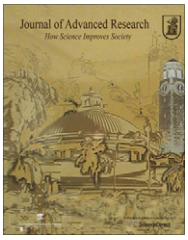
Journal of Advanced Research (2010) 1, 255–290

Cairo University

Journal of Advanced Research



REVIEW

Synthesis and tautomerism of aryl- and hetaryl-azo derivatives of bi- and tri-heterocycles

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Received 29 September 2009; revised 25 November 2009; accepted 2 March 2010
Available online 16 September 2010

KEYWORDS

Heterocycles;
Azodyes;
Azocoupling;
Tautomerism;
Hydrazonoyl halides

Abstract This review summarizes results from the literature concerning synthesis and azo-hydrazone tautomerism of arylazo- and hetarylazo-derivatives of various bi- and tri-heterocycles reported by us and other research groups from 1981 to mid 2009.

Introduction

Aryl- and hetaryl-azo colouring matters have been in use since prehistoric times [1]. The interest in such colouring materials is due to the fact that many derivatives were found useful in the fields of material sciences and theoretical chemistry [2]. For example, many such azo dyes have been extensively used as dyes in various fields such as dyeing of textile fibers, coloured plastics, biological-medical studies and advanced applications in organic synthesis [3]. Recently, applications of such colouring materials to high technology have been attracting much attention. Dyes are used in various fields such as printing, electronic photography, colour formers, liquid crystal displays, laser technology, data storage and solar energy conversion [4]. Also, some of such dyes have found use as non-linear optical (NLO) materials. Such compounds have potential use in optical communications, information processing, frequency doubling and integrated optics [5]. In recent years, arylazo derivatives of various heterocyclic systems have been the subject of intense research by organic chemists [6] and dye manufacturers [7].

It is worth mentioning that azo-hydrazone tautomerism is not only of importance to dyestuff manufacture but also to other areas of chemistry. Also, azo-hydrazone tautomers have different tinctorial strengths (and economics) and different properties, e.g. light fastness. The intention of this review is to focus mainly on publications dealing with the synthesis and azo-hydrazone tautomerism of arylazo derivatives of various bi- and tri-heterocycles that have appeared in Chemical Abstracts during the period 1981–2008. Literature prior to 1981 will not be included unless it is felt essential to use the relevant information to put the problem into a common perspective. Emphasis is only given to the latest developments in the area.

In this literature survey, the arylazo-heterocycles are reported in order of the increase of (i) the number of rings, (ii) the size of such rings and (iii) the number of heteroatoms

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Peer review under responsibility of Cairo University.
doi:10.1016/j.jare.2010.07.002

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present. The sequence of heteroatoms followed is: nitrogen, oxygen, sulfur, selenium and other elements if there are any. The site of fusion in fused heterocycles is indicated by numbers and letters and the numbering of the heterocyclic ring systems is that reported by chemical abstracts.

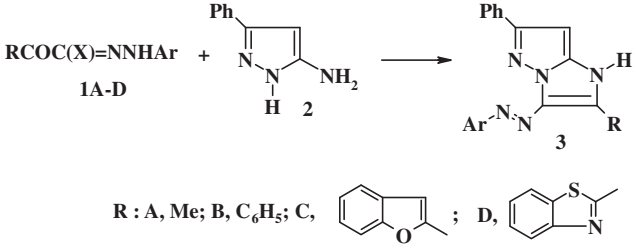
Arylazo dyes of bi-heterocycles

Arylazo derivatives of 5,5-biheterocycles

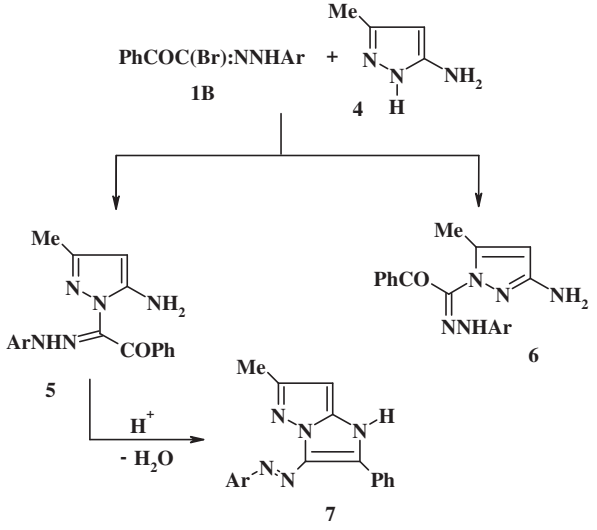
*1H-Imidazo[1,2-b]*pyrazoles

Shawali et al. [8,9] reported that 5-amino-3-phenyl-pyrazole **2** reacted readily with 2-oxohydrazonoyl halides **1A–D** in ethanol and yielded the respective 3-arylazo-2-substituted-*1H*-imidazo[1,2-*b*]pyrazoles **3** (Scheme 1). The spectral data of the latter were reported to be consistent with the depicted arylazo tautomeric structure [9]. Latterly other authors applied the same reaction for synthesis of other derivatives of 3-arylazo derivatives of *1H*-imidazo[1,2-*b*]pyrazole **3** using other hydrazonoyl bromides as precursors [10–15].

Similar reaction of *N*-aryl 2-oxo-2-phenylethanehydrazonoyl bromides **1B** with 3-methyl-5-aminopyrazole **4** was reported, however, to give a mixture of **5** and **6** [16] (Scheme 3). Treatment of **5** with acid resulted in the elimination of water to give the respective *1H*-3-arylazoimidazo[1,2-*b*]pyrazole derivative **7** (Scheme 2) [16]. The product **6** was recovered unchanged upon similar treatment with acid.



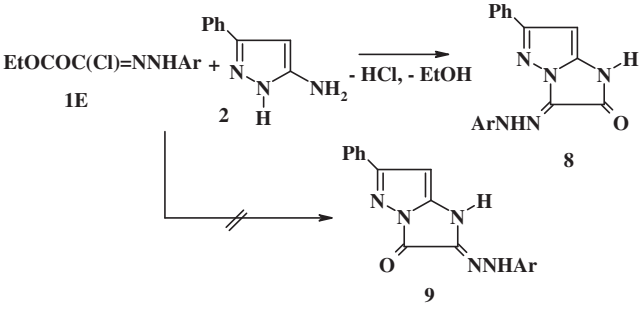
Scheme 1



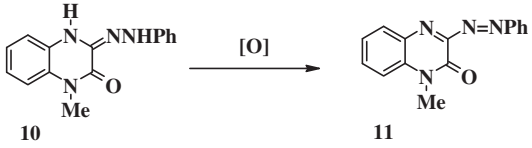
Scheme 2

Also, it has been reported that ethyl *N*-arylhydrazonochloroacetate **1E** reacted with 3-phenyl-5-aminopyrazole **2** to give a product to which structure **8** was assigned (Scheme 3) [8,9]. The isomeric structure **9** was discarded on the basis that the isolated product was recovered unchanged after being subjected to oxidation treatment. Structures of type **9** are expected to be oxidized by analogy with 1-methyl-3-phenylhydrazono-1,4-dihydroquinoxalin-2-one **10** which was reported to give 3-phenylazoquinoxaline derivative **11** upon oxidation (Scheme 4) [17–19].

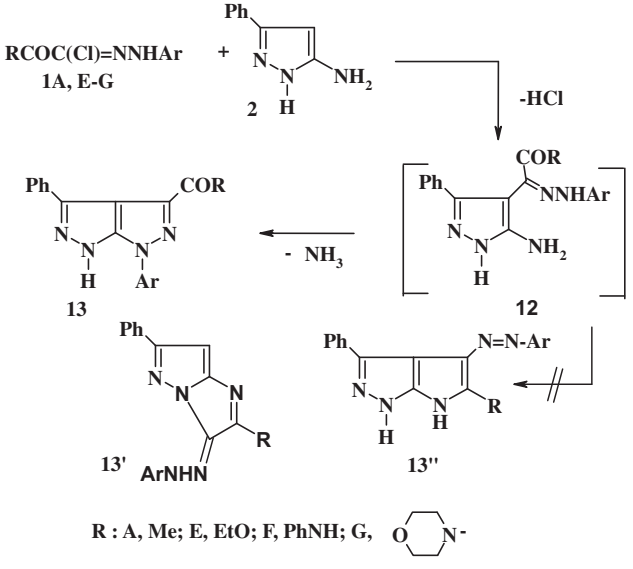
Contrary to the foregoing reports, it was indicated that reaction of 3-phenyl-5-aminopyrazole **2** with each of the hydrazonoyl chlorides **1A, B, C, D** yielded the respective 3-substituted-1-aryl-4-phenyl-*1H,6H*-pyrazolo[3,4-*c*]pyrazoles **13** instead of the expected arylazo imidazopyrazole **13′** or its isomeric arylazo pyrrolopyrazole **13″** (Scheme 5) [20,21]. Such



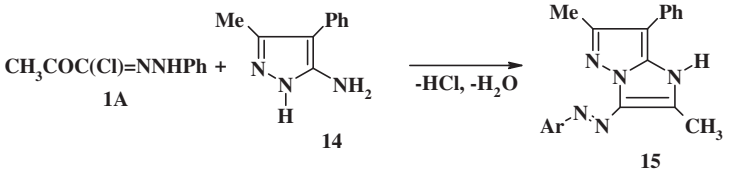
Scheme 3



Scheme 4



Scheme 5



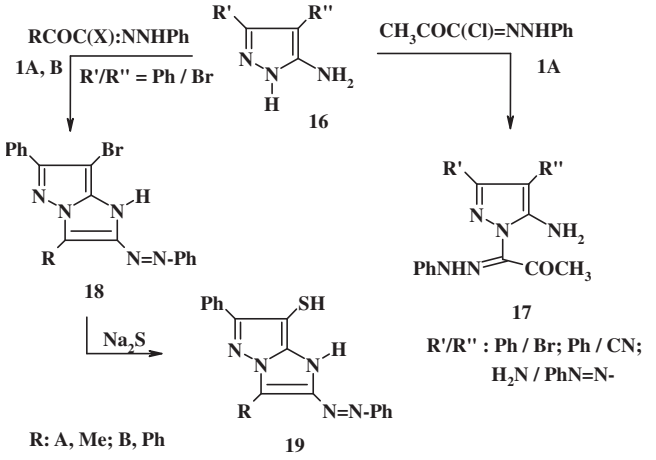
Scheme 6

finding needs further evidence to account for such a suggested pathway.

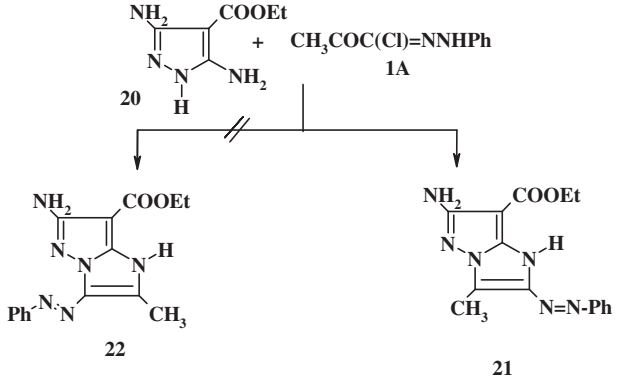
The reaction between 2-oxopropanehydrazonoyl chloride **1A** and 3-methyl-4-phenyl-5-aminopyrazole **14** led, as expected, to *1H*-3-arylazo-imidazo[1,2-*b*]pyrazole derivative **15** (Scheme 6) [22].

Also, it was claimed that reaction of 5-amino-3,4-disubstituted pyrazoles **16** with *N*-phenyl 2-oxopropanehydrazonoyl chloride **1A** afforded the amidrazone derivative **17** (Scheme 7) [22]. In another report [23], reactions of 5-amino-3-phenyl-4-bromopyrazole **16** with the hydrazonoyl halides **1A** and **1B** were reported to yield the respective 2-phenylazoimidazo[1,2-*b*]pyrazole derivative **18** which, upon treatment with sodium sulfide, was converted into **19** (Scheme 7) [24]. No rationalization, however, was offered.

A similar contradiction was also reported, indicating that reaction of ethyl 3,5-diaminopyrazole-4-carboxylate **20** with



Scheme 7

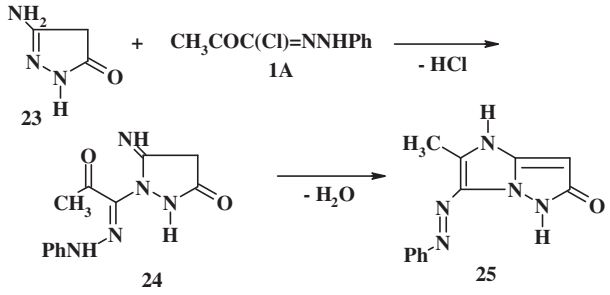


Scheme 8

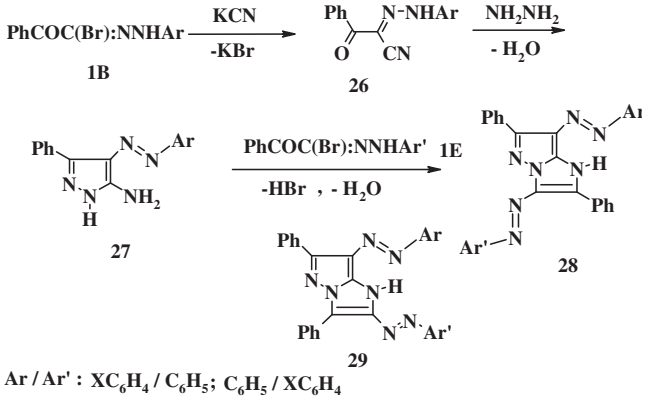
2-oxopropanehydrazonoyl chloride **1A** yielded the 2-phenylazo derivative **21** and not the expected 3-phenylazo derivative **22** (Scheme 8) [25]. The latter isomer is to be the expected product of such a reaction as the pyrazole N(1)H is more basic than the exocyclic 5-amino group and thus the structure of the product isolated from such reaction seems to need further investigation.

Reaction of 3-amino-4,5-dihydropyrazol-5-one **23** with *N*-phenyl 2-oxopropanehydrazonoyl chloride **1A** was reported to yield 3-phenylazo-2-methyl-5,6-dihydro-6-oxo-*1H*-imidazo[1,2-*b*]-pyrazole **25** *via* dehydrative cyclization of the initially formed amidrazone derivative **24** (Scheme 9) [22].

Recently, Shawali et al. [2] reported that when equimolar quantities of *N*-aryl 2-oxo-2-phenylethanehydrazonoyl bromide **1B** (Ar = Ph) and each of the azo derivatives **27a–g** were refluxed in ethanol in the presence of triethylamine, the respective 3,7-*bis*(arylazo)-2,6-diphenyl-*1H*-imidazo[1,2-*b*]pyrazoles **28** were formed. Similar reactions of **27** (Ar = Ph) with each of *N*-aryl 2-oxo-2-phenylethane-hydrazonoyl bromides **1Ba–h**



Scheme 9



Scheme 10

also yielded the respective *bis*-arylazo derivative **28** (Scheme 10). The other regioisomeric structures namely 2,7-*bis*(arylazo)-2,6-diphenyl-*1H*-imidazo[1,2-*b*]pyrazoles **29** were discarded on the basis that reaction of 5-amino-3-phenyl pyrazole with 2-oxohydrazonoyl halides was reported to afford in all cases examined the respective 3-arylazo-2,6-diaryl-*1H*-imidazo[1,2-*b*]pyrazoles and not the isomeric 2-arylazo-3,6-diaryl-*1H*-imidazo[1,2-*b*]pyrazoles [2,8,9,16,22,26,27]

Although, four possible tautomeric structures **A–D** can be written for each of the compounds **28** (Fig. 1), they were found to exist predominantly in the tautomeric form **A** on the basis of their electronic absorption spectra and correlations of their acid dissociation constants in both ground and excited states, p*K* and p*K**, respectively, with Hammett equation. For example, their electronic absorption pattern in dioxane revealed in each case two characteristic intense absorption bands in the regions 600–400 and 350–290 nm, similar to that reported for the azo chromophore [28]. Also, the electronic spectra of **28** (Ar = Ar′ = C_6H_5), in solvents of different polarities showed little, if any, shift. This result indicates that the studied compounds exist in one tautomeric form, namely the *bis*(arylazo) form **A** (Fig. 1). Furthermore, the results of the correlations of their acid dissociation constants by Hammett equation together with the spectral data provided evidence that indicates that such compounds exist predominantly in the *1H-bis*(arylazo) structure, namely the tautomeric form **A** in both ground and excited states (Fig. 1).

Imidazo[2,1-b]thiazoles

6-Arylazoimidazo[2,1-*b*]thiazoles **31** were first synthesized by Shawali et al. [9] by reaction of the appropriate 2-aminothiazole derivatives with hydrazonoyl halides. Thus, reaction of 4-phenyl-2-aminothiazole **30** with 2-oxoalkanehydrazonoyl halides **1A, B, H** were reported to give, in each case, a mixture of three products, namely the hydrohalide salt of the starting 2-aminothiazole, tetrazine derivative and 6-arylazo-3,5-disubstituted imidazo[2,1-*b*]thiazoles **31** [9]. However, when equivalent amounts of hydrazonoyl halide and 2-amino-4-phenylthiazole **30** were refluxed in ethanol in the presence of triethylamine, only the respective azo-products **31** were obtained in 80% yields. Similar reaction of 2-heteroaryl-2-oxohydrazonoyl bromides **1H** with 2-amino-4-phenylthiazole afforded the respective 6-arylazoimidazo[2,1-*b*]thiazoles **31** (Scheme 11) [29]. The other isomeric structure **32** was excluded for the isolated products on the basis that reaction of 2-aminothiazoles with *a*-halo ketones gives 5-substituted imidazo[2,1-*b*]thiazoles [30] and alternate synthesis of **31** by coupling of diazonium salts with 3,5-diphenyl imidazo[2,1-*b*]thiazoles **33** (Scheme 11) [30].

In another report [31], it was indicated that reaction of other 2-amino-4-methylthiazole derivatives **34** with the 2-oxohydrazonoyl halides **1A, B** led to the formation of the respective 5-arylazoimidazo[2,1-*b*]thiazoles **35** (Scheme 12). The other expected regioisomers **36**, however, were not formed.

Reaction of 2-amino-4-phenylthiazole **30** with ethyl *N*-(arylhydrazono)chloroacetate **1B** in the presence of triethylamine was reported to give one product that was assigned the structure **37** (Scheme 13) [9]. The other isomeric structure **38** was discarded and although the isolated products **37** can have two tautomeric forms (**37** and **37′**), they were assigned the ketohydrazone tautomeric structure **37** on the basis that their IR spectra revealed CO and NH bands near 1710 and 3360 cm^{-1}, respectively. Similar reaction of 4-methyl-2-aminothiazole derivatives **34** with ethyl *N*-(arylhydrazono)chloroacetate **1B**

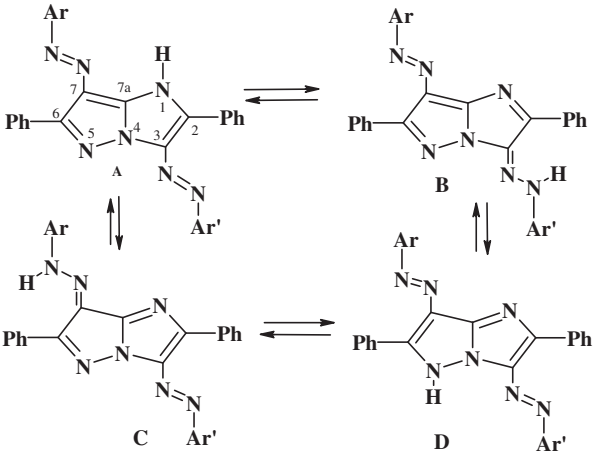
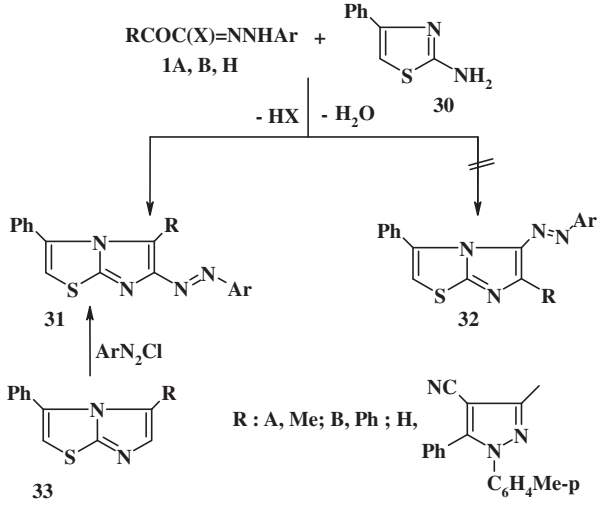
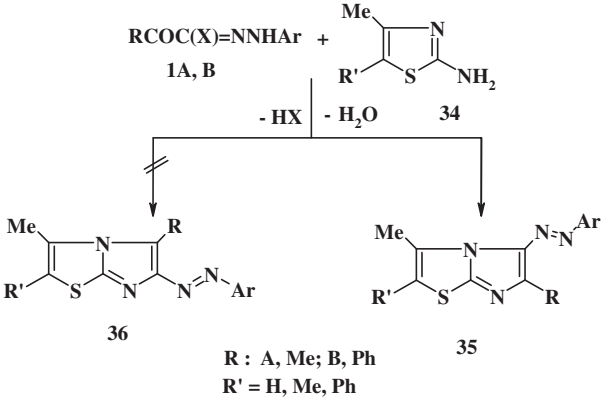


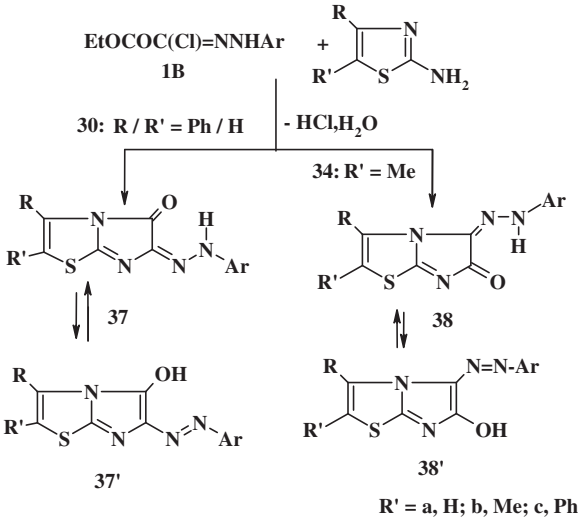
Fig. 1 Possible tautomeric structures for 3,7-*bis*(arylazo)-2,6-diphenyl-*1H*-imidazo[1,2-*b*]pyrazoles.



