Hydrazonoyl Halides: Useful Building Blocks for the Synthesis of Arylazoheterocycles

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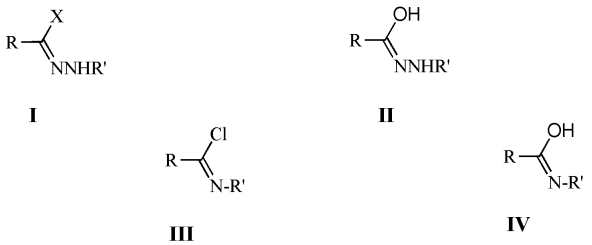
Contents

1. Introduction.

Heterocyclic colouring materials have been in use since prehistoric times. An enormous variety of disperse and cationic heterocyclic azo dyes have been reported in the patent literature. In recent years, arylazo derivatives of various heterocyclic systems have been the subject of intense research by organic chemists [1] and dye manufacturers [2]. Among the various strategies pursued for synthesis of such types of dyes, several procedures have in common either (i) diazotization of the appropriate heterocyclic amines such as 2-aminothiazoles, followed by coupling with an *N*,*N*-dialkylaniline or (ii) condensation of primary amines or their sodio derivatives with suitable nitroso compounds. The resulting azo dyes are then quaternized with suitable alkylating agents to produce the respective cationic azo dyes. Nowadays, the use of hydrazonoyl halides **I** (Chart 1) has become a powerful tool in organic synthetic strategies directed towards the construction of arylazoheterocycles.

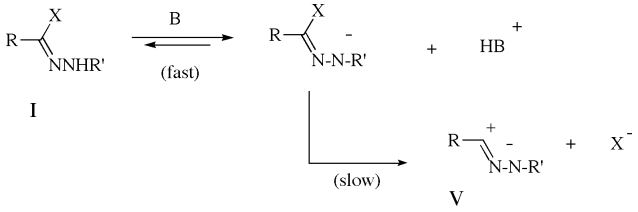
Hydrazonoyl halides are a class of compounds with the general formula **I** where X represents a chlorine or bromine group. These compounds are the halides of the so-called hydrazonic acids **II** as imidoyl chlorides **III** are the chlorides of imidic acids **IV** (Chart 1). Since their discovery, hydrazonoyl halides **I** have emerged as an important class of organic compounds. More than 1300 papers and patents have been reported so far concerning their synthesis, reactions and biological activities. At present, there are several review articles by Shawali *et al*. [3-6] and by others [7] which have been useful to chemists and biologists engaged in synthesis of new heterocyclic systems, new drugs or in other important investigations. Since then, numerous research papers have been published by us and by other research groups describing in detail the varied use of hydrazonoyl halides as reagents and intermediates for the synthesis of arylazoheterocycles. The intention of this review is to focus mainly on publications that have appeared in Chemical Abstracts from 1981 to 2002. Literature prior to 1981 will thus not be included unless it is felt to be essential in bringing the relevant information together and in putting the problem into common perspective. Emphasis will only be given to the latest developments in the area.

Chart 1



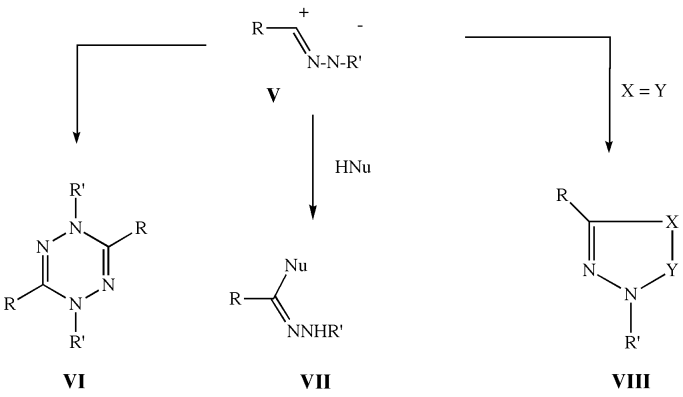
Regarding the reactions of hydrazonoyl halides **I** leading to azoheterocycles, it is noteworthy that they are usually carried out in the presence of a base as catalyst. The function of the latter is to convert **I** into the respective 1,3-dipoles **V**, which are called nitrilimines and sometimes referred to as nitrilium imides *via* a 1,3-elimination reaction. The mechanism of this dehydrohalogenation reaction has been studied by Shawali *et al*. [8,9] who showed that it is as depicted in Scheme 1.

