASTNESS TEMP (°C) AT WHICH STAINING STARTS
I	470	98	5	155
II	538	130	6	185

Fig. 38.

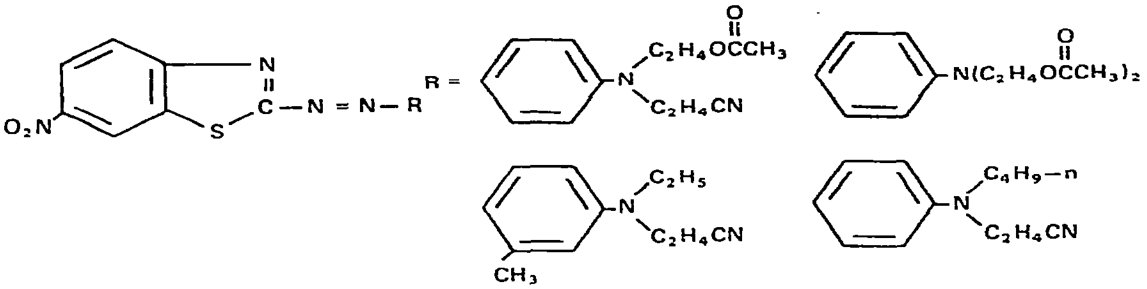
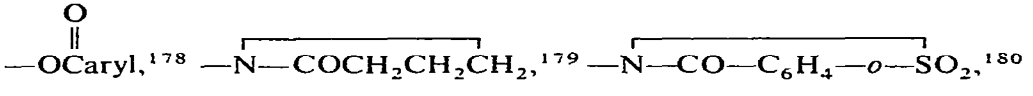


Fig. 39.

lightfastness on cellulose acetate, and 2-amino-6-(cyanoalkylsulphonyl)benzothiazoles[162] give dyes which stain wool less when dyed on polyester–wool blends. Dyes from 2-amino-6-methylsulphonylbenzothiazole and aniline-type couplers containing *N*-carbamylethyl groups[163] have improved dischargeability on cellulose acetate. Also of interest is the observation that 2-amino-5-methyl-6-methlysulphonylbenzothiazole[164] gives a higher yield of dye than the compound without the 5-methyl substituent.

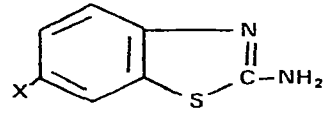
The search for alternative negative groups to occupy the 6-position in 2-benzothiazolylazo dyes has continued, and red dyes were reported having a wide range of substituents in the 6-position (Fig. 40), including acyl,[165] alkoxycarbonyl,[166] —SO_3aryl,[167] arylazo[168] and trifluoromethyl.[169] Introduction of trifluoromethyl and other fluorinated groups enhances volatility of the dyes and renders 2-benzothiazolylazo dyes suitable for heat transfer printing.[169,170] Bright scarlet dyes are obtained from 2-amino-5(7),6-dichlorobenzothiazole[171–173] and are suitable for dyeing polyesters.

To provide increased fastness to light, sublimation, or both, 2-benzothiazolylazo dyes have been prepared from aniline-type couplers containing *N*-alkyl groups substituted with imides[139,174–176] aryl,[149,177]



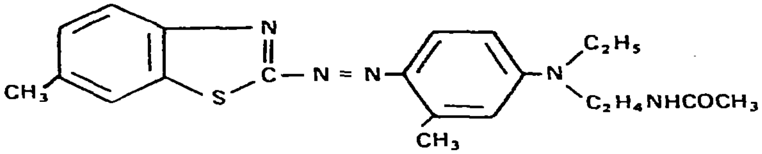
$-O\overset{\overset{O}{\|}}{C}aryl$,[178] $\overline{-N-COCH_2CH_2CH_2}$,[179] $\overline{-N-CO-C_6H_4-o-SO_2}$,[180]

2-benzothiazolylthio[181] and a variety of other groups.

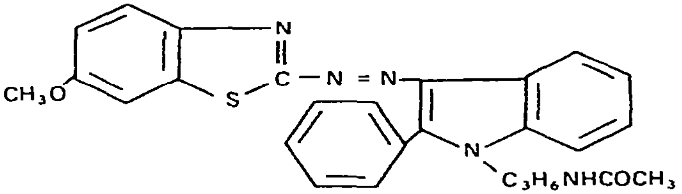


X = $SO_2CH_2CH_2OH$, $SO_2CH_2CH_2CN$, COO ALKYL,
COO ARYL, SO_3 ARYL, N=N—ARYL, CF_3, ETC.

Fig. 40.