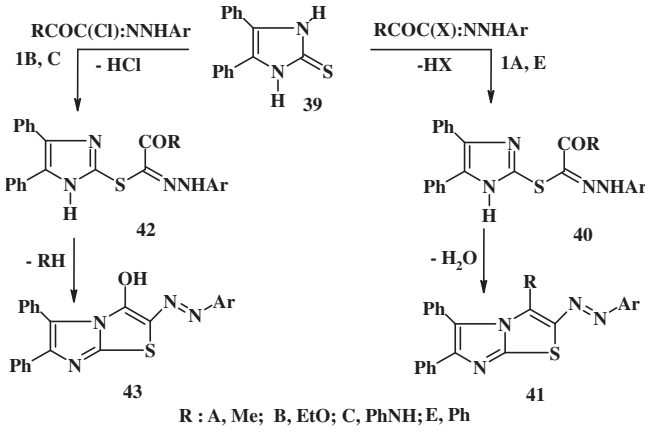
Scheme 11



Scheme 12



Scheme 13



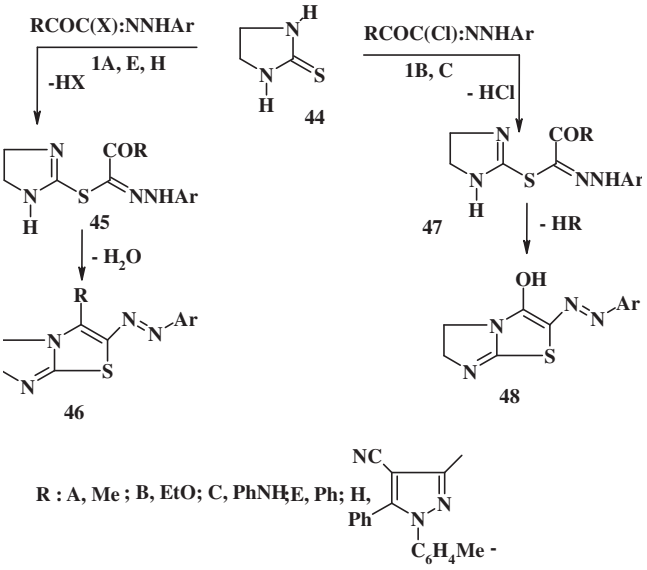
Scheme 14

was reported by Shawali et al. [32] to yield, however, the other isomeric products **38** (Scheme 13) [31].

2-Mercaptoimidazole **39** was reported to react with each of *N*-aryl 2-oxoalkanehydrazonoyl halides **1A, E** in the presence of triethylamine to give the respective thiohydrazonate esters **40** [21,33,34]. Treatment of the latter with polyphosphoric acid resulted in their cyclization to afford **41** (Scheme 14) [33].

Similar reactions of 2-mercaptoimidazole **39** with either ethyl *N*-(arylhydrazono) chloroacetate **1B** or *N*-(arylhydrazono)-chloroacetanilide **1C** yielded one and the same product, namely **43**. The intermediate thiohydrazonate esters **42** were not isolated (Scheme 14) [21,34]. However, in one report [21] such intermediates were said to be the end products.

Reactions of 2-mercapto-4,5-dihydroimidazole **44** with each of *N*-aryl 2-oxoalkanehydrazonoyl halides **1A, E** [23] and **1H** [29] yielded the respective products **46** (Scheme 15). Similar reactions of the 2-mercapto-4,5-dihydroimidazole **44** with either ethyl *N*-arylhydrazonochloroacetate **1B** or *N*-phenyl 2-oxo-2-phenylaminoethanehydrazonoyl chloride **1C** afforded a single product, namely **48** (Scheme 15) [23].



Scheme 15

1H-Pyrazolo[5,1-c][1,2,4]triazoles

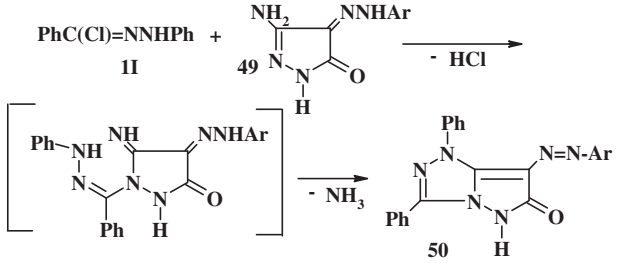
N-Phenyl benzenecarbohydrazonoyl chloride **1I** reacted with 3-amino-4-(arylhydrazono)-pyrazolin-5-ones **49** in refluxing ethanol to yield the respective 7-arylazo-*1H*-pyrazolo[5,1-*c*][1,2,4]triazoles **50** (Scheme 16) [35].

Similar reaction of *N*-phenyl benzenecarbohydrazonoyl chloride **1I** with 3,5-diamino-4-phenylazopyrazole **51** was reported to yield **53** probably via elimination of ammonia from the intermediate amidrazone **52** (Scheme 17) [36,37]. However, reactions of the same diaminopyrazole **51** with 2-oxohydrazonoyl chlorides **1A** and **1C** were reported to give the respective amidrazones **54** (Scheme 17) [21,37]. No attempts to cyclize the latter, however, were reported.

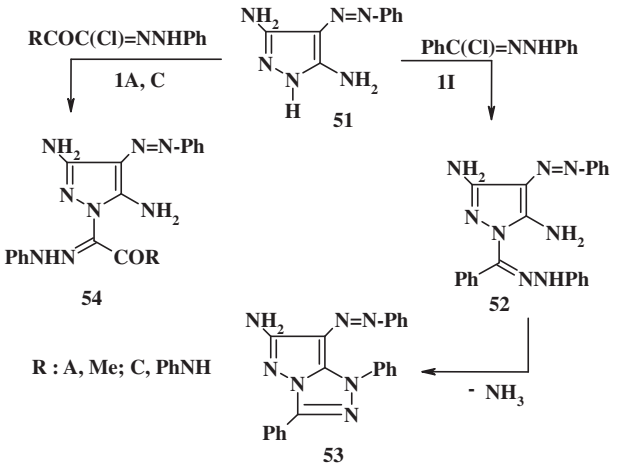
Imidazo[1,2-b][1,2,4]triazoles

Reaction of 3-amino-1,2,4-triazole **55** with 2-oxohydrazonoyl halides **1A, E** in ethanol was first reported by Shawali et al. [9] to yield the respective 5-arylazo-imidazo[1,2-*b*][1,2,4]triazoles **56** (Scheme 18). Similar reaction of the same aminotriazole **55** with the other hydrazonoyl bromides **1G** was latterly reported by others [15] to afford the respective **56**. The other isomeric 6-arylazo derivatives **57** were not produced.

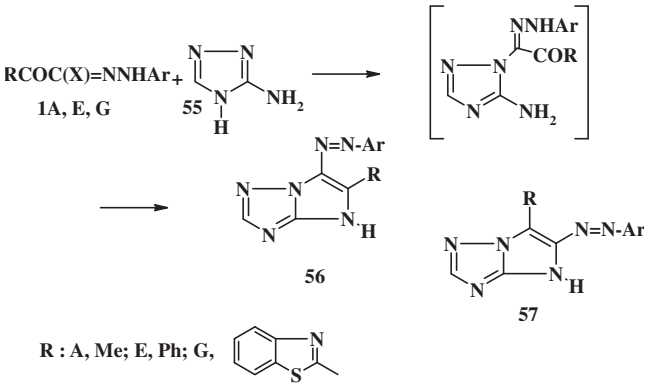
Similar reaction of 3-amino-1,2,4-triazole **55** with ethyl *N*-arylhydrazonochloroacetate **1B** was reported by Shawali et al. [9] to give **58** (Scheme 19). The other two isomeric structures namely **59** and **60** were discarded [9]. Structure **60** was discarded on the basis that the product isolated was recovered unchanged upon treatment with oxidizing agents.



Scheme 16



Scheme 17



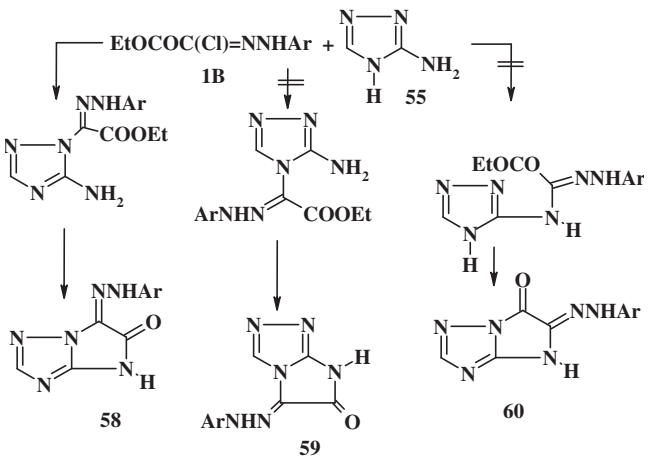
Scheme 18

Arylazo derivatives of 5,6-biheterocycles

Indoles

Reaction of *N*-aryl 2-oxoalkanehydrazonoyl halides **1A, E** each with aniline or *N*-methylaniline in ethanol in the presence of triethylamine afforded the respective amidrazone derivatives **61**. Addition of the latter to preheated polyphosphoric acid at 80 °C yielded the corresponding 2-arylazoindoles **62** (Scheme 20) [38,39].

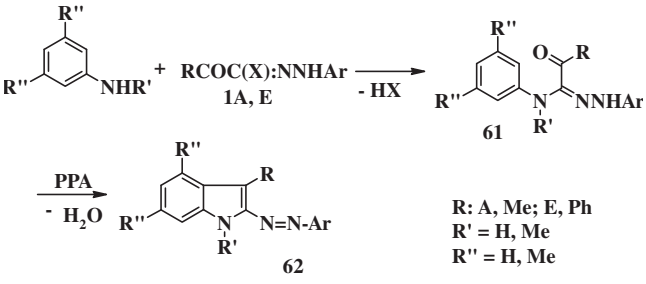
Similar treatment of the amidrazones **63** (R″ = H or Me), prepared from the hydrazonoyl chloride **1J** and *N*-methylaniline, was reported to yield the isatin derivatives **65** and **66** (Scheme 21) [39,40]. The formation of the latter products was considered to result from atmospheric oxidation of the cyclized intermediates **64**, followed, in the case of **66**, by hydrolysis.



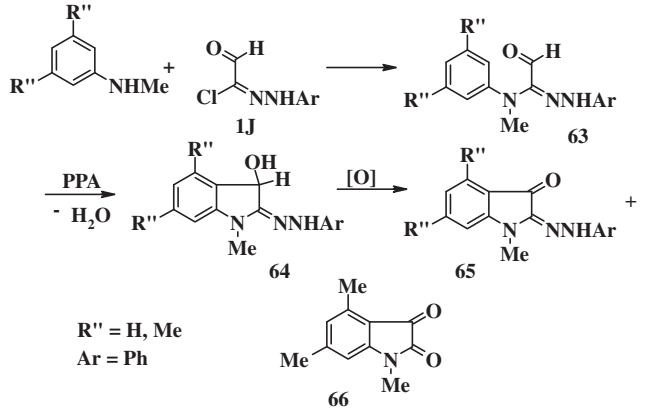
Scheme 19

Benzofurans

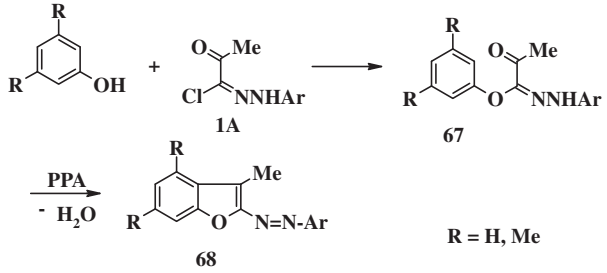
2-Arylazo-3-methyl benzofuran **68** were synthesized by reaction of 2-oxoalkanehydrazonoyl halides **1A** with phenols in the presence of base catalyst such as triethylamine or ethoxide anion and cyclization of the resulting aryl hydrazonate esters **67** via treatment with polyphosphoric acid (Scheme 22) [38].



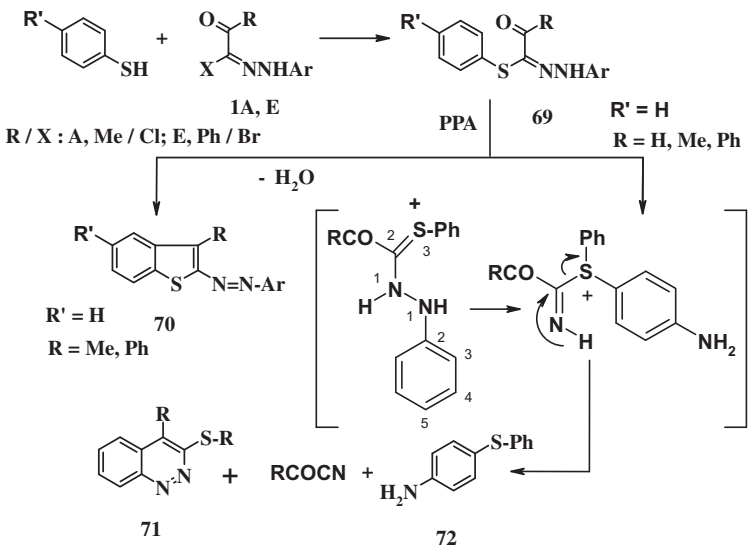
Scheme 20



Scheme 21



Scheme 22



Scheme 23

Benzothiophenes

2-Arylazo-3-substituted-benzothiophenes **70** were obtained from the reactions of thiophenol with 2-oxoalkanehydrazonoyl halides **1A, E** in the presence of base catalyst and treatment of the resulting aryl thiohydrazonate esters **69** with polyphosphoric acid (Scheme 23) [38].

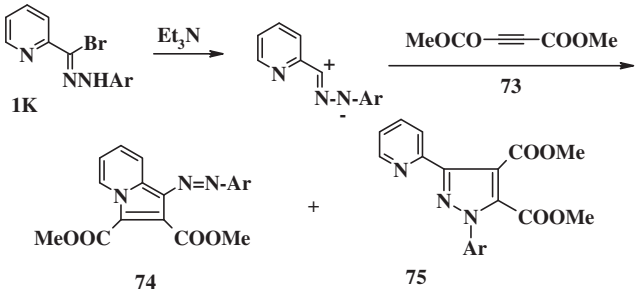
It is worth mentioning that treatment of some phenyl thiohydrazonate ester **69** (Ar = Ph, R = H) with PPA was reported to give the 3-(phenylthio) cinnolines **71** as the main product, with an 18% yield. On the other hand, similar treatment of the esters **69** (Ar = Ph, R = Me, Ph) afforded the respective products **71** (27–35% yield) together with 4-aminophenyl sulfide **72** (32–60% yield) and acylcyanide (Scheme 23) [39]. The formation of **72** was considered to result through a cyclodehydration path involving the aromatic ring of the hydrazone moiety. The mechanism suggested to account for the formation of **72** involves a rather unprecedented [3,5] rearrangement in which the sulfur atom is one of the termini, as depicted in Scheme 23 [39].

Pyrrolo[1,2-a]pyridines

Reaction of *N*-aryl 2-pyridinecarbohydrazonoyl bromide **1K** with dimethyl acetylene-dicarboxylate **73** was reported to afford a mixture of 1-arylazopyrrolo[1,2-*a*]pyridine **74** and the usual 1,3-dipolar cycloadduct **75** (Scheme 24) [41].

Imidazo[1,2-a]pyridines

In 1983 Shawali et al. [9] reported that reactions of 2-oxohydrazonoyl halides **1A, E–G** and **1L** each with 2-aminopyridine **76** in ethanol under reflux gave the respective 3-arylazo-2-substitutedimidazo[1,2-*a*]pyridine **78** (Scheme 25) [9]. The other regioisomeric products **80** were discarded on the basis that 2-aminopyridine **76** has been known to react with *a*-halo ketones to give **85** (Scheme 26) [8,9,13–15,42,43]. Furthermore, the assigned structure **78** was confirmed by the fact that coupling of 2-substitutedimidazo[1,2-*a*]pyridine **79** with *N*-nitrosoacetanilide or diazotized aniline in ethanol was found to yield a product identical in all respects with **78** (Ar = Ph) [9,14].



Scheme 24

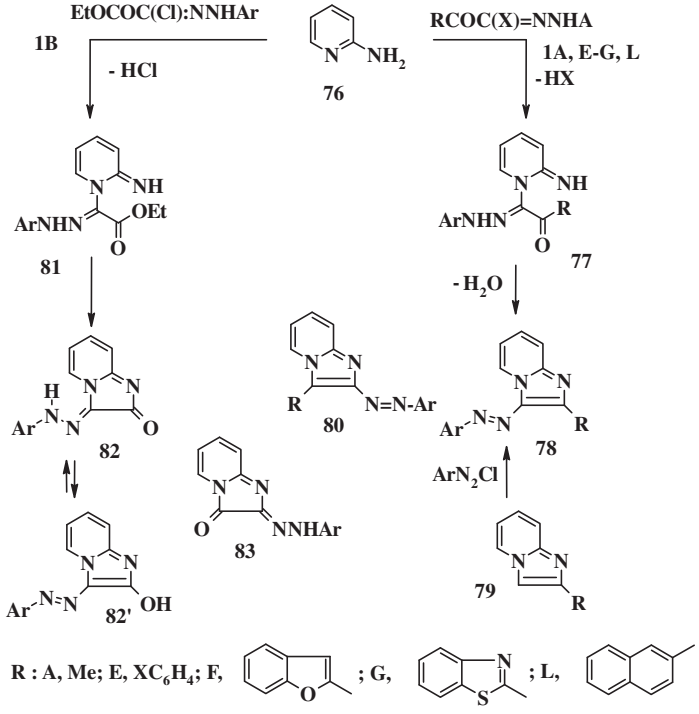
Ethyl *N*-(arylhydrazono)chloroacetates **1B** reacted similarly with 2-aminopyridine **76** and afforded **82** which was shown to have the keto-hydrazone structure (Scheme 25) [9]. The other possible regioisomeric structure **83** was discarded on the basis that reactions of 2-aminopyridine **76** with α-halo-esters were reported to give **84** (Scheme 25) [9,17,18].

Similar reactions of 2-aminopyridine **76** with *N*-(pyrazol-5-yl) 2-oxohydrazonoyl halides **1M, N** in refluxing ethanol in the presence of triethylamine or piperidine were reported not to give the respective arylazo derivatives **87** [44,45]. They yielded instead pyrazolotriazoles **86** probably via cyclization of the nitrilimine intermediates (Scheme 27). In this case it seems that 2-aminopyridine **76** acted as a base catalyst.