Scheme 1



When such nitrilium imides are generated in the presence of a heterocyclic nucleophile HNu or dipolarophile X=Y, they undergo 1,3-addition or cycloaddition to give adducts **VII** or **VIII**, respectively (Scheme 2). In the absence of such reagents, the nitrilimines **V** undergo head-to-tail dimerization to yield the respective tetrazine derivatives **VI** (Scheme 2).

Scheme 2



Furthermore, it should be mentioned that two or more tautomeric structures such as azo and hydrazone forms can be written for some of the arylazoheterocycles covered in this review. In some reports, this problem of tautomerism has been studied and the actual tautomeric form(s) of the studied arylazoheterocycles have been pointed out.

In this article, the arylazoheterocycles are reported in order of increasing (i) number of rings, (ii) size of such rings and (iii) number of heteroatoms present. The heteroatoms have been arranged in the sequence: nitrogen, oxygen, sulfur, selenium and other elements. Fused heterocycles follow the

IUPAC convention and the numbering of ring systems is that of Chemical Abstracts. The various hydrazonoyl halides that have been used hitherto in the synthesis of arylazoheterocycles are presented in Chart 2.

Chart 2

1 $HCOC(Cl)=NNHAr$

2 $CH_3COC(Cl)=NNHAr$

3

$CH(CN)COC(Br)=NNHAr$

4 $MeOCO(CH_2)_3COC(Cl)=NNHAr$

5 Ar'COC(Br)=NNHAr

Ar' : A, Ph; B, 1-Naphthyl; C, 2-Naphthyl;

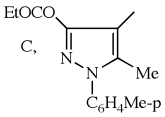
D, 4-$((CH_2)_5N\text{-}SO_2)C_6H_4$

6 Het-COC(X)=NNHAr

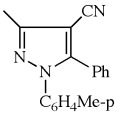
Het : A,

; B,

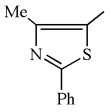
C,



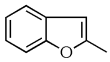
D,



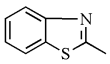
E,



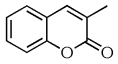
F,



G,

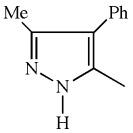


H,

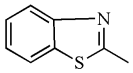


7 $CH_3COC(Cl)=NNH\text{-Het}$

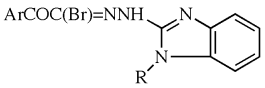
Het : A,



; B,



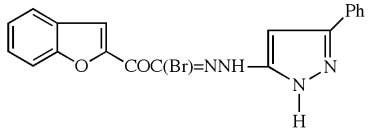
8



R : A, H; B, $PhCH_2$

9 A, $ClCOC(Cl)=NNHAr$

B,

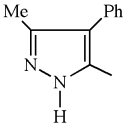


10 $ROCOC(Cl)=NNHAr$

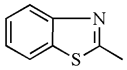
R : A, Me; B, Et

11 $EtOCOC(Cl)=NNH\text{-Het}$

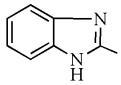
Het : A ,



; B ,



; C,



12 A, $PhNHCOC(Cl)=NNHAr$

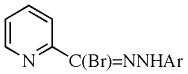
B, 1-Morpholinyl-$COC(Cl)=NNHAr$

13 $Ar\text{-}N=N\text{-}C(Cl)=NNHAr$

14 A, $ArC(Cl)=NNHAr$

B, $PhCH=CHC(Cl)=NNHPh$

15



16 $PhNHN=C(Cl)\text{-}C(Cl)=NNHPh$

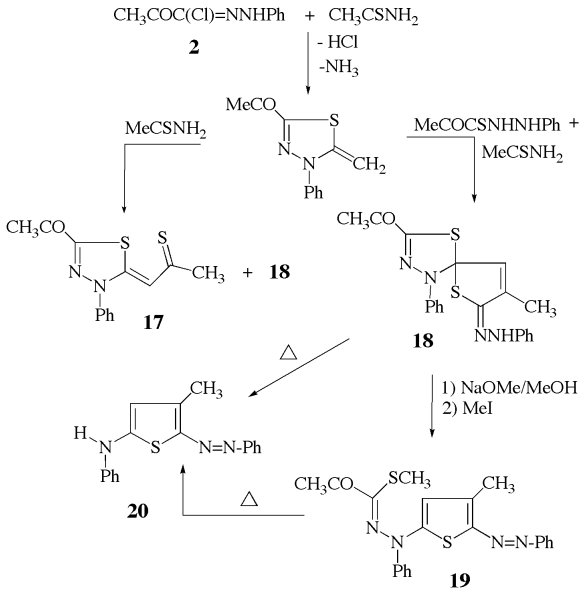
It is hoped that this review will demonstrate the usefulness of hydrazonoyl halides in synthesis of heterocyclic azo dyes and stimulate further work in this area.