RED



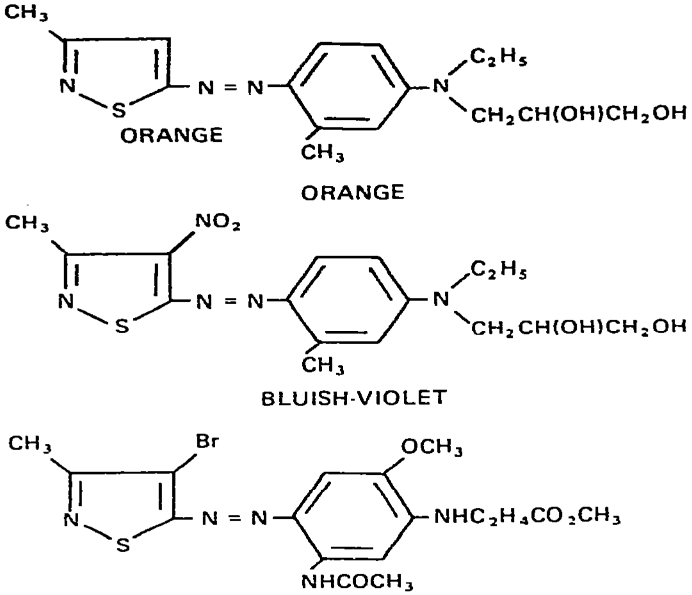
ORANGE

Fig. 41.

Red to bluish-red dyes having improved lightfastness (Fig. 41) on polyamide fibres have been prepared from certain 2-aminobenzothiazoles void of strongly electron withdrawing groups in the 6-position and couplers such as *N*-alkyl-*N*-(2-acylamidoethyl)anilines[182] and selected 1,2,3,4-tetrahydroquinolines.[183] Lightfast reddish-yellow to orange shades on nylon carpet fibre are produced from indole couplers[184] (Fig. 41). Recent patents on dyes from 2-aminobenzothiazoles and aromatic amine couplers containing *N*-(3-sulphopropyl),[185] *N*-(2-sulphoethyl),[186] *N*-(sulphophenoxyalkyl),[187] and *N*-(sulphatoalkyl)[188] groups have shown the utility of 2-aminobenzothiazoles in preparing lightfast acid dyes for polyamide carpet fibres. In summary, the 2-benzothiazolylazo structures provide several large volume commercial dyes used for dyeing polyesters, cellulose acetate and, to a lesser degree, polyamides.

4.3. *Dyes from 5(4)-aminoisothiazoles*

Aminoisothiazoles have received little attention as diazo components, probably because of the lack of attractive synthetic routes, since the dyes themselves produce bright shades and have good fastness. Bright orange to red dyes can be prepared from 5-amino-3-methylisothiazole and have good lightfastness, particularly on cellulose acetate[25] (Fig. 42). Introduction of a nitro group in the 4-position results in a strong bathochromic shift in the absorption maxima of the dyes,[25] thus giving violet to blue dyes; however, the dyes are not as bathochromic as the corresponding isomeric 5-nitro-2-thiazolylazo dyes. 5-Aminoisothiazoles containing halogen and cyano substituents in the 4-position when coupled with aniline couplers produce bright scarlet to violet hues[189] with good lightfastness on polyamides, polyesters, and cellulose acetate. Red acid dyes prepared from aromatic amine couplers containing *N*-(sulphonalkyl) groups have been prepared from diazotized 5-aminoisothiazoles.[188]



ORANGE

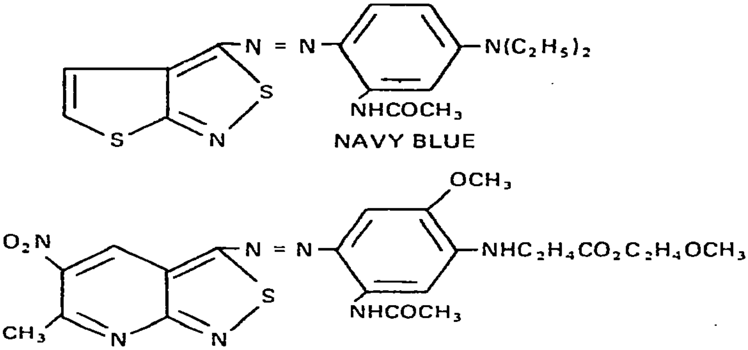
ORANGE

BLUISH-VIOLET

BLUISH-RED

Fig. 42.

Disperse dyes have been prepared from the isomeric 4-aminoisothiazoles.[189,190] Azo dyes from 5-aminoisothiazoles with fused hetero rings (Fig. 43) have been recently reported. Examples of such systems are 3-aminothieno[2,3-*c*]isothiazoles,[59] 3-amino-7-azabenz-2,1-isothiazoles,[60] and 3-aminoisothiazolo[3,4-*d*]-pyrimidines.[61] All these dyes are significantly more bathochromic than the dyes from 5-aminothiazoles, thus allowing the preparation of even blue to green dyes for polyesters.