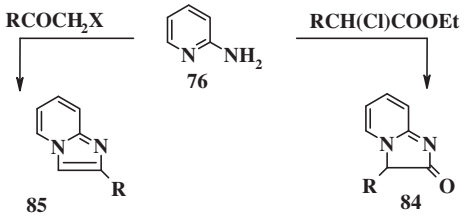
Thieno[2,3-b]pyridines

5-Arylazothieno[2,3-*b*]pyridines **89** were obtained by reaction of phenacyl bromide with 3-arylazopyridine-6(*1H*)-thiones **88** (Scheme 28) [46].

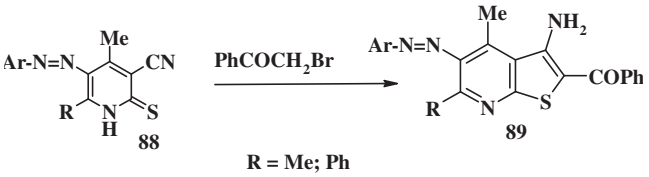
4,6-Dimethyl-2-arylhydrazonothieno[2,3-*b*]pyridin-3-ones **91** were prepared by coupling 4,6-dimethyl-thieno[2,3-*b*]pyridin-3-one **90** with diazotized anilines in ethanol in the presence of sodium acetate (Scheme 29) [47]. On the basis of their IR (*v*CO 1680, *v*NH 3350) and ^{1}H NMR spectra (δNH 11.2–13.2), such products were assigned the indicated ketohydrazone tautomeric structure **91**.



Scheme 25



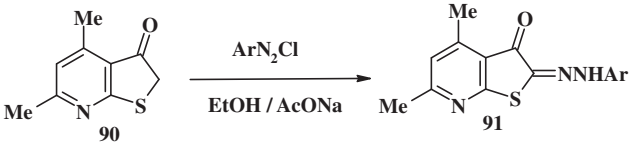
Scheme 26



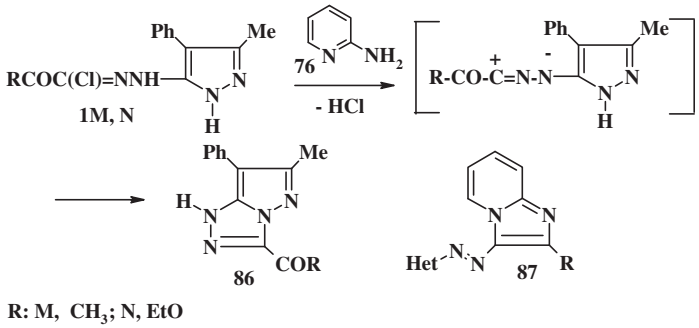
Scheme 28

Pyrazolo[3,4-b]pyridines

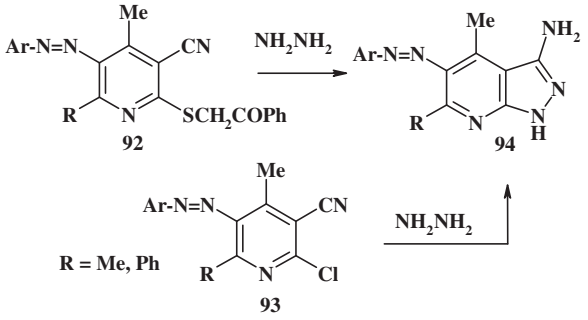
Hydrazinolysis of either **92** or **93**, each in refluxing ethanol containing a catalytic amount of triethylamine, was reported to give 5-arylazo derivatives of *1H*-pyrazolo[3,4-*b*]pyridine **94** (Scheme 30) [46]. Such azo dyes were assigned the azo tautomeric structure as their ^{1}H NMR spectra showed signal at δ 5.5 assignable to NH_2 protons and a broad signal at δ 12.0 assignable to pyrazole NH proton.



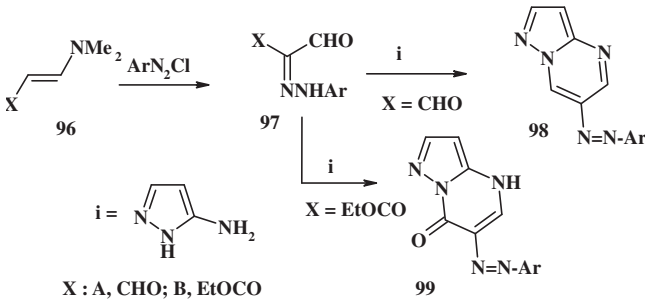
Scheme 29



Scheme 27



Scheme 30



Scheme 32

A study of the electronic absorption spectra of 3-(2,4-dihydroxy-1-naphthylazo)-4,6-dimethylpyrazolo[3,4-*b*]pyridine **95a** and 3-(2-hydroxy-1-naphthylazo)-4,6-dimethylpyrazolo-[3,4-*b*]pyridine **95b** in a number of organic solvents indicated that they exist in basic solvents as azo-hydrazone tautomeric equilibrium. However, in acetone, acetonitrile and carbon tetrachloride, they exist mainly in the arylazo tautomeric form **95A** (Scheme 31) [48].

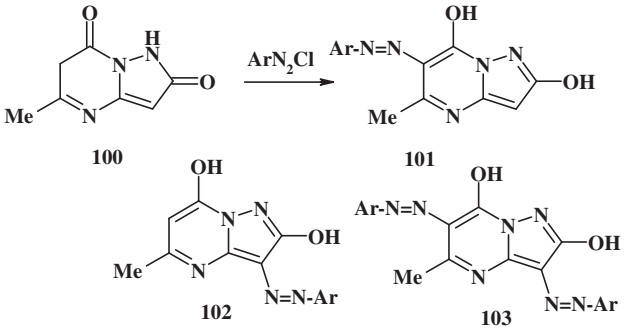
Pyrazolo[1,5-a]pyrimidines

Coupling of enaminal **96A** and enamino ester **96B** each with diazonium salts gave the respective hydrazones **97A** and **97B**, respectively (Scheme 32). Condensation of the latter hydrazones each with aminopyrazole yielded the respective arylazo derivatives of pyrazolo[1,5-*a*]pyrimidines **98** and **99**, respectively (Scheme 32) [49,50]. No discussion of the tautomerism of products **99,** however, was presented.

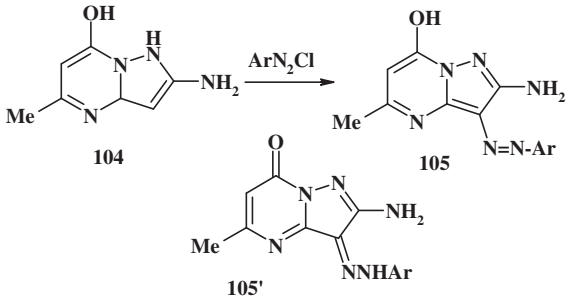
Three series of mono-arylazo- and bis-arylazo- derivatives of pyrazolo[1,5-*a*]pyrimidine ring system **101**–**103** were prepared via coupling of the respective diazotized anilines with 2-methyl-pyrazolo[1,5-*a*]pyrimidin-2,7(1H,7H)-dione **100** (Scheme 33) [51]. Such derivatives were reported to exist predominantly in the indicated arylazohydroxy tautomeric form.

Similarly, a series of 2-amino-3-arylazo-7-hydroxy-5-methyl-pyrazolo[1,5-*a*]pyrimidines 105 was prepared via coupling the respective diazotized anilines with 2-amino-7-hydroxy-5-methyl-pyrazolo[1,5-*a*]pyrimidine 104 (Scheme 34) [52]. Their electronic spectra in different solvents indicated that they exist mainly in the azo tautomeric form 105.

Also, hydrazinolysis of **106** gave 5-amino-4-phenylpyrazole **107**. Cyclization of the latter with diethylmalonate afforded 108 which, upon coupling with diazotized anilines, afforded the respective 6-arylazo derivatives **109** [53]. Treatment of the latter with Phosphorusoxy chloride gave **110** which, upon reaction with secondary amines, yielded **111** (Scheme 35) [53].

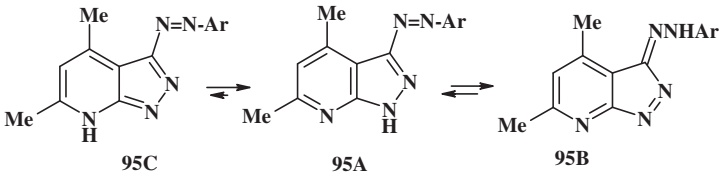


Scheme 33



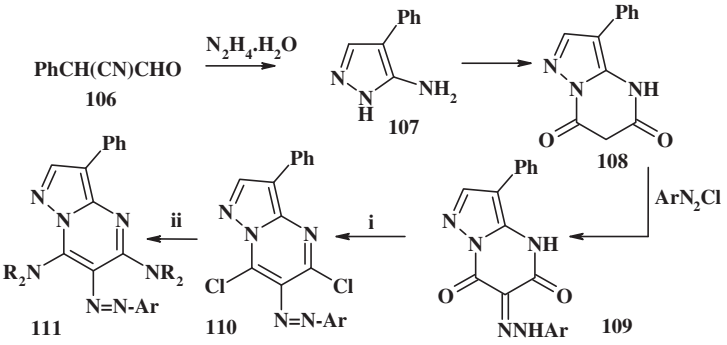
Scheme 34

Another synthetic strategy for 3-arylazopyrazolo[1,5-*a*]pyrimidine dyes involves condensation of 5-amino-4-arylazo-pyrazole derivatives with various reagents. For example, reaction of 5-amino-4-arylazopyrazole derivatives **112** with enaminones **113** afforded the respective 3-arylazopyrazolo[1,5-*a*]pyrimidine dyes **114** (Scheme 36) [26,54,55].

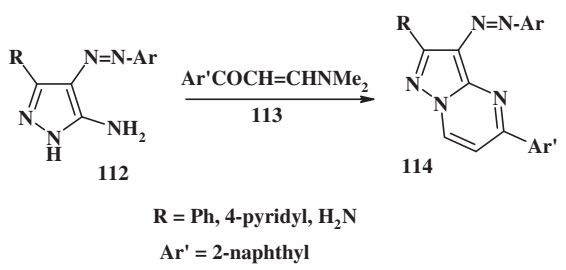


Ar : a, 2,4-(HO)2-1-naphthyl ; b, 2-HO-1-naphthyl

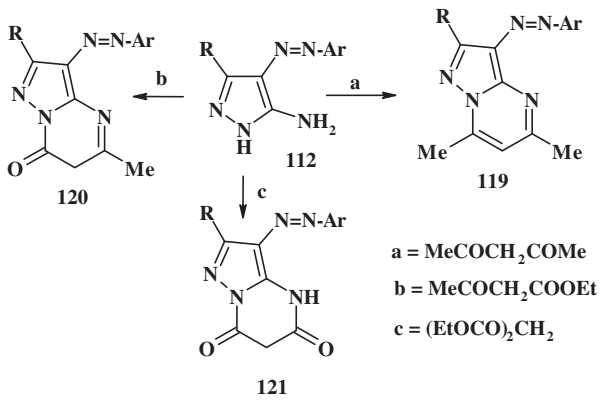
Scheme 31



Scheme 35



Scheme 36



Scheme 38

Reaction of enaminonitrile **115** with 3,5-diamino-4-phenylazopyrazole **117** was reported to follow different regiochemistry and gave 2-amino-3-phenylazo-pyrazolo[1,5-*a*]pyrimidin-7(*4H*)-one **118** (Scheme 37). The latter product was also obtained by refluxing the same pyrazole derivative **117** with ethyl propiolate **116** in pyridine [54]. This product, although it can have two possible tautomeric forms, was assigned the azo tautomeric form **118A** (Scheme 37). No interpretation for this or the change in regiochemistry was given.

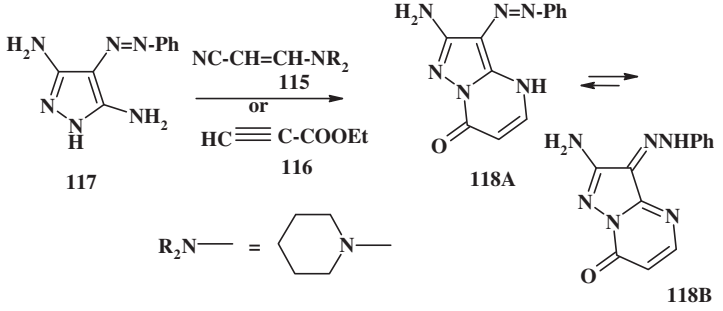
Similar condensation of 5-amino-4-arylazopyrazole derivatives **112** with ß-diketones, ß-keto esters and diester afforded the respective 3-arylazopyrazolo[1,5-*a*]pyrimidine dyes **119–121** (Scheme 38) [36,56].

Reaction of [*bis*(methylthio)methylene]malononitrile and ethyl 2-cyano-3,3-*bis*(methylthio)acrylate each with 3,5-diaminopyrazole **117** in refluxing ethanol in the presence of catalytic amount of piperidine gave the corresponding 7-(methylthio)pyrazolo[1,5-*a*]pyrimidine **122**. Treatment of the latter with aromatic amines yielded the respective aniline derivatives **123** (Scheme 39) [57].

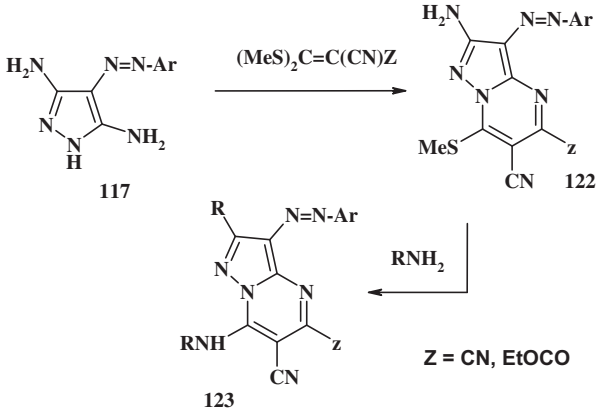
Reaction of ethyl arylhydrazonocyanoacetate **124** with 3-amino-4-arylazo-5-substituted pyrazoles **112** afforded the *bis*-arylazo derivatives **125** (Scheme 40) [58].

Also, reaction of cyanoacetic hydrazide with arylhydrazonomalononitrile **126** yielded 3,5-diamino-4-arylazopyrazole **117**. Treatment of the latter with arylhydrazonomalononitrile afforded the corresponding 2,5,7-triamino-3,6-*bis*-arylazopyrazolo[1,5-*a*]pyrimidines **127** (Scheme 41) [55,59,60].

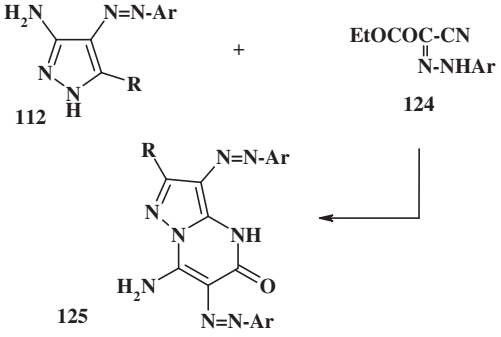
In a similar manner, heating a mixture of each of 5-amino-3-methyl-4-arylazopyrazoles **112** with 2-arylhydrazono-3-ketiminobutyronitriles **128** yielded the respective *bis*-arylazo



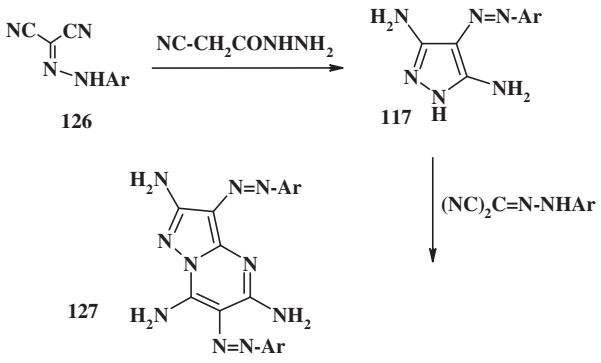
Scheme 37



Scheme 39



Scheme 40

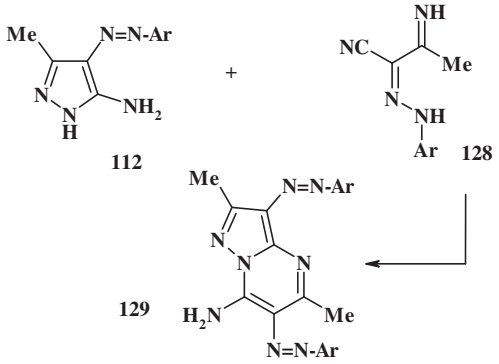


Scheme 41

derivatives of pyrazolo[1,5-*a*]pyrimidines **129** (Scheme 42) [58].

Imidazo[1,2-a]pyrimidines

Reactions of 2-aminopyrimidine **130** with 2-oxohydrazonoyl halides **1A, G** were first studied by Shawali et al. [9] and were reported to yield the respective 3-arylazoimidazo[1,2-*a*]pyrimidines **131** (Scheme 43). The other regioisomers **131A** were discarded on the basis that reactions of 2-aminopyrimidine with *a*-halo ketones give 2-substituted imidazo[1,2-*a*]pyrimidines [9]. Other substituted 2-oxohydrazonoyl halides namely **1E** were reported to react similarly with 2-aminopyrimidine **130** to give the respective **131** (Scheme 43) [15,43].

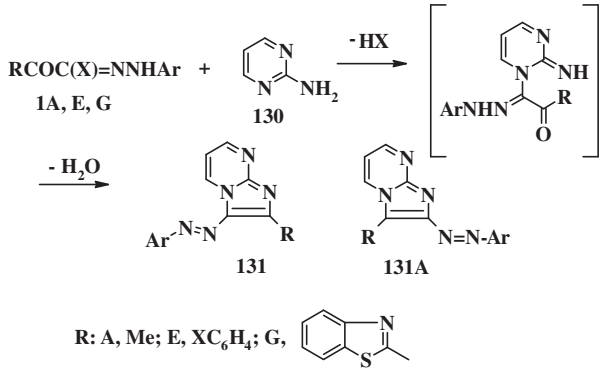


Scheme 42

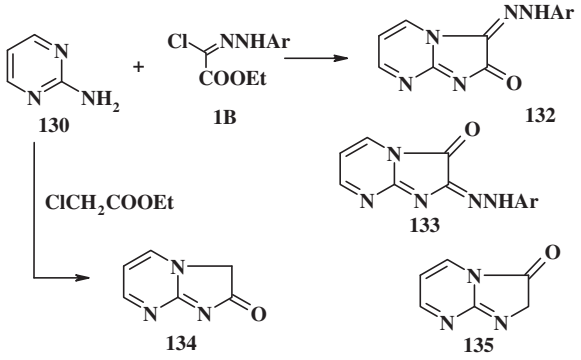
Reaction of 2-aminopyrimidine **130** with the hydrazonoyl chloride **1B** afforded **132** and not **133** (Scheme 44) [9]. The latter structure was rejected on the basis that reactions of haloesters with 2-aminopyrimidine **130** were reported to give **134** and not **135** (Scheme 44) [9].