2. Arylazo Derivatives of Monoheterocycles.

2.1 Thiophenes.

Reaction of *N*-phenyl 2-oxopropanehydrazonoyl chloride **2** with thioacetamide in refluxing toluene was reported to give a mixture of the thiadiazoline derivative **17** and the spiro compound **18** in 30 and 5% yields, respectively (Scheme 3). The latter product **18** was obtained in better yield (25%) by the reaction of **2** with a mixture of thioacetamide and thiopyruvic acid phenylhydrazide [10]. Treatment of **18** with sodium methoxide in methanol followed by methyl iodide afforded 1-methylthio-1-*N*-[2-(4-methyl-5-phenylazo)thienyl]-*N*-phenylhydrazonopropanone **19**. Pyrolysis of **18** and **19** in refluxing mesitylene gives one product that was identified as 2-anilino-4-methyl-5-phenylazothiophene **20** (Scheme 3) [10].

Scheme 3

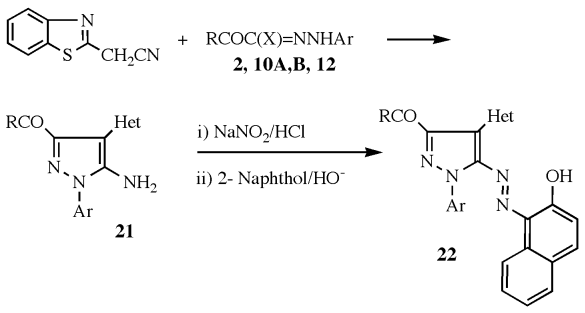


2.2 Pyrazoles.

Reaction of 2-cyanomethylbenzothiazole with each of the hydrazonoyl halides **2, 10A,B** and **12** in ethanol in the presence of sodium ethoxide afforded the respective

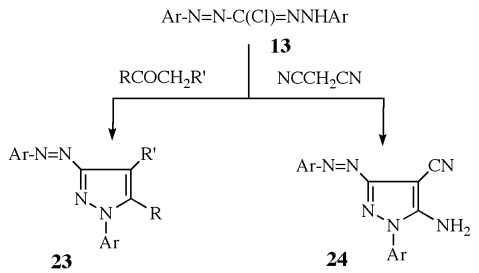
5-amino-4-(benzothiazol-2-yl)pyrazoles **21** (Scheme 4) [11]. Diazotization of the latter followed by coupling of the resulting diazonium salt with 2-naphthol in sodium hydroxide solution afforded the corresponding 5-(2-hydroxy-1-naphthylazo)pyrazole derivatives **22** (Scheme 4) [11].

Scheme 4



Condensation of *N*-aryl arylazomethanehydrazonoyl chlorides **13**, which are commonly referred to as 3-chloroformazans, with various active methylene compounds such as α,β-diketones, β-ketosulfones, β-ketoanilides and phenacyl cyanide in ethanol in the presence of sodium ethoxide afforded the respective 3-arylazopyrazoles **23** (Scheme 5) [12]. A similar reaction of **13** with malononitrile under the same conditions afforded 3-arylazo-4-cyano-5-aminopyrazoles **24** (Scheme 5) [12].