NAVY BLUE

BLUISH-GREEN

Fig. 43.

4.4. *Dyes from 3-amino-2,1-benzisothiazole*

The discovery by BASF workers[191] that dyes from 3-amino-5-nitro-2,1-benzisothiazole (Fig. 44) were more bathochromic than the corresponding dyes from 2-amino-6-nitrobenzothiazole or even 2-amino-5-nitrothiazole gave considerable impetus to the investigation of 3-amino-2,1-benzoisothiazoles as diazo components for blue disperse dyes.[192–197] It should be noted that the absorption maxima of the benzisothiazole dye is shifted 23 nm bathochromically compared with the normal benzothiazole dye and 11 nm compared with the 5-nitro-2-thiazolyl structure when a coupler such as *N*,*N*-dimethylaniline is used.[191] These 5-nitro-2,1-benzisothiazolyl-2-azo dyes have in general better lightfastness than the 5-nitro-2-thiazolylazo dyes, but are usually slightly less lightfast than dyes from 2-amino-6-nitrobenzothiazole. Overall, they have good sublimation fastness and fastness to oxides of nitrogen and ozone. Important dyes in the class are shown in Fig. 45.

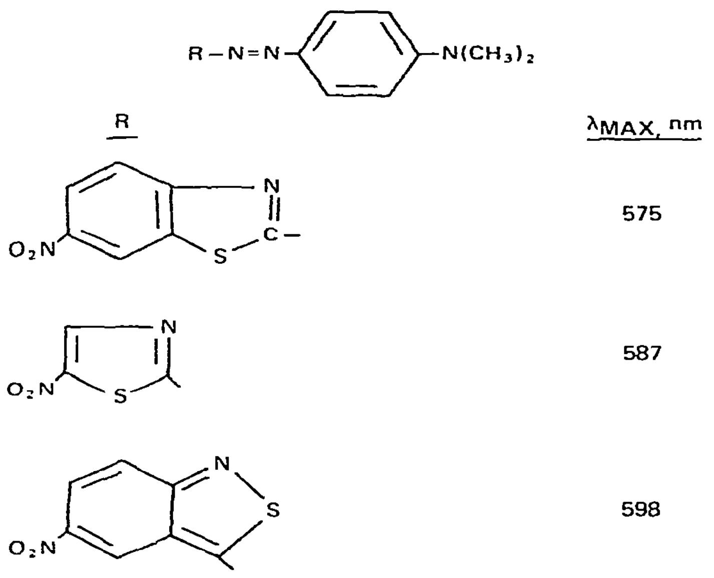
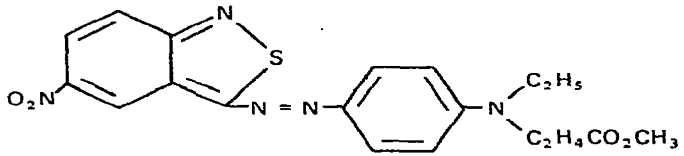


Fig. 44.

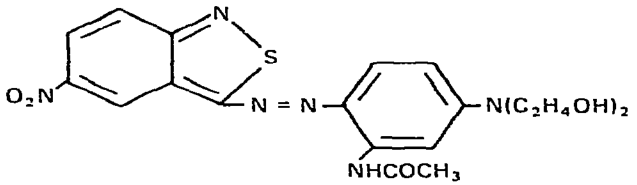
Lightfast violet to blue dyes for polyamides can be prepared by coupling certain diazotized 3-amino-2,1-benzisothiazoles with 1,2,3,4-tetrahydroquinolines,[198] benzomorpholines[198] and *N*-alkyl-1-naphthylamines.[199] Blue azo dyes from 3-amino-2,1-benzisothiazole-7-disulphonic acid[200,201] have been reported recently, illustrating the utility of this type of diazo for acid dyes for polyamides. Acid dyes for polyamides have also been prepared from 3-amino-2,1-benzisothiazoles and aromatic amine couplers containing *N*-sulphatoalkyl groups.[188]

4.5. Dyes from 2-amino-1,3,4-thiadiazoles

This class of diazo components has been studied extensively over the past 20 years because of their brightness and good lightfastness on polyesters and polyamides. In 1963, dyes from 2-amino-5-alkyl(aryl)-1,3,4-thiadiazoles[23] and selected aniline-type couplers were shown to produce very bright red shades on synthetic fibres. Shortly thereafter, 2-amino-5-alkylthio-1,3,4-thiadiazoles[202] were found to produce dyes with similar bright red hues. 2-Amino-5-alkoxy-1,3,4-thiadiazoles[203] produce dyes that are hypsochromic to the 5-alkylthio derivatives, but the lightfastness is good and the dyes are bright. New diazo components which have recently been utilized in this class of dyes include 2-amino-5-thiocyano-,[204] 5-halo-,[205,206] 5-alkylsulphonyl-,[205,206] 5-styryl-[207] and 5-(*p*-carbomethoxy)phenyl-1,3,4-thiadiazoles.[208]



BLUE



GREENISH-BLUE

Fig. 45.