[1,2,4]Triazolo[4,3-a]pyrimidines

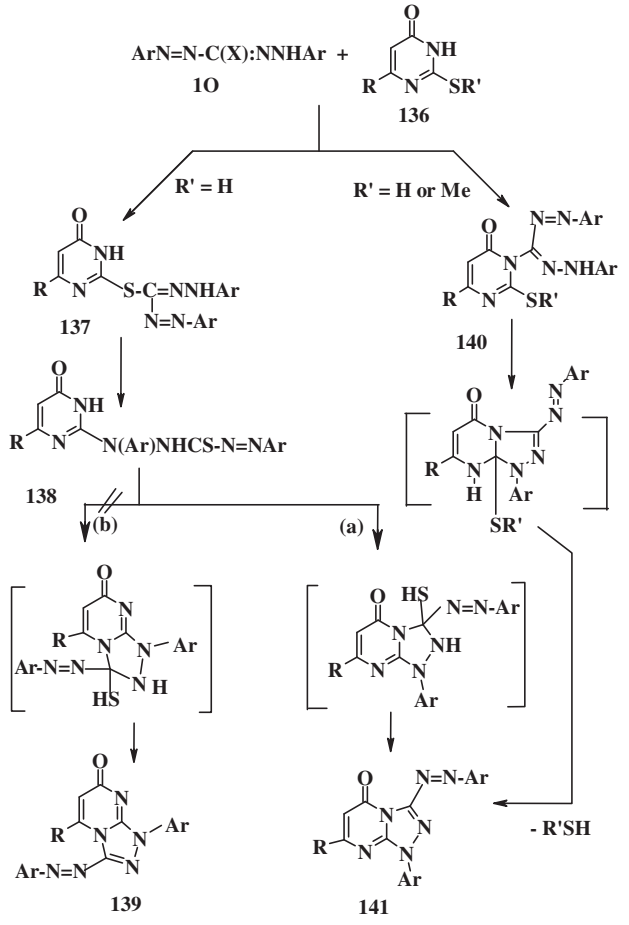
Recently, Shawali et al. [63] reported one-pot synthesis of a series of 3-arylazo-[1,2,4]triazolo[4,3-*a*]pyrimid-5(*1H*)-ones **141** via reactions of 2-thiouracil derivatives **136** (R′ = H) with *N*-aryl arylazomethanehydrazonoyl chlorides **1O** in chloroform in the presence of triethylamine at reflux. Although the studied reactions can lead to the formation of products that



Scheme 43



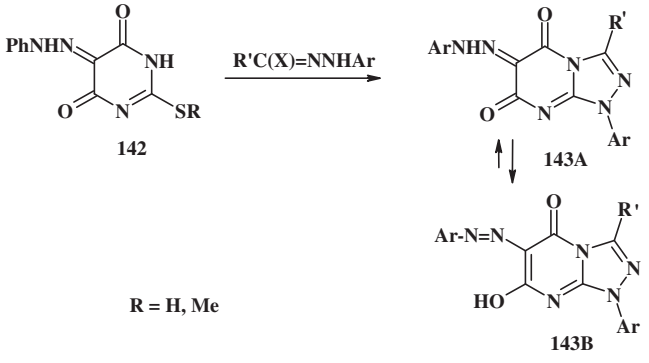
Scheme 44



Scheme 45

can have either structure **139** or **141** (Scheme 45), the isolated products were assigned structure **141**. Such structural assignment was based on ^{13}C NMR and IR spectral data. For example, the ^{13}C NMR spectra of the products **141** revealed their carbonyl carbon resonance at δ 161.7–162.8 and their IR spectra showed the CO bands at 1680–1700 cm^{-1} [63]. These values, while they are similar to those reported for the "ring-acylated" [1,2,4]triazolo[4,3-*a*]pyrimidin-5-one derivatives (δ **161**–**164** and ν_{CO} 1690 cm^{-1}), are different from those reported for the isomeric "acylimino" [1,2,4]triazolo[4,3-*a*]pyrimidin-7-one analogues (δ **170**–**175** and 1660 cm^{-1}) [64–66].

3-Chloroformazans **1O** were also reported by Shawali et al. [63] to react similarly with 2-methylthiouracils **136** (R′ = Me)



Scheme 46

and afforded the same products **141**. This finding was considered by the authors [63] to indicate that route (a) in (Scheme 45) is the most possible mechanism for the reactions of **1O** with both 2-thiouracil **136** and its 2-methylthio derivative.

Reaction of 5-phenylhydrazono-2-thioxopyrimidin-4,6(1H,3H)-dione or its methylthio analog **142** with various hydrazonoyl halides was reported to give the respective 6-phenylazo derivatives of 1H-[1,2,4]triazolo[4,3-*a*]pyrimidin-5(4H)-one that were assigned the tautomeric structure **143A** (Scheme 46) [67].

[1,2,4]Triazolo[1,5-a]pyrimidines

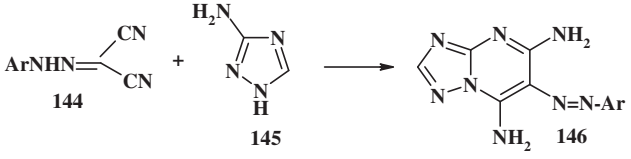
Reaction of arylhydrazonomalononitrile **144** with 3-amino-1,2,4-triazole **145** afforded the respective 6-arylazo derivatives of 1,2,4-triazolo[1,5-*a*]pyrimidine 146 (Scheme 47) [59,60].

Recently, it was reported that condensation of 3-amino-1,2,4-triazole **145** with each of arylhydrazonals 97 yielded the respective 6-arylazo derivatives of [1,2,4]triazolo[1,5-*a*]pyrimidines 148 and **149,** respectively, (Scheme 48) [49].

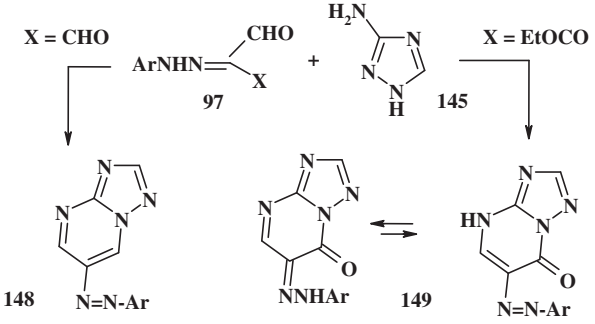
Similarly, reaction of 3-amino[1,2,4]triazole **145** with 2-arylhydrazono-3-oxo-butanoate **97′** in absolute ethanol afforded also the respective arylazo derivative of 1,2,4-triazolo[1,5-*a*]pyrimidines **146′** [50] (Scheme 48A).

Pyrazolo[3,4-c]pyridazines

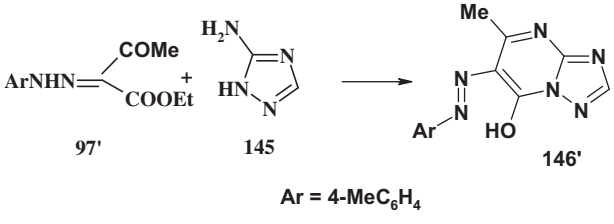
Azocoupling of diazotized 3-aminopyrazolo[3,4-*c*]pyridazine **150** with various aromatic amines and phenols afforded the respective azo derivatives **151** (Scheme 49) [68].



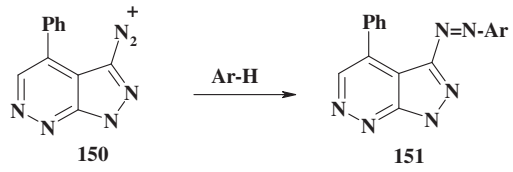
Scheme 47



Scheme 48



Scheme 48A



Ar = 4-$Me_2NC_6H_4$; 2-amino-1-naphthyl;
2-hydroxy-3-(RNHCO)-1-naphthyl
R = Ph, 2,5-$(MeO)_2$, 4-ClC_6H_4

Scheme 49

Imidazo[3,2-d]pyrimidines

Reaction of guanine **152** with diazonium salts was first reported to give **153** [69]. Later it was shown that this conclusion is erroneous and the actual structure of the products is **154** (Scheme 50) [70]. In 1991 Slouka et al. [71] prepared a series of **154** and showed that they have the arylazo tautomeric structure **154B** on the basis of their ^{13}C and ^{15}N NMR spectra.

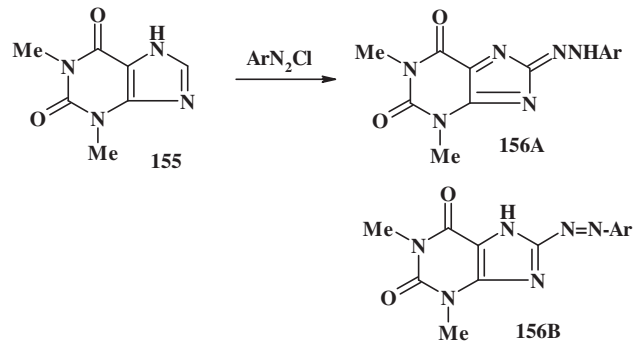
Similar reactions of aromatic diazonium salts with theophylline **155** were reported to give 8-arylazotheophylline derivatives **156** (Scheme 51) [72]. The results of electronic absorption spectra and quantum chemical calculations of such compounds revealed that they exist in the hydrazone form **156A**. Electron withdrawing substituents and polar solvents favour the azo form **156B**.

7H-Pyrazolo[4,3-b][1,4]thiazines

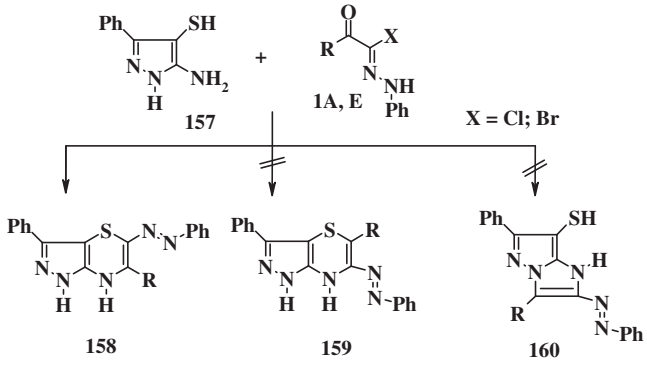
Reaction of 5-amino-4-mercapto-3-phenylpyrazole **157** with *N*-phenyl 2-oxohydrazonoyl halides **1A, E** in ethanol in the presence of triethylamine yielded 2-(phenylazo)-3-substituted-7-phenylpyrazolo[4,3-*b*]-1,4-thiazines **158** (Scheme 52) [23]. The other regioisomeric product **159**, as well as the imidazopyrazole derivative **160**, were not formed [23].

Pyrazolo[1,5-a][1,3,5]triazines

When compound **161** was coupled with diazotized 4-methoxyaniline in pyridine, it afforded the hydrazone derivative **162**. When the latter compound **162** was treated with aqueous 5% potassium hydroxide, it underwent intramolecular cyclization to furnish the respective 8-arylazo-2-phenyl-4-thioxo-3,4-dihydropyrazolo[1,5-*a*][1,3,5]triazine **163** (Scheme 53) [73].



Scheme 51



R: A, Me; E, Ph

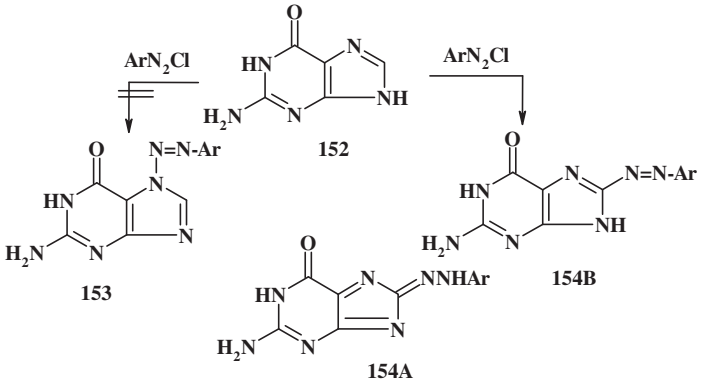
Scheme 52

Imidazo[1,2-b][1,2,4]triazines

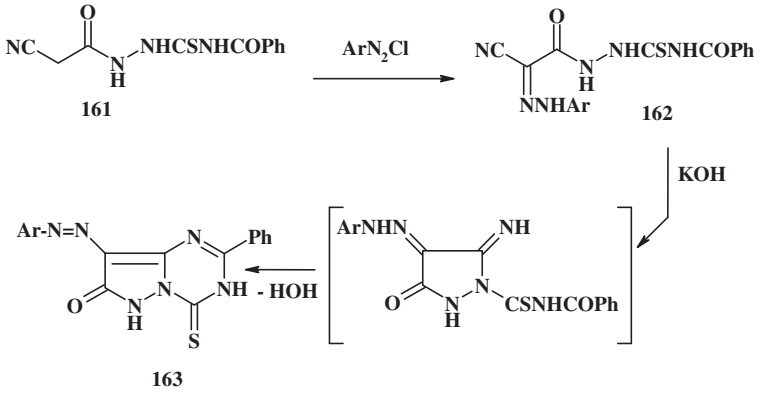
N-aryl 2-aryl-2-oxo-ethanehydrazonoyl bromides **1E** was reported to react with 3-amino-1,2,4-triazine **164** to afford 3-arylazo-imidazo[1,2-*b*][1,2,4]triazine **165** via dehydrative cyclization of the initially formed amidrazone (Scheme 54) [74].

[1,2,4]Triazolo[3,4-b][1,3,4]thiadiazines

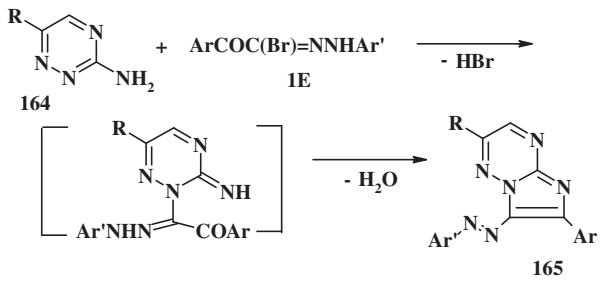
Recently, Shawali et al. [75] reported that reaction of 4-amino-3-phenyl-*1H*-1,2,4-triazole-5-thiol **166** with 2-aryl-2-oxoetha nehydrazonoyl bromides **1E** in ethanol in the presence of sodium ethoxide afforded the respective thiohydrazonates **167**.



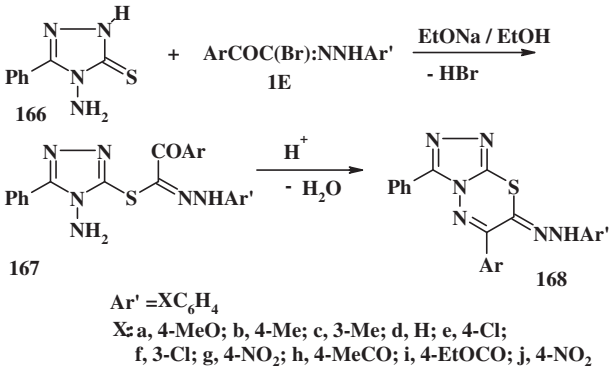
Scheme 50



Scheme 53



Scheme 54



Scheme 55

Similar reacions of the 4-amino-1,2,4-triazole-4(1H)-thione with the hydrazonoyl bromide having electron-withdrawing substituents in the *N*-aryl moiety directly afforded, however, the respective 7-arylhydrazono-3,6-diaryl[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazines **168** as end products probably via in situ dehydrative cyclization of the respective thiohydrazonates **167** [75]. The isolated thiohydrazonates **167** were converted into the respective triazolothiadiazines **168** by treatment with acetic acid (Scheme 55) [75].

Also, reaction of 1,2-*bis*(4-amino-5-mercapto-*4H*-1,2,4-triazol-3-yl)ethane **169** with two molar equivalents of each of *N*-aryl 2-oxopropanehydrazonoyl chlorides **1A** in ethanol in the presence of sodium ethoxide at room temperature gave in each case a single product proved to be the respective 1,2-*bis*(7-arylhydrazono-*7H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazin-3-yl)ethane **171** (Scheme 56). The direct formation of **171** indicates that the initially formed *bis*-thiohydrazonates **170** undergo in situ dehydrative cyclization under the employed reaction conditions to give **171** as end products (Scheme 56). The intermediacy of **170** was confirmed by their isolation and conversion into **171**. For example, reaction of **1A** (Ar = Ph), taken as a typical example of the series studied, with two molar equivalents of 1,2-*bis*(4-amino-5-mercapto-*4H*-1,2,4-triazol-3-yl)ethane in benzene in the presence of triethylamine at room temperature afforded **170** (Ar = Ph) in 92% yield. When the latter ester **170** was refluxed in acetic acid for 1 h, it yielded the respective 1,2-*bis*(7-phenylhydrazono-7H-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazin-3-yl)-ethane **171** (Ar = Ph) in 90% yield (Scheme 56) [76].

Reaction of the *bis*-triazolethione with one mole equivalent of *N*-(p-chlorophenyl) 2-oxopropanehydrazonoyl chloride **1A** (Ar = 4-ClC_6H_4) in ethanol in the presence of sodium ethoxide yielded one product which was identified as **172** (Scheme 56). This product was used as precursor for synthesis of a series of 1-(7-(4-chlorophenylhydrazono)-*7H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazin-3-yl)-2-(7-arylhydrazono-*7H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazin-3-yl)ethanes **171**. Thus, treatment of **172** with *N*-aryl 2-oxopropanehydrazonoyl chlorides **1A** in ethanol in the presence of sodium ethoxide gave after workup the corresponding **171** in an overall good yield (72–92%) (Scheme 56) [76].

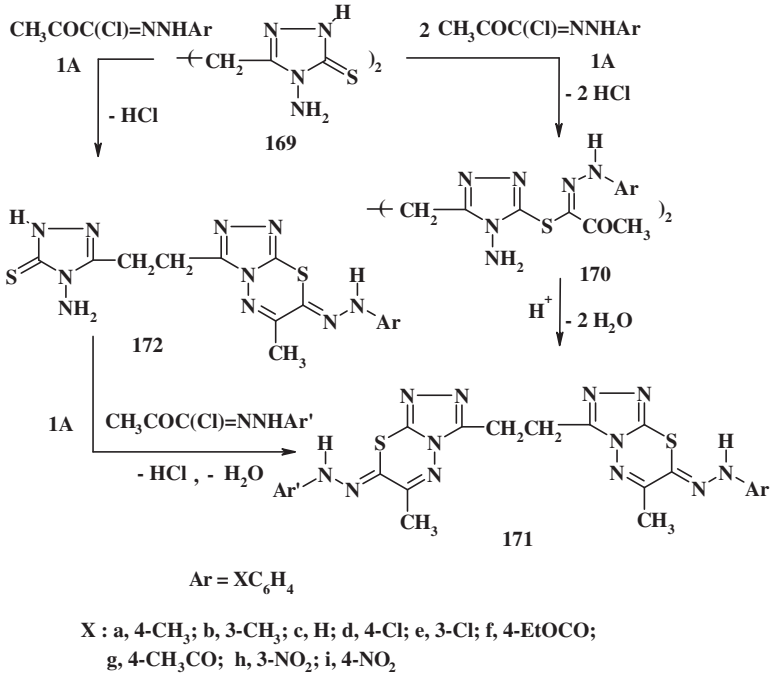
Arylazo derivatives of 6,6-biheterocycles

Quinolines

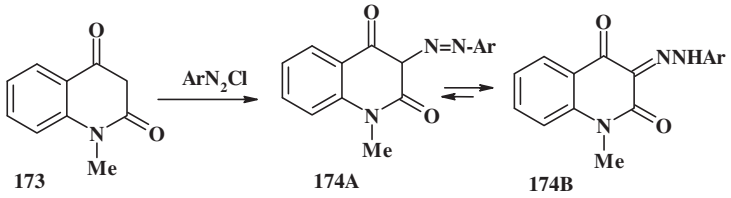
A series of 3-arylazo-1-methylquinolines **174** was prepared by reaction of the respective diazotized anilines with 1-methylquinoline derivative **173** in ethanol in the presence of sodium acetate (Scheme 57) [77,78]. The IR spectra indicate that such dyes exist predominantly in the ketohydrazone form **174B**.

Isoquinolines

A series of 4-arylazo-1-ethylthio-3(*4H*)-isoquinolinones **176** was prepared by reaction of the respective diazotized anilines with 1-ethylthio-3(*4H*)-isoquinolinone **175** in ethanol in the presence of sodium acetate (Scheme 58) [79]. The IR spectra and the polarographic reduction data indicate that such dyes in aqueous solution and in solid state exist predominantly in the azo form **176C**.



Scheme 56



Scheme 57

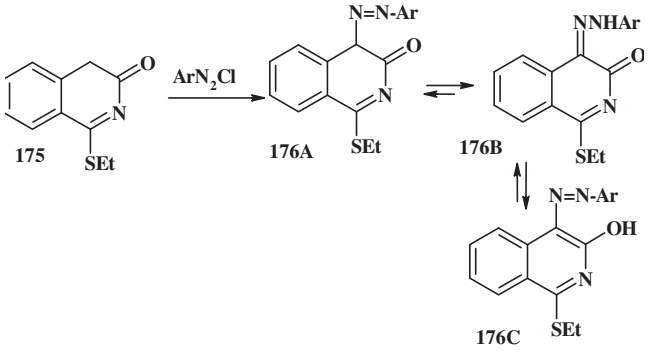
Coumarins

Shawali et al. [28] studied the ^{1}H NMR, IR and UV spectra of the diazonium coupling products of 4-hydroxycoumarin **177**. The results of such study indicated that such dyes exist in the keto hydrazone form **178B** both in solid and solution states (Scheme 59).

Quinoxalines

Reactions of o-phenylenediamine **179** with the various hydrazonoyl chlorides **1A, E, F**, **P** were reported to yield the respective 2-arylazo-1,2-dihydroquinoxaline derivatives **180** (Scheme 60) [14,80–82]. The salts of the latter products are deep coloured substances similar to compounds described as dyes [80], and the free bases of **180** were reported to be unstable in contact with air oxygen and to easily undergo oxidation to the red quinoxaline derivatives **181** [80]. Reduction of the formed azo derivative **181** with sodium dithionite afforded the aminoquinoxaline derivative **182** (Scheme 60) [80].