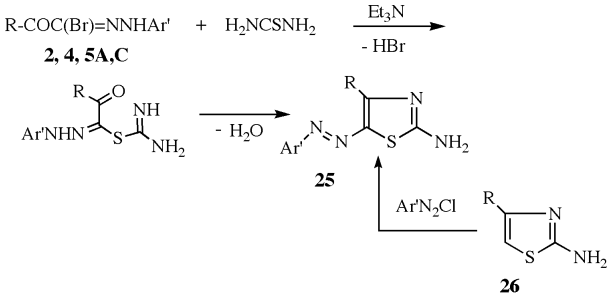
Scheme 5



2.3 Thiazoles.

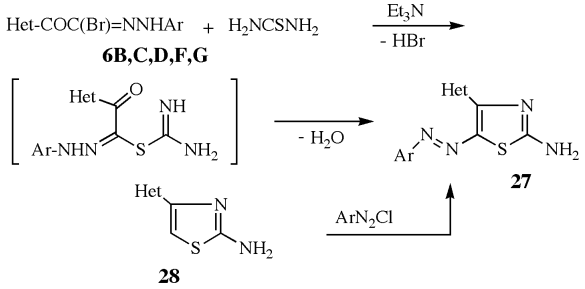
Reaction of thiourea with hydrazonoyl halides **2, 4**, **5A,C** and **6C** in refluxing ethanol afforded the respective 2-amino-5-arylazo-4-substituted thiazoles **25** (Scheme 6) [13-17]. The structure of the latter products was confirmed in some cases by their alternate synthesis *via* coupling of the respective 2-aminothiazole derivatives **26** with a diazotized aniline (Scheme 6). Although three possible tautomeric structures can be written for such arylazo derivatives, they were assigned the indicated aminoazo tautomeric form **25**, based on the results of a polarographic study of a series of such compounds (R = Ph), and HMO calculations of bonding energies of the various tautomeric forms [18].

Scheme 6



N-aryl 2-oxo-2-heteroarylethanehydrazonoyl bromides **6B-G** react similarly with thiourea to give the respective 5-arylazothiazoles **27** (Scheme 7) [19-24]. The structure **27** assigned to these products was confirmed in some cases by their alternate synthesis *via* coupling of **28** with diazotized anilines (Scheme 7).

Scheme 7

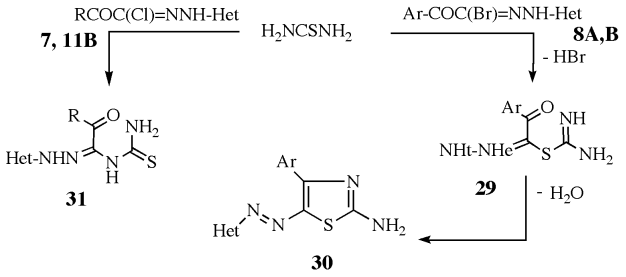


Reaction of thiourea with each of the *N*-heteroaryl hydrazonoyl halides **8A,B** was also reported to give the respective 2-amino-5-heteroarylazothiazoles **30** (Scheme 8) [25].

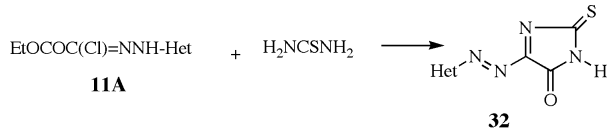
Contrary to the foregoing results, reactions of thiourea with *N*-heteroaryl 2-oxopropanehydrazonoyl chloride **7** and ethyl *N*-heteroarylhydrazono chloroacetate **11B** were reported to afford the corresponding amidrazone derivatives **31** as end products (Scheme 8) [26]. No rationalization was presented to account for this unexpected finding, although it is well known that the sulfur atom in thiourea and thiosemicarbazide is a more nucleophilic site than the nitrogen atoms.

Another unexpected result was also reported for the reaction of ethyl *N*-(3-methyl-4-phenyl-pyrazol-5-yl)hydrazono chloroacetate **11A** with thiourea. Such a reaction was reported to yield the azo derivative **32** instead of the expected 2-amino-5-arylazo-4(5*H*)-thiazolone (Scheme 9) [27]. No rationalization for that finding was given.

Scheme 8

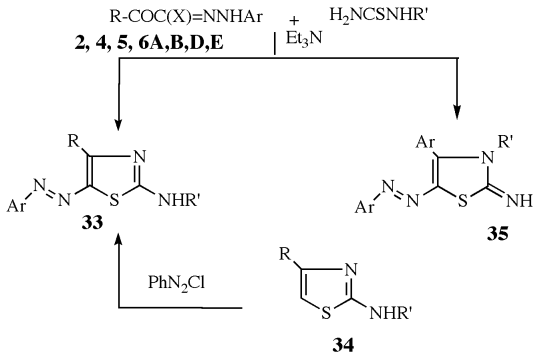


Scheme 9



Reaction of the hydrazonoyl halides **2, 4, 5** and **6A,B,D,E** , each with a monosubstituted thiourea, was reported to follow a similar pathway to that of thiourea and give the respective 5-arylazo-2-(substituted amino)thiazole derivatives **33** (Scheme 10) [17,28-30]. The structures of the latter products were confirmed by their alternate syntheses [17,28-30]. A similar reaction of 2-aryl-2-oxoethanehydrazonoyl bromides **5** with *N*-(4-ethoxyphenyl)thiourea in ethanol afforded 5-arylazo-4-aryl-2-iminothiazoles **35** (Scheme 10) [16,31].