The early deficiency of poor sublimation fastness in this series of dyes was corrected by utilizing couplers containing dicarboximide,[205,209] vinylsulphonyl,[206] and aryl groups.[149,210] Coupling components such as 3′-(*N*,*N*-dialkylamino)acylanilides,[203] 3′-(*N*-alkylamino)-4-methylacylanilides,[203] 3′-(cyclohexylamino)-acylanilides,[211] *N*-alkyl-*N*-(2-carbamylethyl)-*m*-toluidines,[212] *N*-alkyl-*N*-(2-acylamidoethyl)-*m*-toluidines,[212] and indoles[213] produce orange to red dyes with excellent lightfastness on polyamide carpet fibres when coupled with diazotized 2-amino-5-alkylthio-1,3,4-thiadiazoles (Fig. 46). *N*-Alkyl-1-naphthylamines[214] gave violet dyes with good lightfastness on polyamides. Red azo acid dyes from 2-amino-1,3,4-thiadiazoles and aniline, 1,2,3,4-tetrahydroquinoline and benzomorpholine couplers containing *N*-(sulphatoethyl) groups also have excellent lightfastness on polyamides.[188] This class of dyes has also been studied as dyes for heat transfer printing.[215]

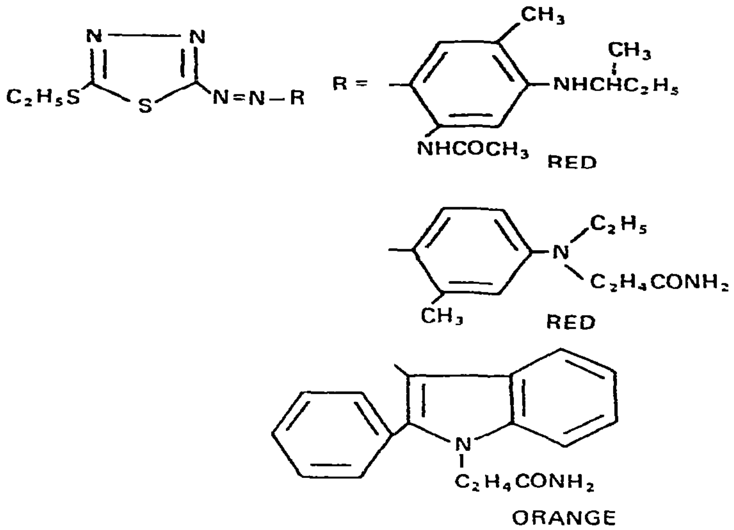


Fig. 46.