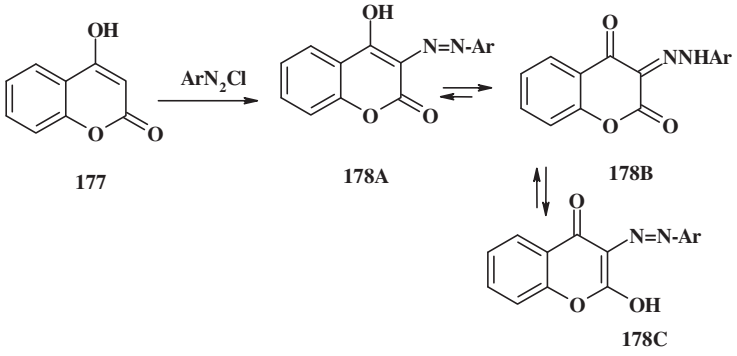
Reaction of o-phenylenediamine **179** with ethyl *N*-(arylhydrazono)chloroacetates **1B** was reported by several authors to yield 3-arylhydrazono-1,2,3,4-tetrahydroquinoxalin-2-ones **184** [81–83] (Scheme 60). Such products were said to exist as a mixture of two tautomeric forms as their ^{1}H NMR spectra revealed the presence of six protons that exchange with deuterium oxide [81].



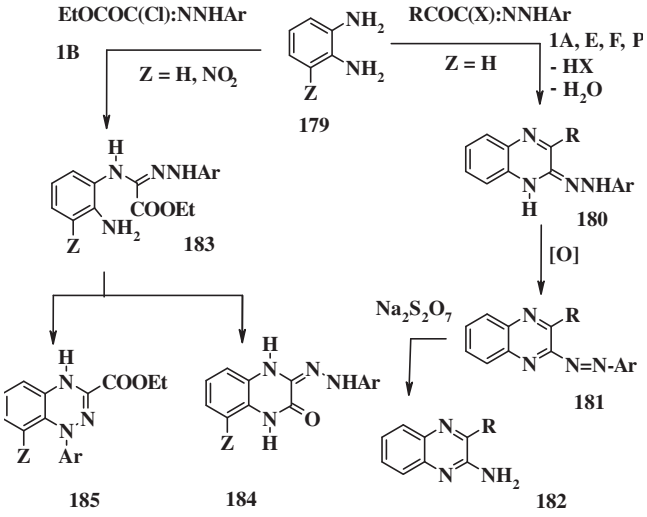
Scheme 58

In contrast to the foregoing established findings, it was reported that reactions of *o*-phenylenediamine **179** with ethyl *N*-(arylhydrazono)chloroacetate **1B** afforded ethyl 1-aryl-*4H*-benzo[*c*][1,2,4]triazine-3-carboxylate **185** via elimination of the aromatic amino group as ammonia from the initially formed amidrazone intermediate **183** (Scheme 60) [20]. This unexpected result needs further investigation.

1-Alkylbenzimidazole **186** reacted with hydrazonoyl chlorides **1B** and gave the corresponding salts **187**. The latter

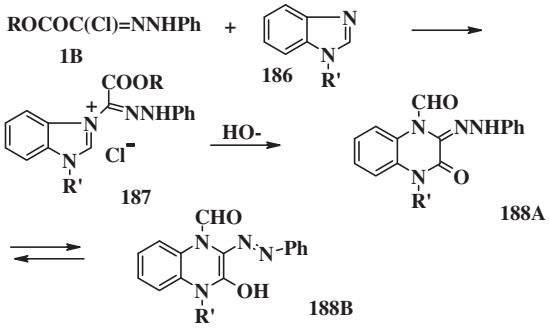


Scheme 59



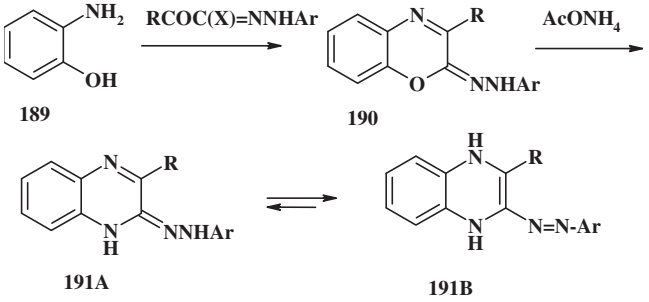
R : A, Me; E, XC_6H_4; F, benzofuran-2-yl; P, $MeOCO(CH_2)_3$-

Scheme 60



Scheme 61

yielded the 3,4-dihydroquinoxalin-2-one derivatives **188** when treated with aqueous sodium hydroxide in ethanol (Scheme 61) [19]. HOMO calculations of the bonding energies of the two possible tautomeric forms indicated that the ketohydrazone structure **188A** is more stable than the azo form **188B** [83].



Scheme 62

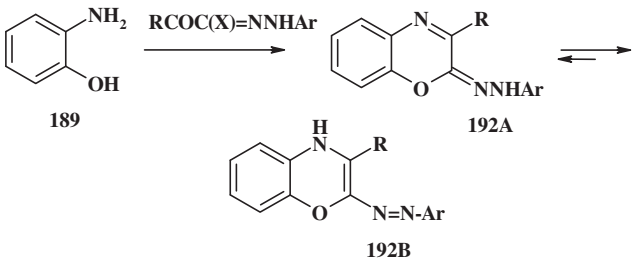
Treatment of 2-arylhydrazonobenzo-1,4-oxazines **190** with ammonium acetate was reported to give the respective 2-arylazoquinoxaline derivatives **191** (Scheme 62) [84,85].

4H-1,4-Benzoxazines

o-Aminophenol **189** was reported to react with the hydrazonoyl halides in ethanol in the presence of sodium ethoxide to yield the respective 2-arylhydrazonobenzo-1,4-oxazine **192A** or their 2-arylazo-tautomers **192B** (Scheme 63) [14,23,43,83,84].

In contrast to the foregoing literature reports, it was indicated that reaction of 2-aminophenol **189** with ethyl *N*-(arylhydrazono) chloroacetate **1B** afforded 2-substituted 1,3,4-oxadiazines **193** (Scheme 64) [20]. This reaction requires further confirmation.

Reaction of 2-aminophenol **189** with the 2-oxohydrazonoyl bromide **1R** was reported to afford the tricyclic compound **194**



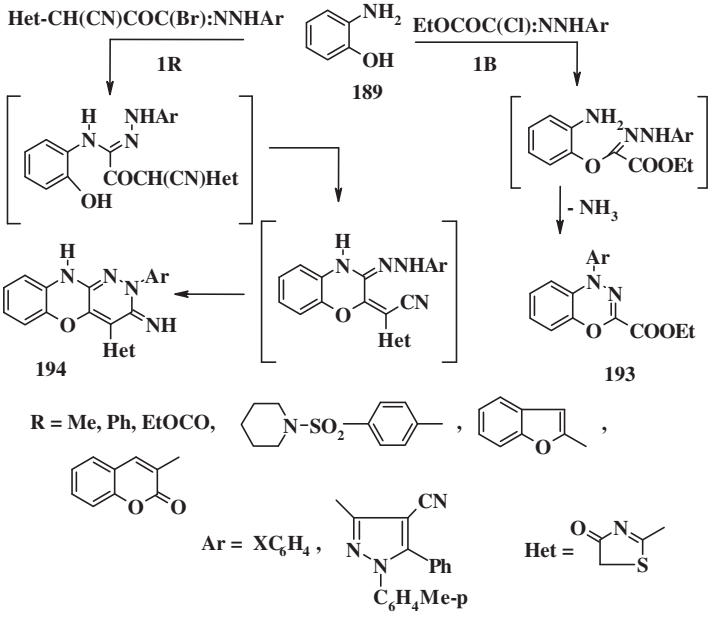
Scheme 63

as the sole end product and no arylazo-1,4-oxazine was produced (Scheme 64) [20].

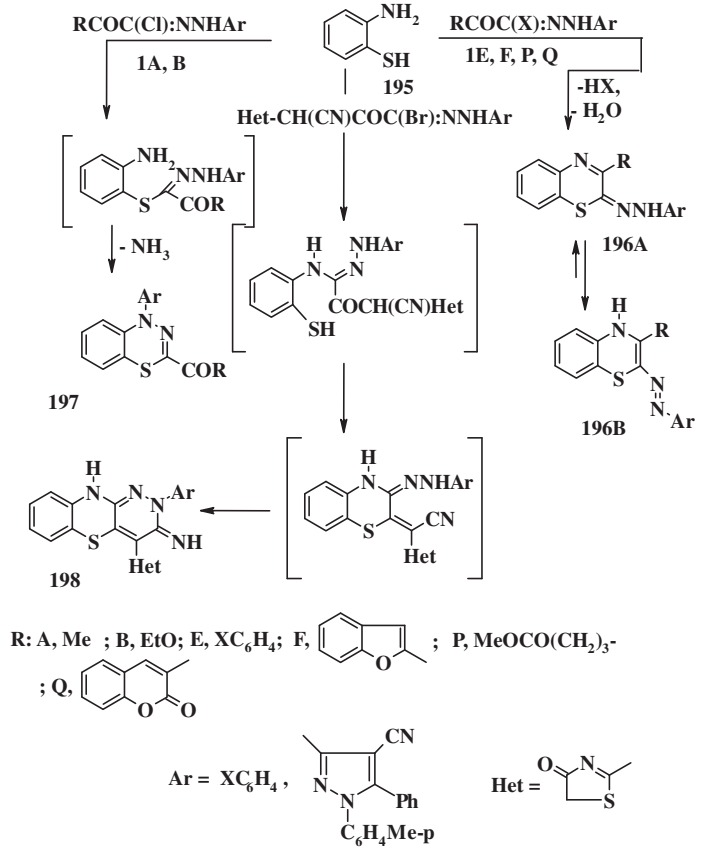
4H-1,4-Benzothiazines

Reactions of *o*-aminothiophenol **195** with the hydrazonoyl halides were studied by several groups of authors in ethanol in the presence of base catalyst and in all cases they were reported to give the respective 2-arylazo-1,4-benzothiazine **196** (Scheme 65) [14,29,43,80,83,85–89].

In contrast to the foregoing results, it was indicated that reactions of 2-aminothiophenol **195** with *N*-aryl 2-oxopropane hydrazonoyl chloride **1A** and ethyl *N*-(arylhydrazono)chloro-



Scheme 64



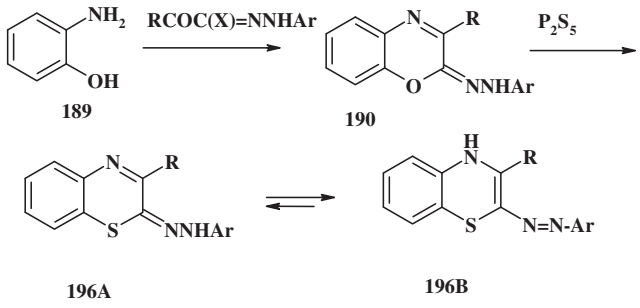
Scheme 65

acetate **1B** afforded the respective 2-substituted 1,3,4-thiadiazines **197** (Scheme 65) [20,21]. Such reactions need further reinvestigation to confirm such ambiguous results.

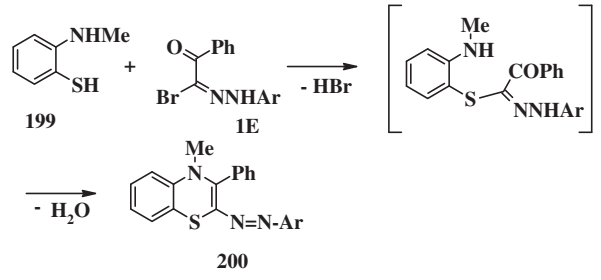
In another report, it was indicated that reaction of 2-aminothiophenol **195** with the hydrazonoyl bromide **1A, B** afforded no arylazobenzothiazine; instead it yielded the tricyclic compound **198** as the sole product (Scheme 65) [90].

Treatment of 2-arylazobenzo-1,4-oxazines **190** with phosphorus pentasulfide was reported to give the respective 2-arylazo-1,4-benzothiazine derivatives **196** (Scheme 66) [84,85].

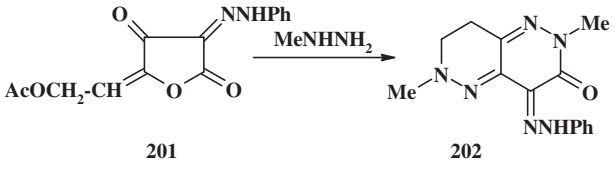
2-Methylaminothiophenol **199** reacted similarly with *N*-aryl 2-oxo-2-phenylethanehydrazonoyl bromides **1E** and gave the corresponding 2-arylazo-3-phenyl-4-methylbenzothiazines **200** (Scheme 67) [86].



Scheme 66



Scheme 67



Scheme 68

Pyridazino[4,3-c]pyridazines

Treatment of **201** with methylhydrazine was reported to give 2,6-dimethyl-3-oxo-2,3,4,6,7,8-hexahydropyridazino[4,3-*c*]pyridazine-4-arylhydrazone **202**. The structure of the latter was based on its IR and ^{1}HNMR spectra together with X-ray analysis (Scheme 68) [91].

Arylazo derivatives of 5,5,6-triheterocycles

Indeno[2,1-b]thiophenes

Recently three series of 2-(4-substituted-phenylazo)-3-cyano-8-substituted-indeno[2,1-*b*]thiophenes **204** were prepared by coupling diazotized 2-amino-3-cyano-8-substituted-indeno[2,1-*b*]thiophene **203** with dialkylaminobenzene (Scheme 69) [92].

Pyrrolo[2,1-b]benzothiazoles

2-Cyanomethylbenzothiazole **205** was reported to react with the *bis*-hydrazonoyl chlorides **1S** in ethanol in the presence of sodium ethoxide to give the respective *bis*-hydrazone derivative **206**. Oxidation of the latter with lead tetraacetate (LTA) afforded 1,2-*bis*-(arylazo)-3-cyanopyrrolo[2,1-*b*]benzothiazoles **207** (Scheme 70) [93].

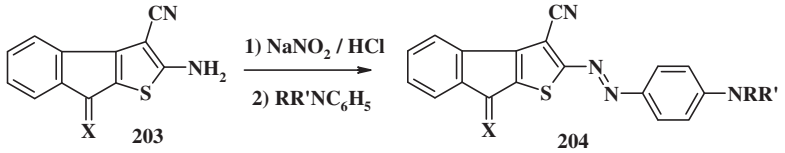
Imidazo[1,2-a]benzimidazoles

When the hydrazonoyl bromide **1G** was refluxed with 2-aminobenzimidazole **208** in ethanol, it furnished 3-arylazo-2-(benzothiazol-2-yl)-1H-imidazo[1,2-*a*]benzimidazoles **209** (Scheme 71) [15].

Imidazo[2,1-b]benzothiazoles

Reactions of 2-aminobenzothiazole **210** with *N*-aryl 2-oxopropanehydrazonoyl chloride **1A** and *N*-aryl 2-oxo-2-phenylethanehydrazonoyl bromides **1E** were reported to give the respective 3-arylazoimidazo[1,2-*a*]benzothiazoles **211** (Scheme 72) [31]. In another report, it was indicated, however, that reaction of the hydrazonoyl chloride **1A** with 2-aminobenzothiazole yielded the unexpected amidrazone derivative **214** which was not cyclized. No rationalization, however, was given [22].

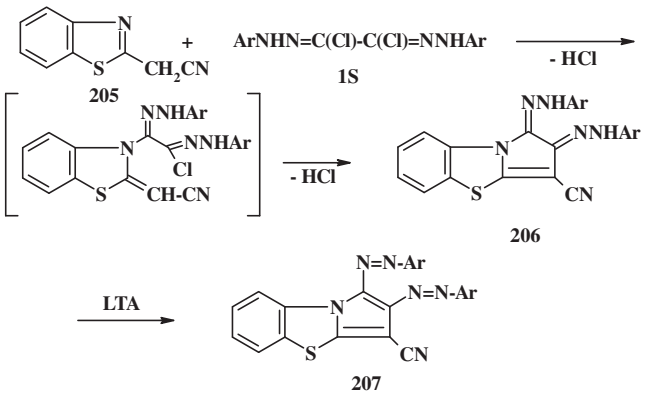
When *N*-phenyl 2-oxo-2-(pyrazol-3-yl)ethanehydrazonoyl bromide **1H** was used in reaction with 2-aminobenzothiazole **210**, it was claimed that it gave rise to the formation of 2-phenylazoimidazo[1,2-*a*]benzothiazoles **213** (Scheme 72) [29].



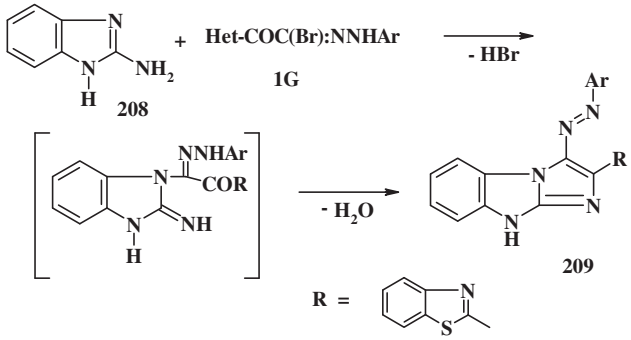
X = O, $(CN)_2C$

R/R' = Me / Me, Et / Et, Et / $HOCH_2CH_2$, $HOCH_2CH_2$ / $HOCH_2CH_2$

Scheme 69



Scheme 70



Scheme 71

No rationalization was given to account for this different regiochemical result.

Similar reaction of 2-aminobenzothiazole **210** with ethyl *N*-(arylhydrazono)chloroacetate **1B** afforded **212** via cyclization of the initially formed respective amidrazone (Scheme 72) [31].

Thiazolo[3,2-a]benzimidazoles

2-Mecrapto-1H-benzimidazole **215** was reported to react with ethyl (*N*-arylhydrazono)chloroacetate **1B** and 2-phenylamino-2-oxoethanehydrazonoyl chloride **1C** in the presence of base catalyst and yielded the corresponding thiohydrazonate esters **216** (Scheme 73) [23]. Acid treatment of the latter products resulted in their cyclization to give 2-arylhydrazono-thiazolo[3,2-*a*]benzimidazol-3-one **217** (Scheme 73) [23].

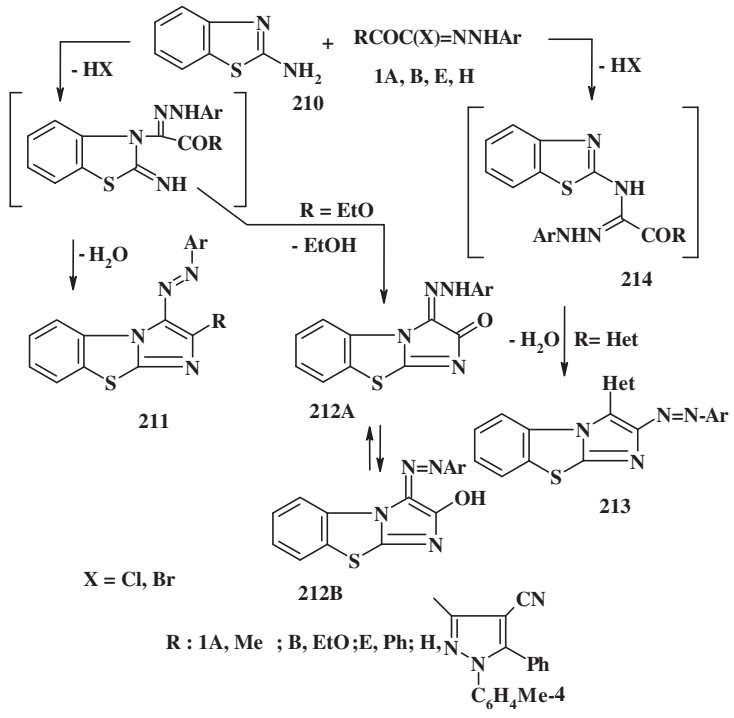
Similar reaction of 2-oxopropanehydrazonoyl chloride **1A** [23] and 2-oxo-2-(hetaryl)ethanehydrazonoyl bromide **1T** [23,29,89,94] each with **215** afforded the respective thiohydrazonate esters **216** that cyclized upon heating to give the corresponding arylazo thiazolobenzimidazoles **218** (Scheme 73).