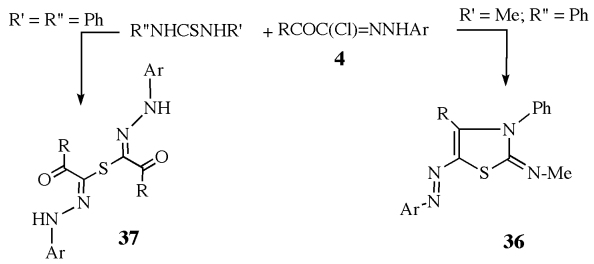
Scheme 10



N,*N*'-Disubstituted thioureas were reported to react with the hydrazonoyl chloride **4** to yield either 5-arylazothiazoles **36** or the sulfide **37** according to the type of substituents present (Scheme 11) [17,32].

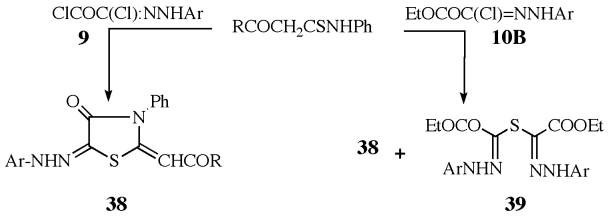
The reaction of ethyl *N*-(arylhydrazono)chloroacetate **10B** with 3-oxo-thioanilides in ethanolic sodium ethoxide was reported [33] to give a mixture of the arylhydrazonothiazoline derivative **38** and the hydrazonoyl sulfide **39** (Scheme 12). Reaction of the same thioanilides with

Scheme 11



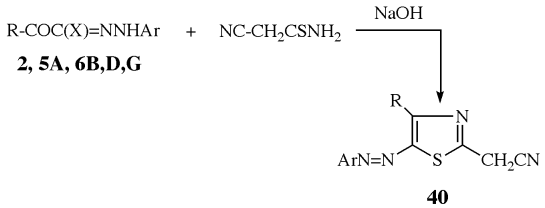
N-aryl 2-oxo-2-chloroethanehydrazonoyl chloride **9** afforded only the azo derivative **38** (Scheme 12) [34].

Scheme 12



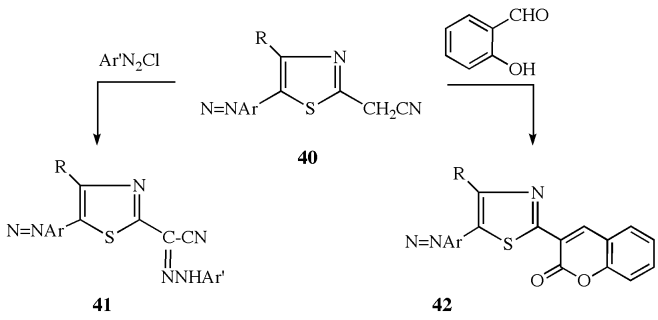
The reactions of *N*-aryl 2-oxopropanehydrazonoyl chlorides **2**, 2-oxo-2-phenylethanehydrazonoyl bromides **5A** [35] and *N*-aryl 2-heteroaryl-2-oxo-ethanehydrazonoyl bromides **6B,D,G** [21,23,36] each with cyanothioacetamide were reported to give the respective 5-arylazo-4-substituted thiazole derivatives **40** (Scheme 13). The latter products **40** were reported to couple with diazotized anilines to give **41** (Scheme 14) [23,35,36], and to condense with salicylaldehyde to afford 5-arylazo-2-(coumarin-3-yl)- 4-substituted thiazoles **42** (Scheme 14) [35,36].

Scheme 13



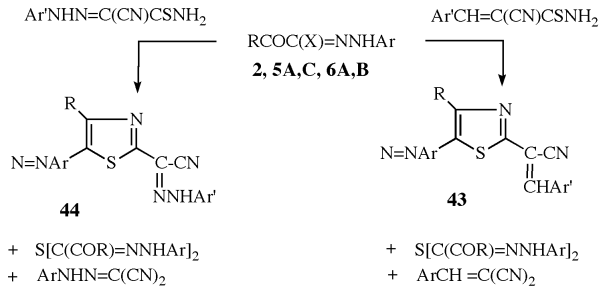
Treatment of 2-oxohydrazonoyl halides **2, 5A,C** and **6A,B** with 2-arylmethylenecyanothioacetamide was reported to give the corresponding 5-arylazothiazole derivatives **43** together with the hydrazonoyl sulfide and arylidenemalonitrile as by-products (Scheme 15) [37]. Similar reaction of such hydrazonoyl halides with 2-arylhydra-