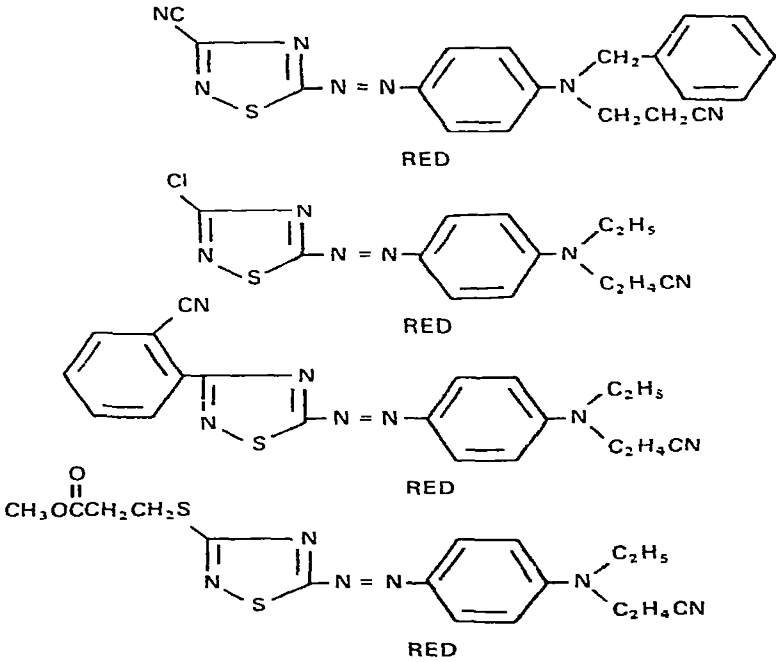


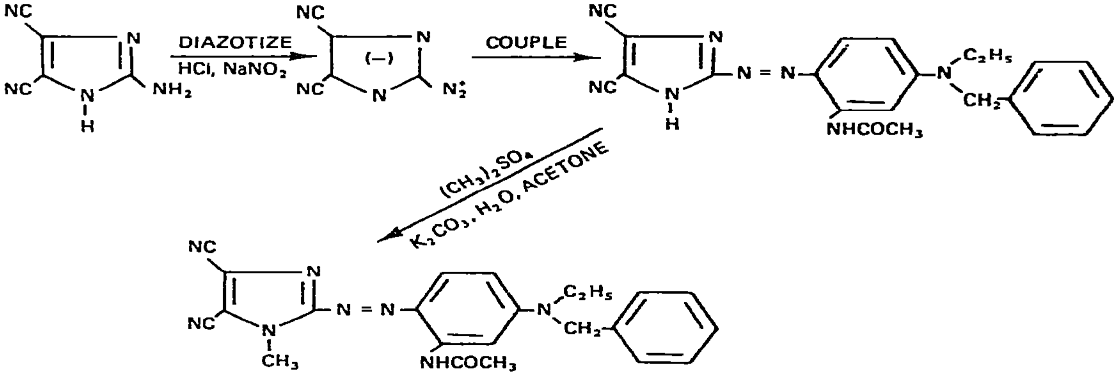
Fig. 47.

4.6. *Dyes from 5-amino-1,2,4-thiadiazoles*

The isomeric 5-amino-1,2,4-thiadiazoles produce dyes having very similar overall fastness properties to the 2-amino-1,3,4-thiadiazoles; however, they are somewhat more bathochromic and usually suffer a slight disadvantage in dullness of shade. The first dyes patented in this series were prepared from 5-amino-1,2,4-thiadiazole[24] and the 3-alkyl,[24] 3-alkoxy,[24] 3-aryl,[24] 3-alkylthio[216] and 3-alkylsulphonyl[216] derivatives. More recently red dyes have been prepared from such diazo components as 5-amino-3-cyano-,[217] 3-chloro(bromo)-,[218] 3-(2′-cyanophenyl)-[219] and 3-(2-carboalkoxyethylthio)-1,2,4-thiadiazoles[220–222] and simple substituted aniline couplers (Fig. 47). This last mentioned diazo component gives bright red dyes for polyester and cellulose acetate and has a good combination of fastness and dyeing properties. Dyes for heat transfer printing[223] and acid dyes for polyamide carpet fibre[188] from 5-amino-1,2,4-thiadiazoles are also known.