1H-Imidazo[1,2-c]pyrazolo[4,3-e]pyrimidines

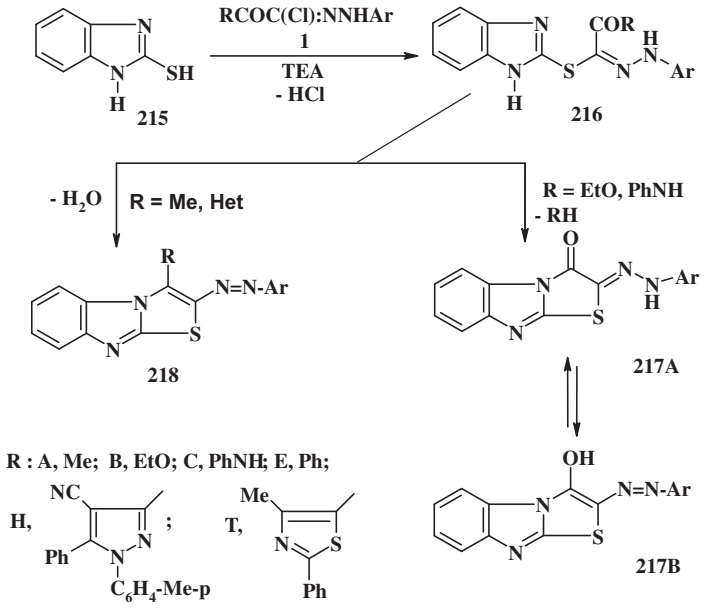
4-Aminopyrazolo[3,4-*d*]pyrimidine **219** was reported by Shawali et al. [95,96] to react readily with 2-oxoalkanehydrazonoyl halides **1A** and **1U** to give the respective 3-arylazo-*1H*-imidazo[1′,2′-*c*]pyrazolo[4,3-*e*]pyrimidines **220** (Scheme 74). When ethyl *N*-(arylhydrazono)chloroacetates **1B** was employed in lieu of **1A** or **1U**, the reaction gave **221** (Scheme 74).

1H-Dipyrazolo[1,5-a:4',3'-e]pyrimidines

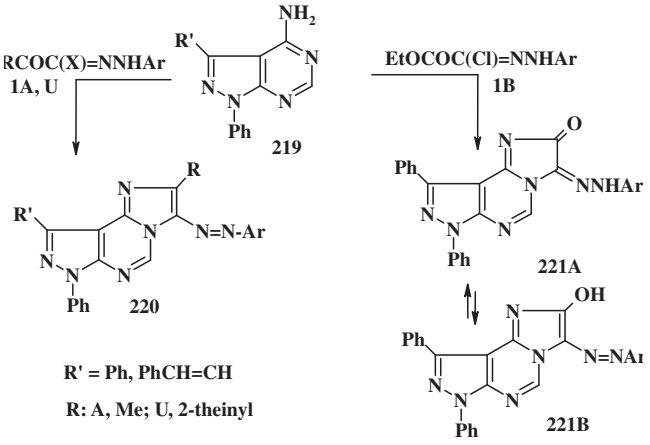
When compounds **222** were treated with hydrazine hydrate, the initially formed hydrazino derivatives **223** underwent in situ cyclization to give the respective *1H*-Dipyrazolo[1,5-



Scheme 72



Scheme 73



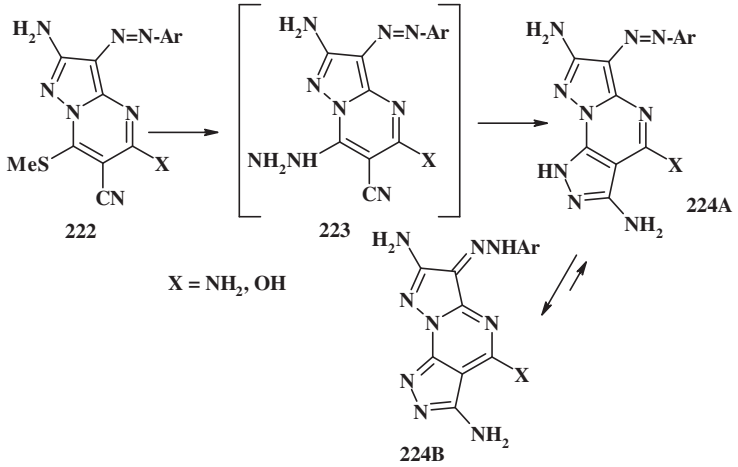
Scheme 74

a:4′,3′-*e*]pyrimidine derivatives **224**. Although two possible tautomeic structures can be written for such products, their ^{1}H NMR data were consistent with the hydrazone structure **224B** (Scheme 75) [57].

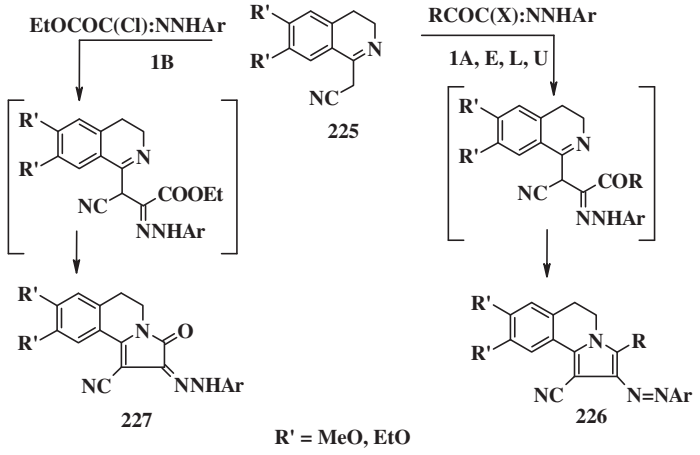
Arylazo derivatives of 5,6,6-triheterocycles

Pyrrolo[2,1-a]isoquinolines

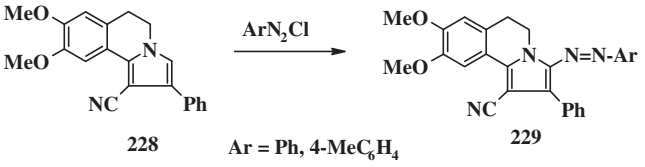
Recently, reactions of 2-(6,7-diethoxy-3,4-dihydroisoquinolin-1-yl)acetonitrile **225** with each of the 2-oxohydrazonoyl halides **1A**, **E**, **L**, **U** have been examined in tetrahydrofuran in the presence of triethylamine and found to result in the formation of the respective 2-(arylazo)pyrrolo[2,1-*a*]isoquinoline derivatives **226** (Scheme 76) [97]. Similar reaction of the same acetonitrile derivative with ethyl *N*-(arylhydrazono)chloroacetate **1B** affor-



Scheme 75



Scheme 76



Scheme 77

ded 2-(arylhydrazono)pyrrolo[2,1-*a*]isoquinolin-1-carbonitrile **227** (Scheme 76) [97,98].

Recently it was reported that 3-(arylazo)pyrrolo[2,1-*a*]isoquinoline derivatives **229** can also be prepared by coupling 2-phenyl-pyrrolo[2,1-*a*]isoquinoline-1-carbonitrile **228** with the appropriate diazonium salts (Scheme 77) [99].

Pyrido[1,2-a]benzimidazoles

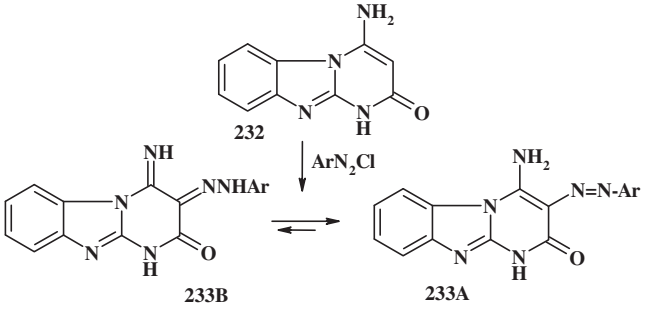
Reaction of arylhydrazonomalononitrile **126** with 2-cyanomethylbenzimidazole **230** was reported to give the respective 1,3-diamino-2-arylazo-4-cyano-pyrido[1,2-*a*]benzimidazoles **231** (Scheme 78) [62].

Pyrimido[1,2-a]benzimidazoles

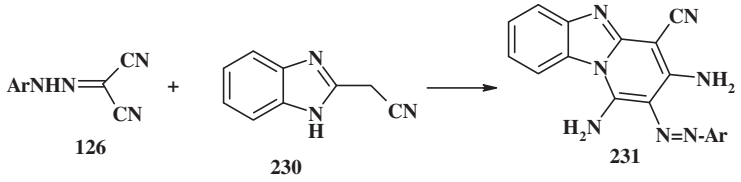
A series of 4-amino-3-arylazo-*1H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-ones **233A** was prepared by coupling of the respective diazotized anilines with 4-amino-*1H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one **232** (Scheme 79) [100]. Their ^{1}H NMR in DMSO-d_6 indicated that such azo derivatives exist as a mixture of the azo and hydrazone tautomeric forms as such spectra showed two signals in the regions δ 10.2–10.1 (N1–H), 11.94–10.76 (NH_2) and 10.2–8.81 (imine NH and hydrazone NH). In solid state such compounds were reported to exist only in the azo tautomeric form **233A** (Scheme 79) because their IR spectra showed bands at ν 3434–3420 and 3395–3371 cm^{-1}. A study of the effect of substituent on their electronic spectra revealed that some of these dyes exist in a single tautomeric form and some others as an equilibrium mixture of the azo and hydrazone forms, according to the nature of the substituent [100].

Reaction of arylhydrazonomalononitrile **126** with 2-aminobenzimidazole **208** yielded 1,3-diamino-2-arylazo-pyrimido[1,2-*a*]benzimidazoles **234** (Scheme 80) [59].

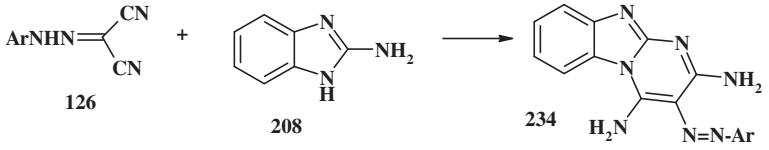
Similarly, condensation of 2-aminobenzimidazole **208** with each of ethyl 2-arylhydrazono-3-oxo-butanoate **126A** [50] and 2-arylhydrazono-3-oxopentanal **126B** [60] in refluxing ethanol afforded the respective 3-arylazo derivative of pyrimido[1,2-*a*]benzimidazole **234A** and **234B**. The isomeric structure of the latter, namely **234C**, was discarded on the



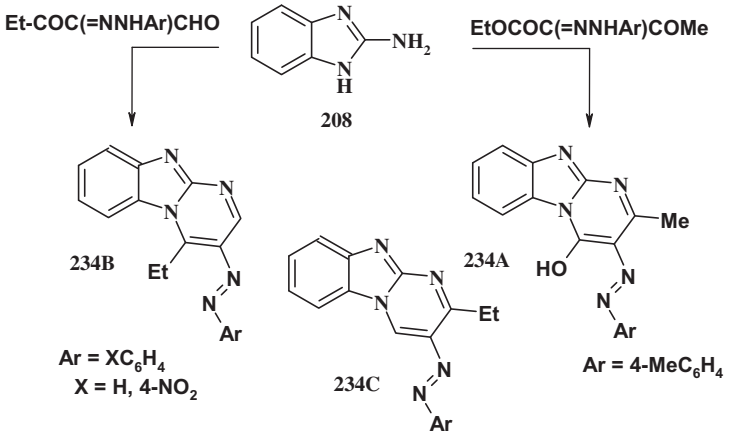
Scheme 79



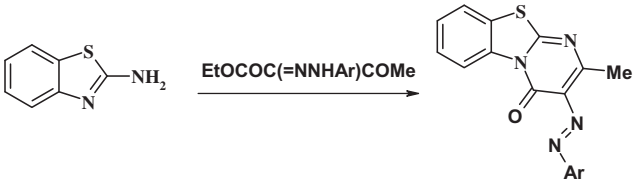
Scheme 78



Scheme 80



Scheme 80A



Scheme 80B

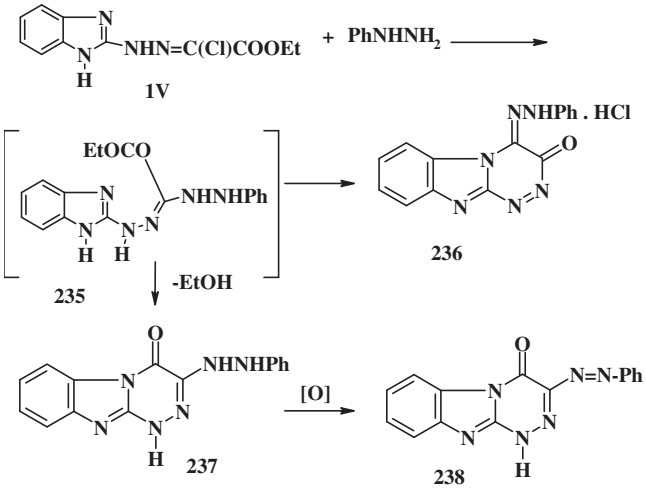
basis of NOE difference that revealed that the ethyl group and benzimidazole-H are spatially proximal (Scheme 80A) [60].

Pyrimido[2,1-a]benzothiazoles

Condensation of 2-aminobenzothiazole with ethyl 2-arylhydrazono-3-oxobutanoate was reported to give the respective 3-arylazo derivatives of pyrimido[1,2-*a*]benzimidazole (Scheme 80B) [61].

Triazino[4,3-a]benzimidazoles

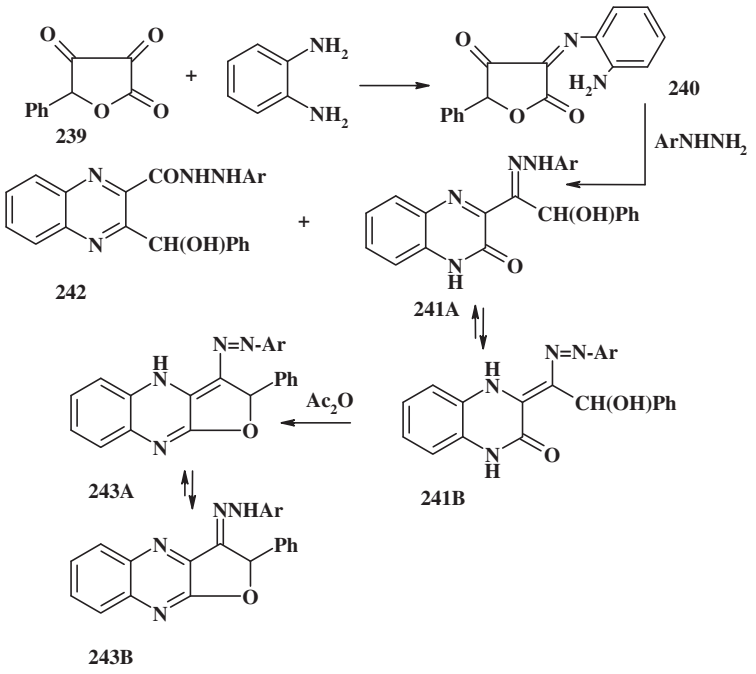
Reaction of phenylhydrazine with ethyl *N*-((benzimidazol-2-yl)hydrazono)chloroacetate **1V** was reported to give the hydrochloride salt of 4-phenylhydrazono-3-oxo-[1,2,4]triazino[4,3-*a*]benzimidazole **236** (Scheme 81) [48]. This result requires further investigation as the expected product from cyclization of the initially formed intermediate **235** is expected to have the isomeric structure **237** or its oxidation product **238** (Scheme 81).



Scheme 81

Furo[2,3-b]quinoxalines

El-Ashry et al. [101] reported that reaction of 5-phenylfuran-2,3,4-(5*H*)-trione **239** with o-phenylenediamine gave **240** (Scheme 82). Treatment of the latter with arylhydrazine gave a mixture of the azo derivative **241** and the hydrazide **242**. The ^{1}H NMR spectra of **241** in DMSO-d_6 revealed that such dyes exist as a mixture of the iminohydrazone **241A** and azo-enamine forms **241B** in a ratio of 3:2, respectively. For example, the spectra showed in each case three different NH proton signals at δ 10.47 (NNH), 10.63 (N4-H) and 11.47 (N1-H). Attempting to acetylate **241** with acetic anhydride in pyridine at room temperature or in refluxing acetic anhydride gave **243** [101]. The ^{1}H NMR spectra of the latter revealed that each of such dyes exist as an equilibrium mixture of the tautomeric forms **243A** and **243B** (Scheme 82).



Scheme 82

Pyrazolo[5,1-c]benzo[1,2,4]triazines

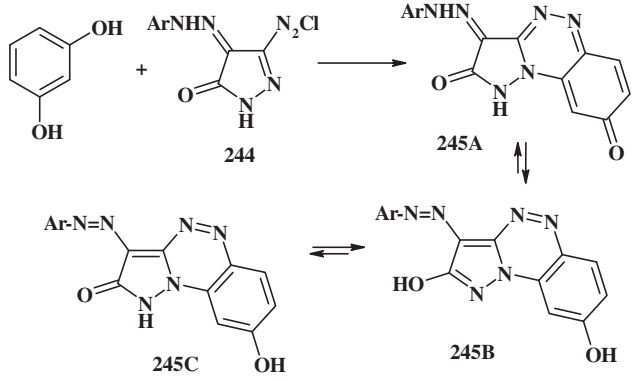
Reaction of resorcinol with diazotized 3-amino-4-phenylhydrazino-*1H*-pyrazolin-5-one **244** was reported to give **245**. The latter was assigned the indicated hydroxyazo tautomeric form **245B** although no spectral data were given to confirm this assignment (Scheme 83) [102].

Dipyrimido[1,2-b:2′,1′-e]pyrazoles

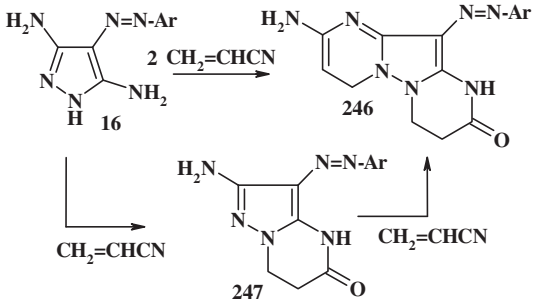
The arylazo derivatives **246** were prepared by either heating **247** with one molar equivalent of acrylonitrile or heating **16** with two molar equivalents of acrylonitrile (Scheme 84) [36].

1H-Pyrazolo[3,4-d]pyrimido[1,6-b][1,2,4]triazines

1-Phenyl-3-substituted-5-amino-4-imino-*1H*-pyrazolo[3,4-*d*]-pyrimidine **248** was reported to react with each of *N*-aryl-2-oxoalkanehydrazonoyl halides **1A, E, U** to give the respective 6-arylazo-pyrazolo[3,4-*d*]pyrimido[1,6-*b*][1,2,4]triazines **249**.



Scheme 83



Scheme 84

When ethyl *N*-(arylhydrazono)chloroacetate **1B** was used in this reaction, it gave **250** (Scheme 85) [96,103].

Arylazo derivatives of 6,6,6-triheterocycles

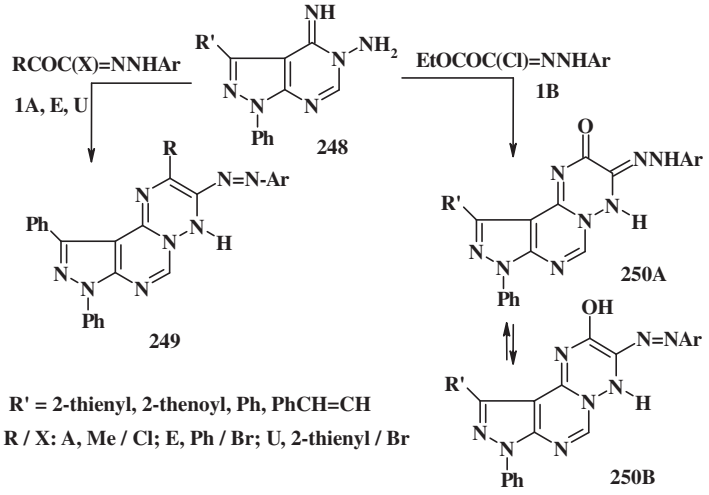
[1,2,4,5]Tetrazino[3,2-b]quinazolines

N-Aryl arylazomethanehydrazonoyl chlorides **1O** have been reported to react with 3-amino-2-thioxo-4(*1H*)quinazolinone **251a** or its methylthio derivative **251b** in refluxing ethanol in the presence of triethylamine (Scheme 86) [104]. Such reactions afforded the respective 3-arylazo-*6H*-[1,2,4,5]tetrazino[3,2-*b*]quinazolin-6-ones **252** via elimination of hydrogen sulphide and methanethiol respectively from the initially formed amidrazone intermediates (Scheme 86).

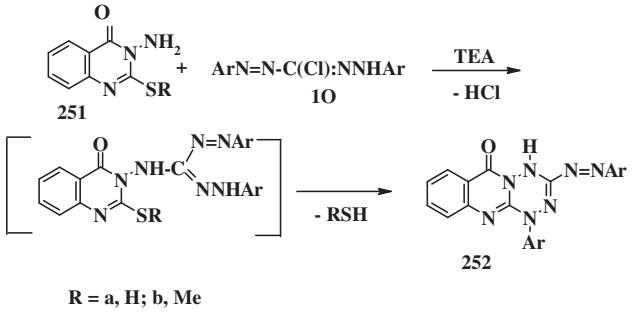
Hetarylazo- of Bi- and Tri-heterocycles

2-[(4-Pyrazolyl)azo]indazoles

Reaction of diazotized 2-aminoimidazole **253** with 3-methyl-1-phenyl-5(*4H*)-pyrazolone **254** yielded the respective azo dye



Scheme 85



Scheme 86

255. Although the latter can have three tautomeric structures **255A–C**, it was assigned the indicated ketohydrazone tautomeric structure **255A** (Scheme 87) [105].

2-[(4-Pyrazolyl)azo]benzothiazoles

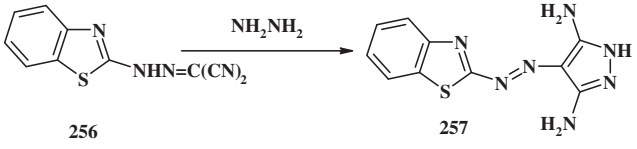
Hydrazinolysis of 2-benzothiazolylhydrazonomalononitrile **256** was reported to give the azo dye **257** (Scheme 88) [106].

Other dyes of this series **259** were prepared by coupling the respective 2-benzothiazole-diazonium salts **258** with the appropriate 5-pyrazolone derivatives **254**. Such dyes were considered to have the indicated hydrazone structure **259A** (Scheme 89) [105].

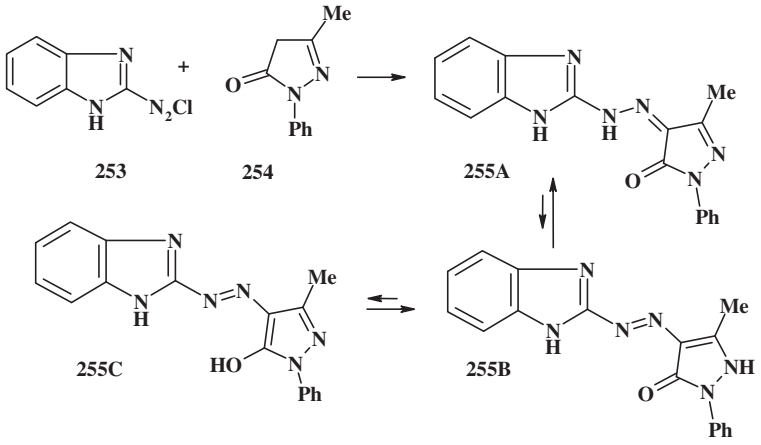
Coupling of diazotized 2-aminobenzothiazole derivative **258** with the enaminonitrile yielded the coupling product **260**. Hydrazinolysis of the latter with hydrazine or phenylhydrazine yielded the respective azo dyes **261** (Scheme 90) [107].

3-[(5-Thiazolyl)azo]pyrazolo[3,4-b]pyridines

Reaction of 2-amino-4-substituted-thiazole **263** with 4,6-dimethylpyrazolo[3,4-*b*]pyridine-3-diazonium nitrate **262** afforded the respective azo dye **264**. The latter products were assigned the azo tautomeric structure although four possible tautomeric structures can be written for each of such dyes (Scheme 91) [108].



Scheme 88



Scheme 87

3-[(3-Isoxazolyl)azo]pyrazolo[5,1-c][1,2,4]triazines

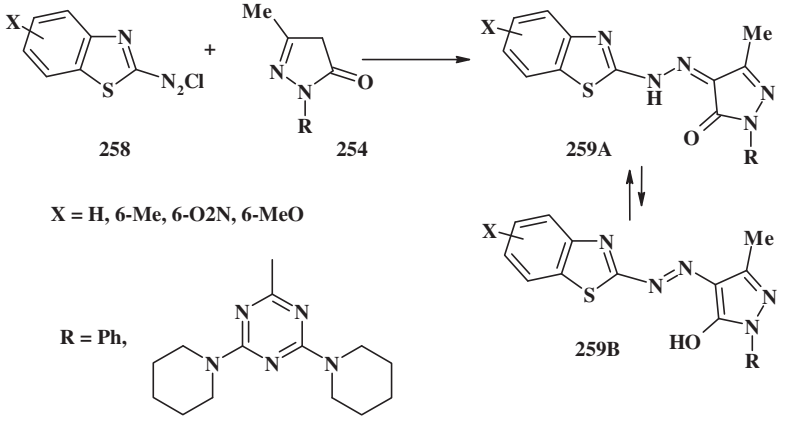
Diazotization of 5-amino-3-methyl-pyrazole derivative **265** and coupling the resulting diazonium salt with each of malononitrile and ethyl cyanoacetate yielded the respective coupling products that cyclized in situ to give 4-amino-7-methyl-8-(3-isoxazolylazo)pyrazolo[5,1-*c*][1,2,4]-triazines **266**. FT-IR spectra of such dyes revealed also that they exist predominantly in the indicated azo-enamine tautomeric form **266** (Scheme 92) [109].

3-[(2-Thiazolyl)azo]pyrazolo[5,1-c][1,2,4]triazines

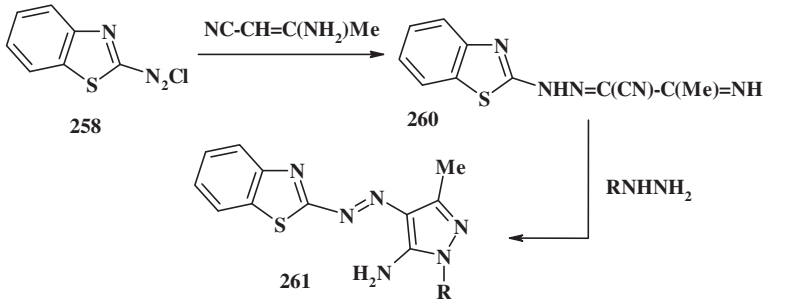
Diazotization of 5-amino-3-methyl-4-(thiazolylazo)-*1H*-pyrazole **267** with sodium nitrite in sulfuric acid in acetic acid gave the corresponding diazonium salt. Treatment of the latter with each of malononitrile and ethyl cyanoacetate yielded the respective coupling products that cyclized in situ to give 4-amino-7-methyl-3-substituted-8-(2-thiazolylazo)pyrazolo[5,1-*c*][1,2,4]triazines **268**. FT-IR spectra of such dyes revealed that they exist predominantly in the indicated azo-enamine tautomeric form (Scheme 93) [109].

3-[(3-Pyrazolyl)azo]quinolines

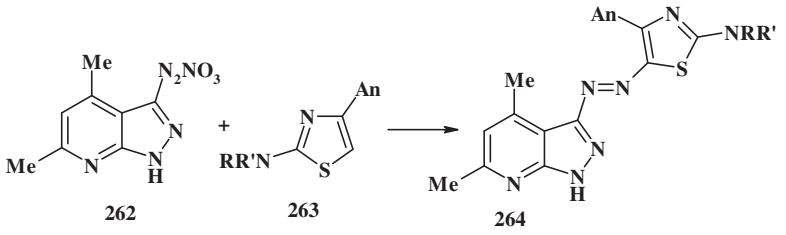
Coupling of diazotized 3-amino-pyrazole derivatives **269** with 2,4-dihydroxyquinoline **270** yielded the corresponding azo dye **271** (Scheme 94) [3]. The IR spectrum of such a dye showed no C═O bands and its ^{1}H NMR spectrum revealed NH proton signals at δ 13.98–13.85 and in addition two OH



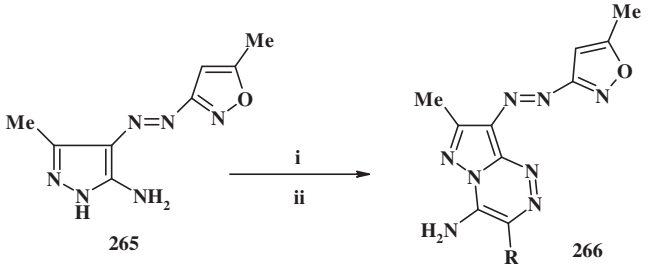
Scheme 89



Scheme 90



Scheme 91



i = $NaNO_2$ / H_2SO_4 / AcOH
ii = NC-CH_2R, R = CN, EtOCO

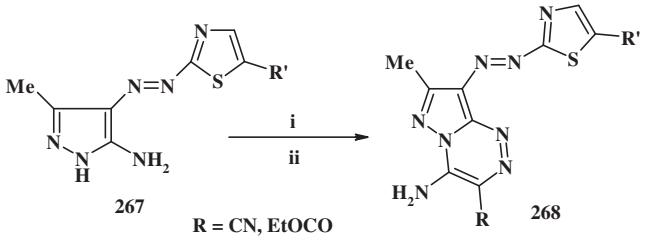
Scheme 92

signals at δ 10.41 and 19.97. On the basis of these data such dyes were assigned the indicated azo-hydroxy tautomeric structure [3].

3-[(3-Isoxazolyl)azo]quinolines

The title azo dye **273** was prepared by coupling 2,4-dihydroxyquinoline **270** with diazotized 3-amino-5-methylisoxazole **272** (Scheme 95). This dye was proved on the basis of its IR (no tCO) and ^{1}H NMR (δ 10.84, OH) and was assigned the indicated azo-hydroxy tautomeric form **273** [3].

Also, diazotized 3-amino-5-methyl-isoxazole **272** was coupled with 8-hydroxyquinoline **274** and gave the respective azo dye **275** (Scheme 96) [110].

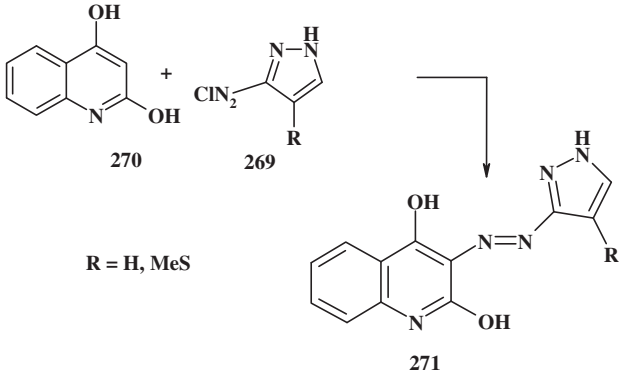


R = CN, EtOCO

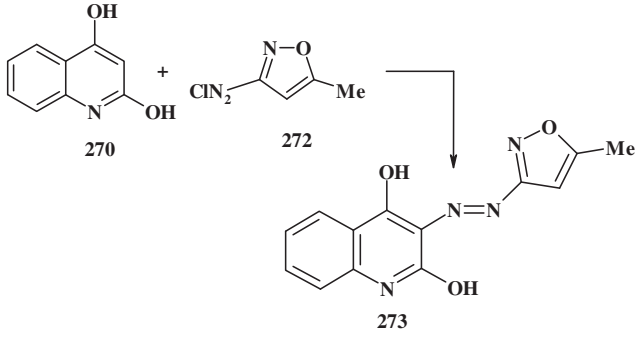
i = $NaNO_2$ / H_2SO_4 / AcOH
ii = NC-CH_2R

R' = H, Me

Scheme 93



Scheme 94



Scheme 95

3-[(5-Methyl-isoxazol-3-yl)azo]coumarins

3-[(5-Methyl-isoxazol-3-yl)azo]coumarin **277** was prepared by coupling 4-hydroxy-coumarin **276** with diazotized 3-amino-5-methylisoxazole **272** (Scheme 97). This dye, on the basis of its IR (tCO 1740 cm^{-1}) and ^{1}H NMR (δ 14.7) spectral data, was assigned the keto-hydrazone form **277B** [111].

3-[(5-Thiazolyl)azo]quinolines

The 3-(2-methyl-5-thiazolylazo)quinoline-2,4-dione dye **278** was prepared by coupling diazotized 2-amino-5-methylthiazole derivative with 4-hydroxy-2(*1H*)quinolinone **270** (Scheme 98). In solution, this dye **278** may exist in four possible tautomeric structures. However, its FT-IR spectra showed no carbonyl band and its ^{1}H NMR spectrum in DMSO-d_6 did not show NH signal. These findings were considered as evidence that it has the indicated azo-hydroxy form in solid state and in solution [3].

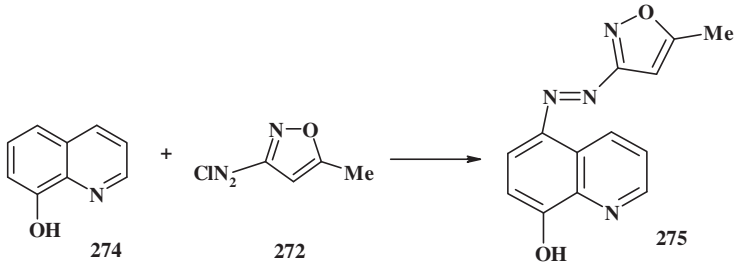
3-[(5-Thiazolyl)azo]coumarins

The 3-(2-thiazolylazo)coumarin dyes **279** were prepared by coupling diazotized 2-aminothiazole derivatives in nitrosyl sulfuric acid with coumarin derivative **276** (Scheme 99) [111]. Although four possible tautomeric structures can be written for such dyes, they were assigned the azo-hydroxy forms **279A** and **279B** according to the nature of the substituent R. For example, the ^{1}H NMR spectra revealed that dye **279** (R = H) exists in one tautomeric form whereas dye **279** (R = Me) exists as a mixture of two tautomers [111].

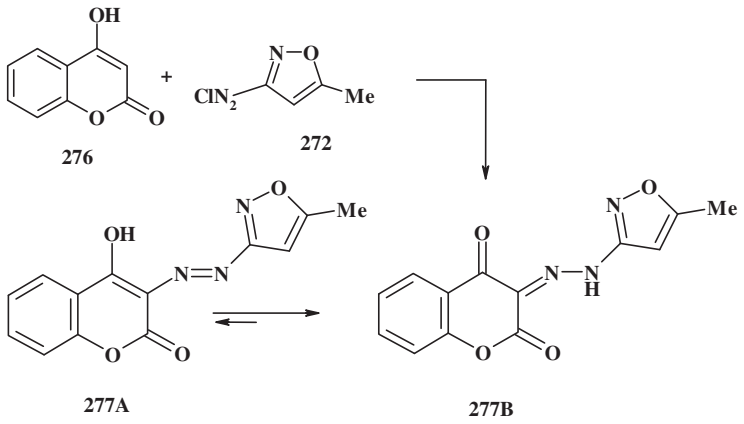
3-[(1,2,4-Triazol-3-yl)azo]quinolines

Similar coupling of diazotized 3-amino-1,2,4-triazole derivatives **280** with quinoline derivative **270** afforded the respective coupling products **281** (Scheme 100) [111]. On the basis of their ^{1}H NMR spectral data such dyes were assigned the two azo-hydroxy tautomeric forms **281A** and **281B** according to the substituent present. For example, compound **281a** (R = H) exists in one tautomeric form, namely **281A**, whereas, compound **281b** (R = MeS) exists as a mixture of azo-hydroxy and keto hydrazone forms **281A** and **281B**, respectively [111].

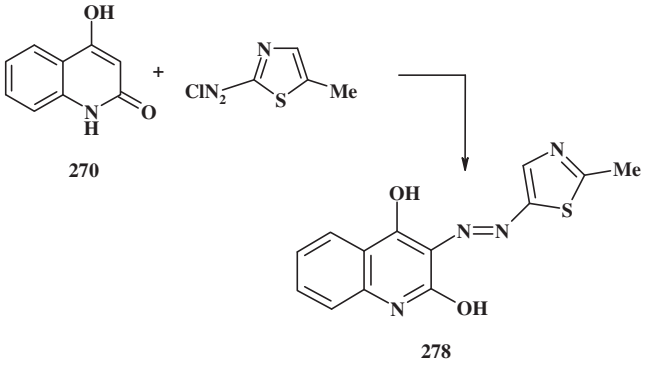
Recently a series of 8-hydroxy-5-[(1,2,4-triazol-3-yl)azo] quinolines **282** were prepared by the coupling of diazotized



Scheme 96



Scheme 97

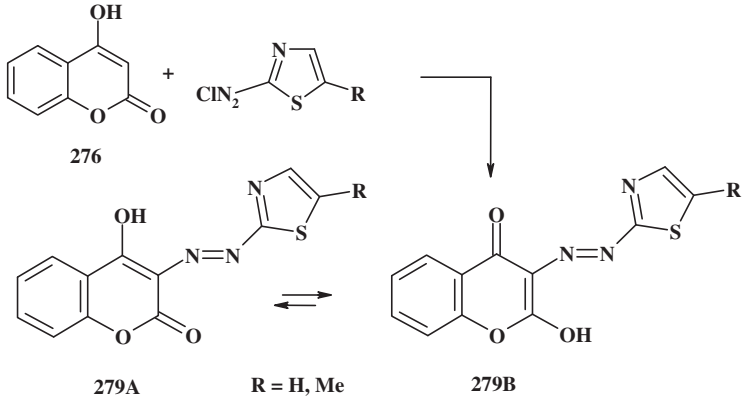


Scheme 98

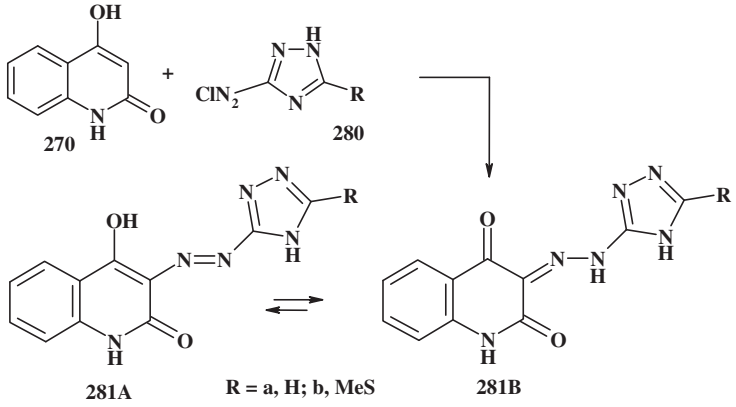
3-amino-1,3,4-triazoles **280** with 8-hydroxyquinoline **274** (Scheme 101) [110].

3-[(1,2,4-Triazol-3-yl)azo]coumarins

Coupling of diazotized 3-amino-1,2,4-triazole derivatives **280** with 4-hydroxy-coumarin **276** afforded the respective coupling products **283** [111] (Scheme 102). On the basis of their ^{1}H NMR spectral data such dyes were reported to have one of the two tautomeric forms **283A** and **283B** according to the substituent present. For example, compound **283a** (R = H) exists in one tautomeric form, namely **283A**, whereas compound **283b** (R = MeS) exists as a mixture of



Scheme 99



Scheme 100

azo-hydroxy and keto hydrazone forms **283A** and **283B**, respectively [111].

3-[(1,3,4-Thiadiazol-2-yl)azo]quinolines

Coupling of diazotized 3-amino-1,3,4-thiadiazole derivative with 2,4-dihydroxyquinoline **270** afforded the respective azo dye **284** [111]. On the basis of its IR spectrum, which showed HO and C═O bands, such a dye was considered to exist as a mixture of the four tautomeric forms **284A–D** (Scheme 103) [111].

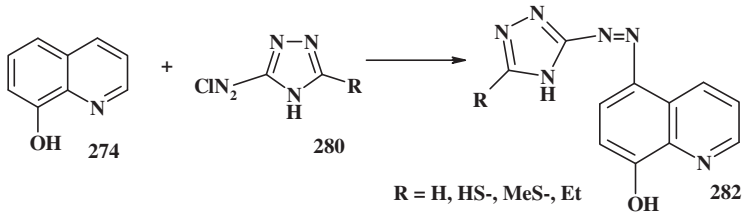
Also, diazotized 2-amino-1,3,4-thiadiazoles couples with 8-hydroxyquinoline **274** to give the respective thiadiazolylazo derivatives **285** (Scheme 104) [110].