4.7. *Dyes from 2(5)-aminoimidazoles*

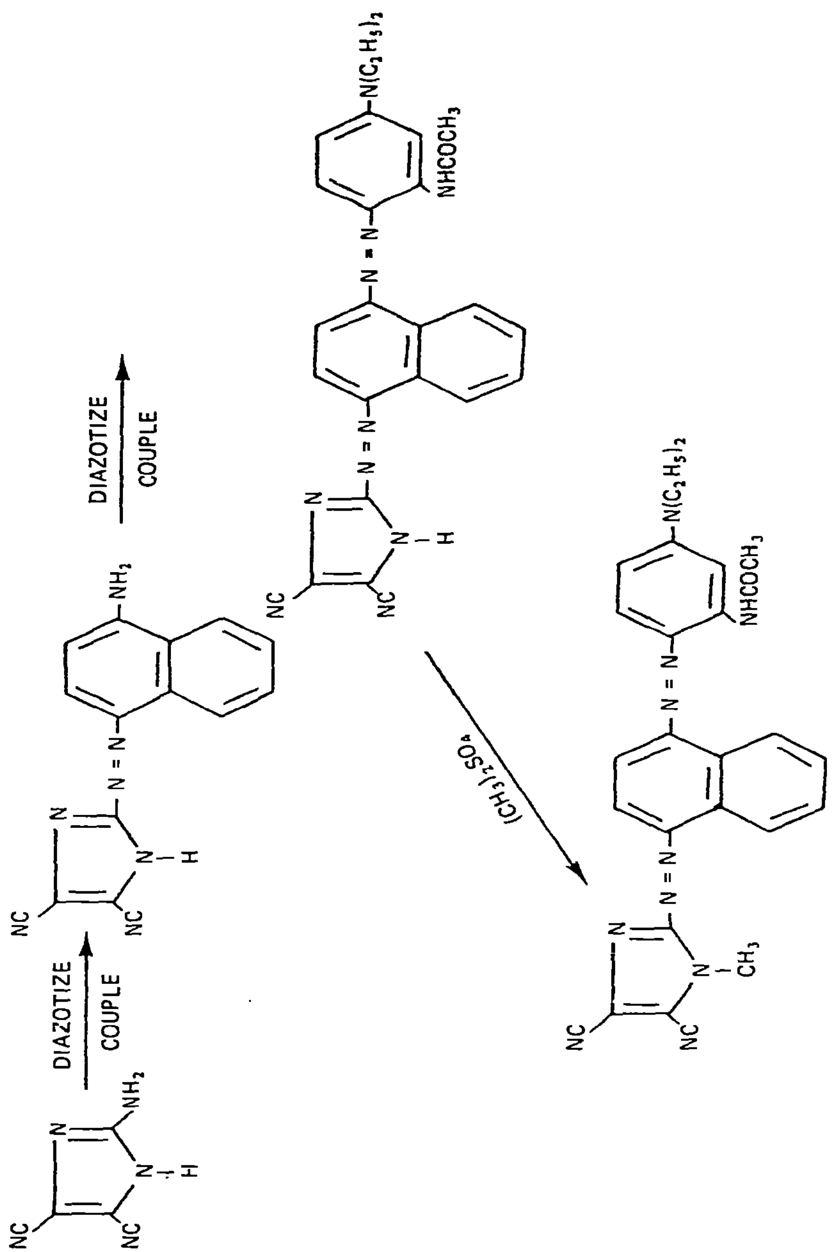
Aminoimidazoles have received little attention as diazo components. Red to violet dyes derived from 5-amino-4-nitro-1-alkylimidazole[88] have been prepared, but they have only moderate fastness. One important development in this chemistry is the recent discovery that bright red dyes having good lightfastness on polyester and polyamides can be prepared from 2-amino-4,5-dicyanoimidazole[224] (Fig. 48). Upon diazotization with hydrochloric acid and sodium nitrite, an insoluble diazonium zwitterion precipitates. The diazo dicyanoimidazole is highly shock sensitive when dry[92] and the diazotization slurry is coupled to give a high yield of dye. For example, *N*-benzyl-*N*-ethyl-*m*-acetamide aniline coupler gives dye in 99 %



λ_{MAX} = 527 nm

a_{MAX} = 141 lg^{-1}cm^{-1}

Fig. 48.



λ_{MAX} = 638 nm

a_{MAX} = 98 $lg^{-1}cm^{-1}$

Fig. 49.

yield.[224] The lightfastness of this dye can be improved considerably by alkylation of the imidazole ring. Alkylation also results in a bathochromic shift in the visible absorption maxima. The dye thus found is bright red (λ_{max} 527 nm), has the high absorptivity typical of heterocyclic azo dyes, and has good fastness to light and sublimation when applied to polyester fibres. It is possible to prepare blue diazo dyes from 2-amino-4,5-dicyanoimidazole[224] (Fig. 49) by using couplers such as 1-naphthylamine, followed by subsequent diazotization and coupling of the intermediate dye. Finally, the diazo dye is alkylated as before. The lack of attractive synthetic routes to this diazo component has no doubt hindered the pursuit of these dyes as commercial candidates.

2-Benzimidazole dyes (i.e. imidazoles with a fused benzo ring) are difficult to prepare by diazotizing and coupling 2-aminobenzimidazoles directly. An alternative synthesis for dyes of this type was reported[225] for use of conventional coupler molecules with an amino group *para* to the coupler nitrogen. The amino group is diazotized and converted to a diazocyanide, which reacts with *o*-phenylenediamine to give the 2-benzimidazolylazo dye.

4.8. *Dyes from 5-aminopyrazoles*

Yellow to violet dyes for hydrophobic fibres have been prepared from 5-amino-4-cyanopyrazoles and the 1-alkyl(aryl) compounds.[226] Corresponding dyes from 5-amino-4-cyano(or COO—alkyl)pyrazoles containing alkyl,[227] alkoxy,[227] cyanomethyl,[227] alkylthio[228] and arylthio[228] groups in the 3-position have been patented, as have azo dyes prepared from 5-amino-4-phenyl-3-trifluoromethyl-pyrazole.[229] Developments in this class of dyes have been hindered by the fact that the diazo components are obtainable only in moderate yield and are difficult to diazotize and couple to produce dyes in good yield and high purity. It has been reported recently that a better synthetic route to the 4-cyano-5-pyrazolylazo dyes (Fig. 50) involves

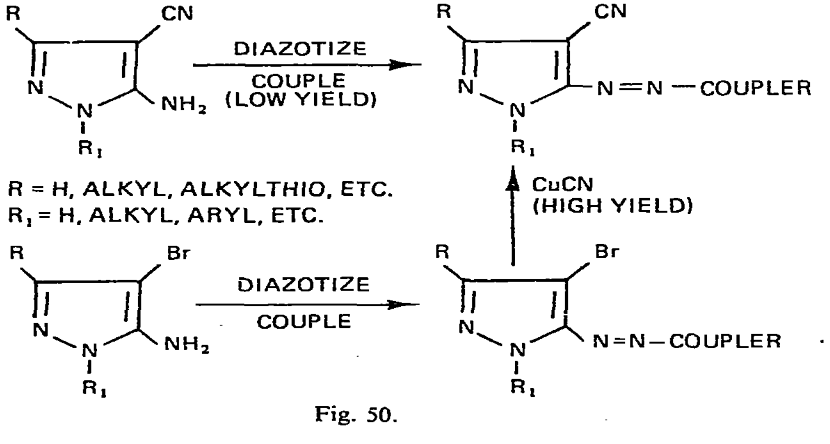
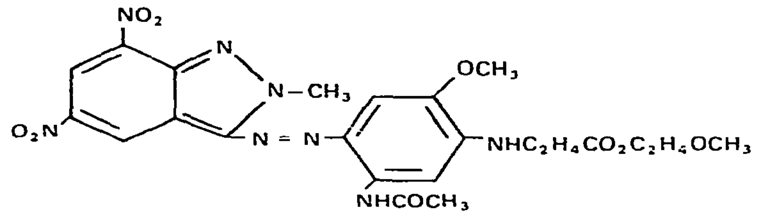


Fig. 50.

diazotization and coupling of 5-amino-4-bromopyrazoles to give bromo intermediates in high yield which can be converted to the cyano dyes by reacting with metal cyanides.[230] Bright red dyes with good lightfastness on polyesters are obtained in this series of dyes when 3′-(*N*,*N*-dialkylamino)-acylanilide-type couplers are used.[230] Yellow dyes are obtained when 5-aminopyrazoles are diazotized and coupled with 3-cyano-4-alkyl-6-hydroxy-2-pyridone[228] and indole[231] couplers. Acid dyes have been prepared from these diazo components with aromatic amine couplers which contain *N*-(sulphatoalkyl) groups.[188]



λMAX = 625 nm (CHLOROFORM)

Fig. 51.

Dyes from 5-aminopyrazoles, where the alternative nitrogen atom is substituted, have been prepared.[104] Aminopyrazoles with a fused benzo ring (3-aminoindazoles) have been reported to give dyes[232] that are more hypsochromic than the corresponding 3-amino-(2,1)-benzisothiazoles (i.e. where >N—H and S are exchanged). However, alkylation of the >N—H group does lead to a bathochromic shift, as does further negative substitution in the benzo ring. For example, 3-amino-2-methyl-5,7-dinitroindazole diazotized and coupled to 5-acetamido-2-methoxy-aniline derivatives yields bluish-green dyes for polyesters (Fig. 51).[107]

4.9. Dyes from 2-aminothiophenes

Some of the earliest dyes prepared from 2-aminothiophenes were from2-amino-3-nitro-5-acyl(aryl)thiophenes.[9,10] These dyes were found to have excellent fastness and dischargeability on acetate fibres and produced bright blue hues. These dyes also have utility as polyester dyes.

During the last 10–15 years, developments in the synthetic routes to substituted 2-aminothiophenes (see section 3.9) have resulted in considerable interest in these amines as diazo components for blue dyes for polyester, cellulose acetate and polyamide fibres. Newly investigated and recently developed diazo components include 2-amino-3,5-dinitro-,[117,233] 3-cyano-5-nitro,[120,234] 3-cyano-4-methyl-5-