3-[(3-Isoxazolyl)azo]pyrimido[1,2-a]benzimidazoles

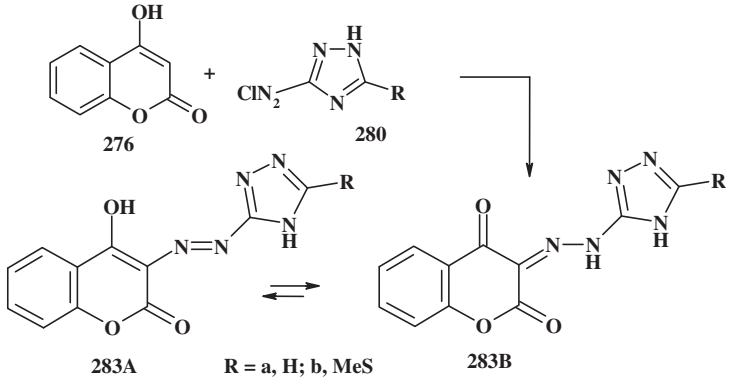
Reaction of diazotized 2-amino-5-methyl-isoxazole **272** with 4-amino-2-oxopyrimido[1,2-*a*]benzimidazole **286** yielded the respective 3-[(3-isoxazolyl)azo]-pyrimido[1,2-*a*]benzimidazole **287**, which was considered to exist as a mixture of the two tautomeric forms **287A** and **287B** (Scheme 105) [112].

3-[(2-Thiazolyl)azo]pyrimido[1,2-a]benzimidazoles

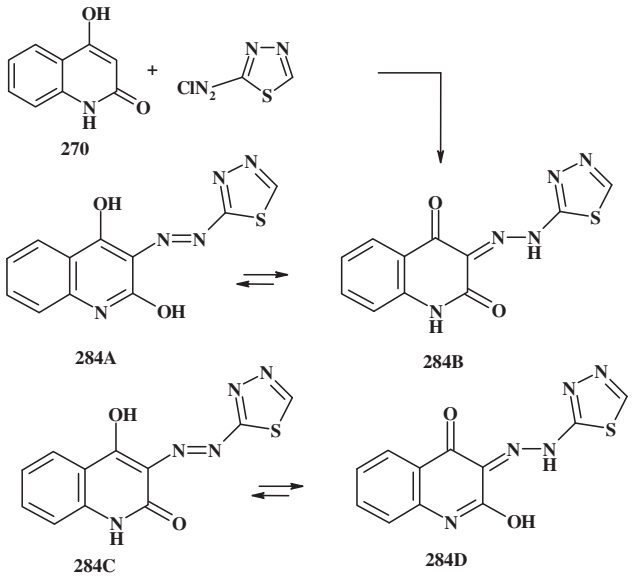
Coupling of diazotized 2-amino-5-substituted-thiazole with 4-amino-2-oxopyrimido[1,2-*a*]benzimidazole **286** yielded the respective 3-[(2-thiazolyl)azo]-pyrimido[1,2-*a*]benzimidazoles **288**, which were considered to exist as a mixture of the two tautomeric forms **288A** and **288B** (Scheme 106) [112].



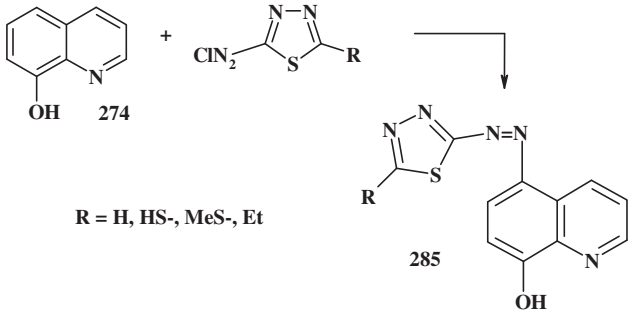
Scheme 101



Scheme 102



Scheme 103



Scheme 104

3-[([1,2,4]Triazol-3-yl)azo]pyrimido[1,2-a]benzimidazoles

Similar coupling of diazotized 2-amino-5-substituted-[1,2,4]triazole with 4-amino-2-oxopyrimido[1,2-*a*]benzimidazole **286** yielded the respective 3-[(3-triazolyl)azo]-pyrimido[1,2-*a*]benzimidazoles **289**, which were also considered to exist as a mixture of the two tautomeric forms **289A** and **289B** (Scheme 107) [112].

2-[(5-Pyrimidinyl)azo]benzothiazoles

Diazotized 2-aminobenzothiazole was reported to couple with 4-hydroxy-6-methyl-2-thiouracil **136** to give the respective azo dyes **290**, which were assigned the indicated azo-tautomeric structure (Scheme 108) [113].

Recently, it was reported that diazotized 3-aminopyridine **291** was coupled with 8-hydroxyquinoline **274** and gave the respective azo dye **292** (Scheme 109) [110].

3-[(2-Benzothiazolyl)azo]pyrazolo[5,1-c][1,2,4]triazines

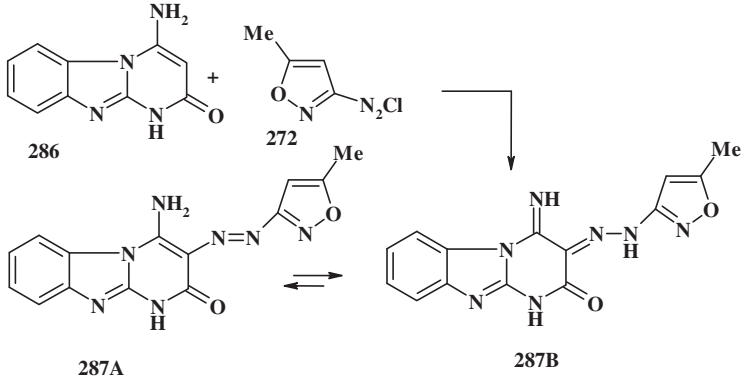
Similar reaction of the diazonium salt, which derived from 5-aminopyrazole derivative **293**, with each of malononitrile and ethyl cyanoacetate yielded the respective coupling products that cyclized in situ to give 4-amino-7-methyl-8-(2-benzothiazolylazo)pyrazolo[5,1-*c*][1,2,4]triazines **294**. FT-IR spectra of such dyes revealed that they exist predominantly in the indicated azo-enamine tautomeric form **294** (Scheme 110) [109].

3-[(2-Benzimidazolyl)azo]quinolines

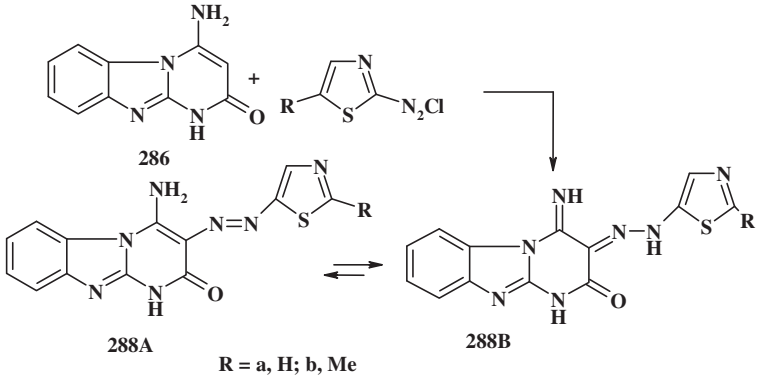
3-[(2-Benzimidazolyl)azo]-2,4-dihydroxyquinoline **296** was prepared by coupling 2,4-dihydroxyquinoline **270** with diazotized 2-aminobenzimidazole **295** (Scheme 111). The ^{1}H NMR of this dye in DMS-d_6 revealed signals at δ 13.98 (NH) and 10.41 (OH), which indicate that such a dye exists as the azo-enol form [3].

3-[(2-Benzothiazolyl)azo]quinolines

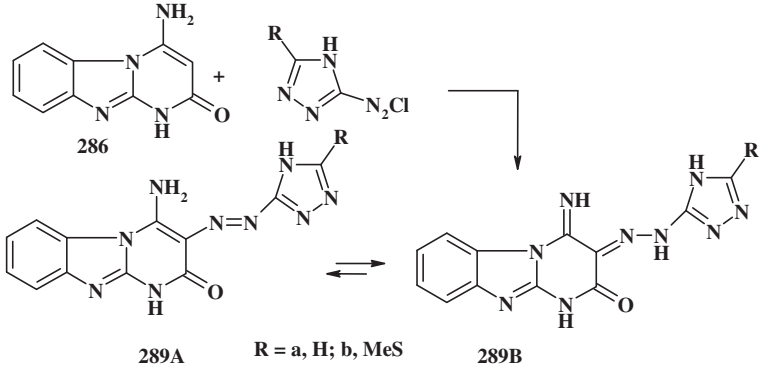
3-[(2-Benzothiazolyl)azo]quinoline**s** **297** were prepared by coupling 2,4-dihydroxyquinoline **270** with diazotized 2-aminobenzothiazoles. The ^{1}H NMR of this dye in DMS-d_6 revealed a broad signal at δ 10.37–10.93 (OH) and its IR spectrum showed no carbonyl absorption band. Such data indicate that such a dye exists in the indicated azo-enol form **297** (Scheme 112) [3].



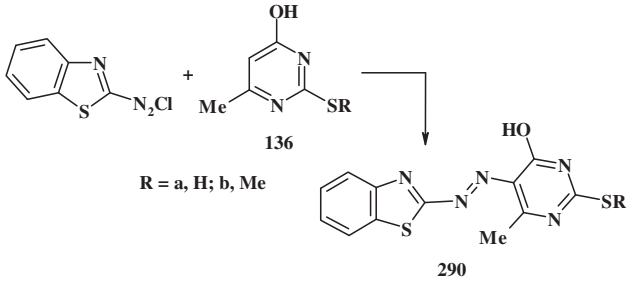
Scheme 105



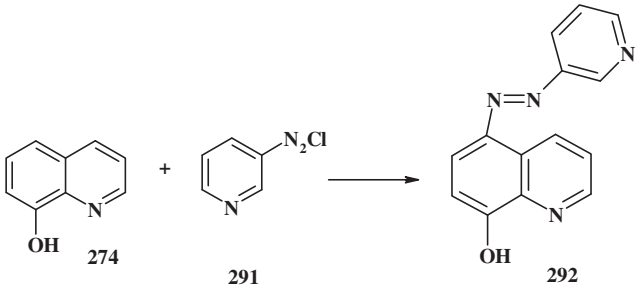
Scheme 106



Scheme 107



Scheme 108



Scheme 109

3-[(2-Benzimidazolyl)azo]coumarins

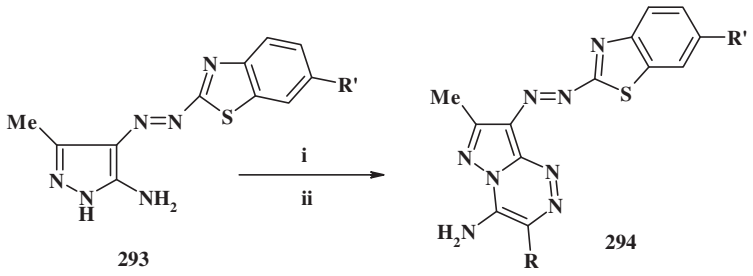
3-[(2-Benzimidazolyl)azo]coumarin **298** was prepared by coupling 4-hydroxycoumarin **276** with diazotized 2-aminobenzimidazole in nitrosyl sulfuric acid. The ^{1}H NMR of this dye in DMS-d_6 revealed signals at δ 12.5 (OH), 14.8 (NH) and 15.3 (NH), which indicate that such a dye exists as an equilibrium mixture of azo-enol and keto-hydrazone tautomeric forms **298A** and **298B**, respectively (Scheme 113) [3].

3-[(2-Benzothiazolyl)azo]coumarins

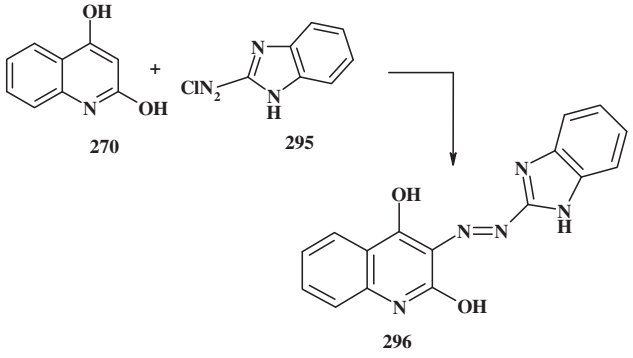
A series of 3-[(2-benzothiazolyl)azo]coumarins **299** was prepared by coupling 4-hydroxycoumarin **276** with diazotized 2-aminobenzothiazoles. The ^{1}H NMR of this dye in DMS-d_6 revealed two broad signals at δ 13.6–13.7 (OH) and 14.7–14.8 (NH), which indicate that each of such dyes exists as an equilibrium mixture of azo-enol and keto-hydrazone tautomeric forms **299A** and **299B** in DMSO-d_6 (Scheme 114) [111].

3-[(2-Benzimidazolyl)azo]pyrimido[1,2-a]benzimidazoles

Diazotized 2-amino-benzimidazole coupled with 4-amino-2-oxopyrimido[1,2-*a*]benzimidazole **288** and yielded the respective 3-[(2-benzimidazolyl)azo]-pyrimido[1,2-*a*]benzimidazole **300**, which was reported to exist as a mixture of the two tautomeric amino-azo form **300A** and the imino-hydrazone form **300B** (Scheme 115) [112]. For example, its ^{1}H NMR



Scheme 110

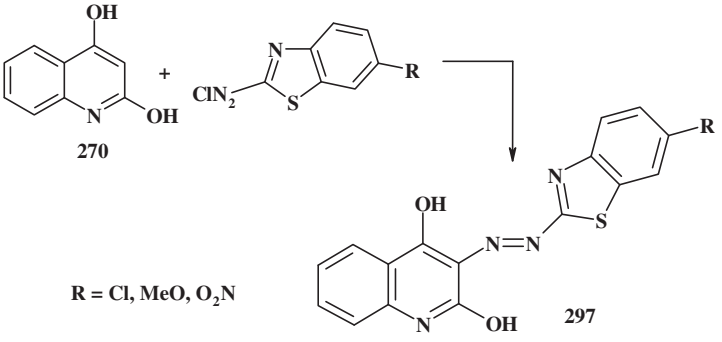


Scheme 111

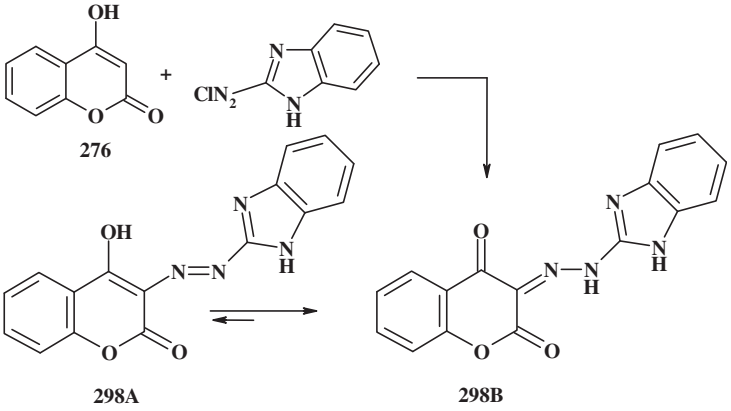
revealed signals at δ 12.45 (NH_2), 11.93 (NHCO) and 9.78 (=NH).

3-[(2-Benzthiazolyl)azo] pyrimido[1,2-a]benzimidazoles

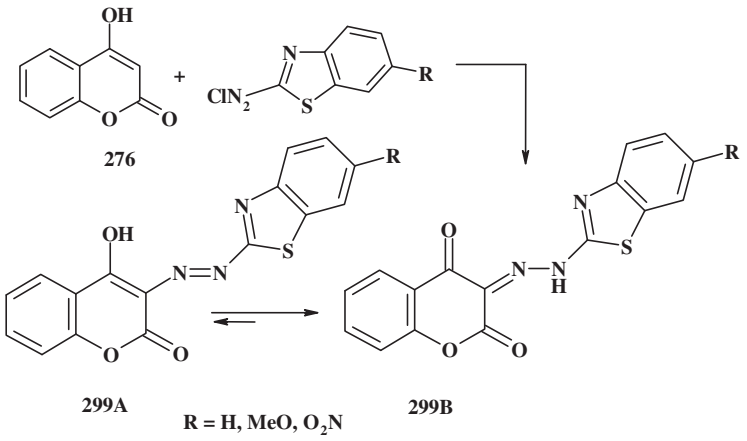
Similarly, three series of 3-[(2-benzthiazolyl)azo] pyrimido[1, 2-*a*]benzimidazoles **301** were prepared by coupling diazotized 2-amino-benzothiazole with 4-amino-2-oxopyrimido[1,2-*a*] benzimidazole **286**. Such dyes were found to exist as equilibrium mixture of the two tautomeric amino-azo form **301A** and the imino-hydrazone form **301B** (Scheme 116) [112]. For example, its ^{1}H NMR revealed signals at δ 12.50–12.40 (NH_2), 10.3–10.32 (NHCO) and 9.60–9.63 (=NH) [112].



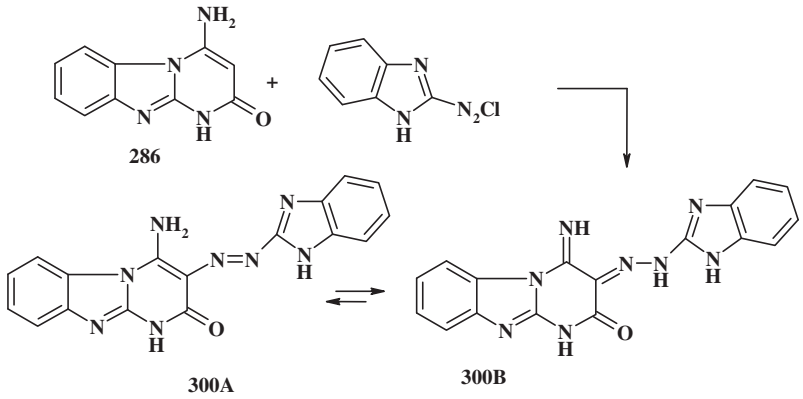
Scheme 112



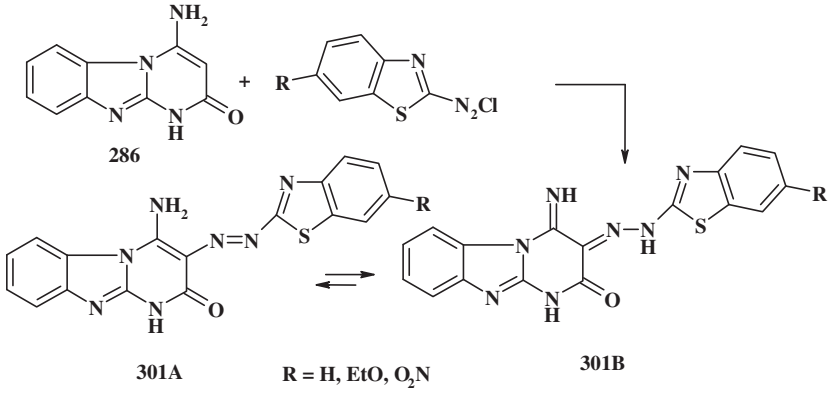
Scheme 113



Scheme 114



Scheme 115



Scheme 116

Conclusion and prospects

The literature survey presented herein indicates that the synthesis and tautomerism of aryl- and hetaryl-azo derivatives of the various heterocycles have attracted the interest of many research groups all over the world. Such colouring compounds seem to be promising dyes. However, the author feels that there are still several problems that need further clarification before application of such colouring compounds in industry. For example, it should be pointed out that the observation of more than one form in the ^{1}H NMR spectra of some compounds could be more probably explained by E/Z isomerism e.g. on the moiety C═N–NH–Ar. A similar case of the E/Z isomerism has been recently reported by Simunek et al. [114], where the isomerism has been proved by means of multinuclear magnetic resonance using isotopically labeled compounds. Also, in most

literature reports covered herein, the quantification of the position of azo-hydrazone equilibria is determined by means of NMR based on comparison of relevant NMR parameters of the equilibrium mixture with the parameters of standards. As the azo-hydrazone equilibrium mixture of a single compound proceeds only through the very fast intramolecular rearrangement of the proton between two atoms (N or O), it seems that the application of N-15 NMR spectroscopy seems to be the best method available for this purpose [115,116]. Furthermore, the literature survey revealed that there are several aspects of such colorants that still need further study. For example, the role of solvent polarity, temperature and other factors that control the existence of such tautomeric mixtures could be elaborated. Also, the tautomerism-coloristic properties correlations of such dyes need to be explored. Finally, it is hoped that this review will encourage many researchers to shed light on such problems, which will facilitate the utility of such azo colouring compounds in industry.

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