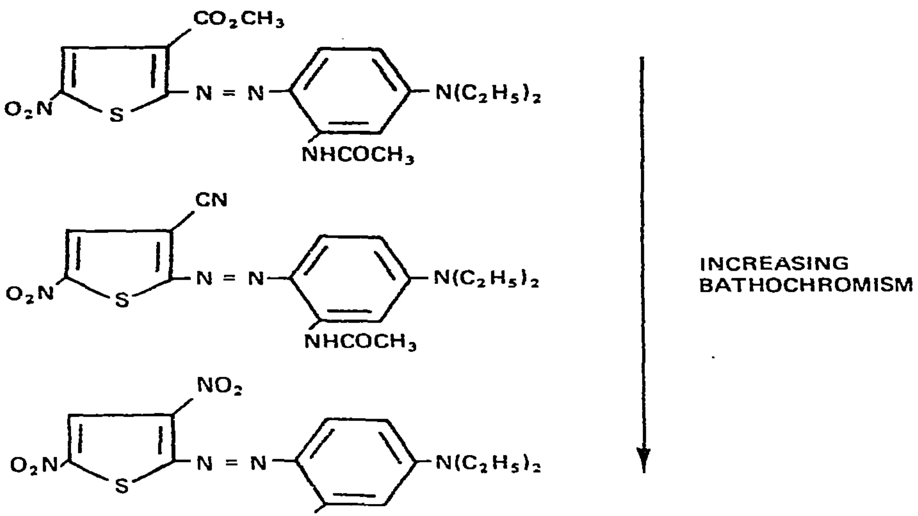


Fig. 52.

nitro,[120,235] 3-carboalkoxy-5-nitro,[120] 3-carboalkoxy-4-methyl-3-nitro-,[120,235] 5-cyano-3-nitro-,[117,236] 5-cyano-4-methyl-3-nitro-,[236] 3-alkylsulphonyl-5-nitro-,[120] 3-carboxy-5-nitro-[237] and 3-formyl-5-nitrothiophene.[238] Dyes prepared from the 2-amino-3,5-dinitrothiophene are the most bathochromic of any dye known in the thiophene series (Fig. 52). When 3'-(*N,N*-dialkylamino)acylanilides are used as coupling components bright greenish-blue dyes with acceptable fastness for polyesters are produced. These dyes also have the valuable property of flaring green when exposed to artificial light, thus rendering them valuable as shading components. The 3,5-dinitro-2-thienylazo dyes are, in general, not as lightfast on polyesters as are dyes from 2-amino-5-acyl-3-nitrothiophenes, and recent patents have claimed dyes from this latter diazo component which have outstanding lightfastness and sublimation fastness on polyesters.[149,239,240] Dyes from 2-amino-3-nitro-5-trifluoroacetylthiophene[241] are also valuable for preparing heat transfer printing dyes.

Violet to blue dyes with moderate to good lightfastness on polyamides have been prepared from new diazo components available by Gewald or similar chemistry. These include 2-amino-3,5-dicyano,[235] 3-carboalkoxy-5-cyano-4-methyl-[120,235] and 3-carbamyl-5-phenylthiophene.[242] Blue acid dyes for nylon carpet fibre have been patented from certain selected 2-aminothiophene diazo components.[119,188]

Based on the number of patents issued, the 2-aminothiophenes have received more attention than any other class of heterocyclic diazo components during the past 5–10 years, and the search for blue azo dyes for application to polyesters and polyamides appears to be continuing.

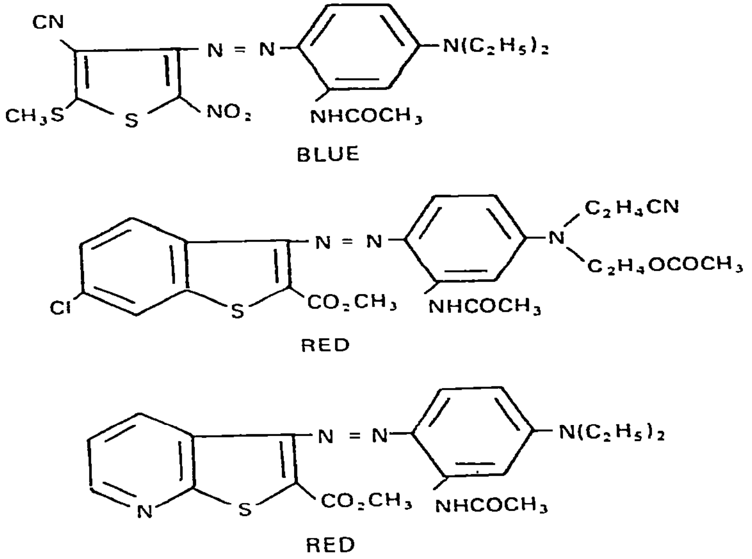


Fig. 53.

Azo dyes have also been reported from negatively substituted 3-aminothiophenes,[127] although they appear to offer no advantages over the 2-amino isomers. Blue dyes are reported,[127] for example, from 3-amino-2-nitro-4-cyano-5-methylmercaptothiophene when diazotized and coupled with *N*,*N*-diethyl-*m*-aminoacetanilide (Fig. 53). 3-Aminobenzo[*b*]thiophenes[243] and 3-amino-[2,3-*b*]pyridines,[244] which are 3-aminothiophenes containing respectively fused benzo and pyridino rings, give orange to red dyes with common aniline-type couplers (Fig. 53).

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