Scheme 14



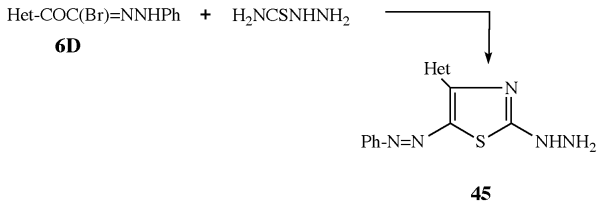
zonocyanothioacetamide yielded the azo derivatives **44** (Scheme 15) [37]. In this case hydrazonoyl sulfide and arylhydrazonomalononitrile were produced as by-products (Scheme 15).

Scheme 15



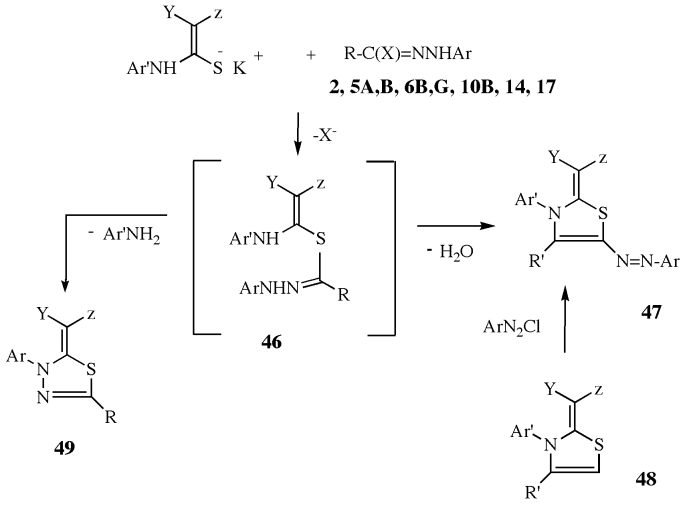
Reaction of hydrazonoyl bromide **6D** with thiosemicarbazide in ethanol was reported to give the 2-hydrazino-5-phenylazo-4-substituted thiazole **45** (Scheme 16) [28].

Scheme 16

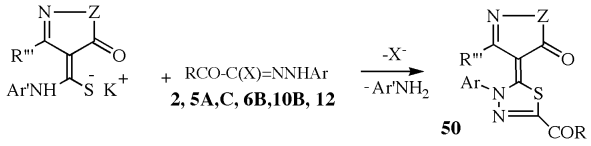


Reactions of hydrazonoyl halides of type **2, 5A** with potassium salts of active methine thioanilides were first reported to give the respective 5-arylazothiazoline derivatives **47** (Scheme 17) [38,39]. Although the latter products were said to be identified by alternate synthesis by coupling of diazotized anilines with the respective thiazole derivatives **48**, other literature reports indicated that reactions of active methine thioanilides with the same hydrazonoyl halides **2** and **5A** as well as other hydrazonoyl halides **5B, 6B,G, 10B**, **B, 6B,G, 10B** and **14A,B** proceed *via* elimination of an arylamine from the initially formed thiohydrazonate esters **46** to give the respective thiadiazoline derivatives **49** (Scheme 17) [40-43]. Similar reactions of cyclic active methine thioanilides with hydrazonoyl halides **2, 5A,C, 6B, 10B** and **12** were reported to yield the respective thiadiazoline derivatives **50** (Scheme 18) [44].

Scheme 17

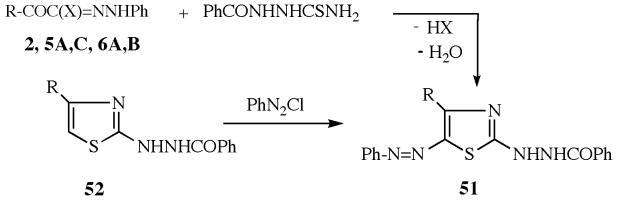


Scheme 18



Recently, it was reported that reaction of 2-benzoylhydrazine-thiocarboxamide with 2-oxohydrazonoyl halides **2, 5A,C and 6A,B** in ethanol in the presence of triethylamine yielded the corresponding 2-(2-benzoylhydrazino)-5-arylazothiazole derivatives **51** [45] (Scheme 19). The structure of the latter products was confirmed by their alternate synthesis by coupling diazotized anilines with the respective thiazole derivatives **52** (Scheme 19).

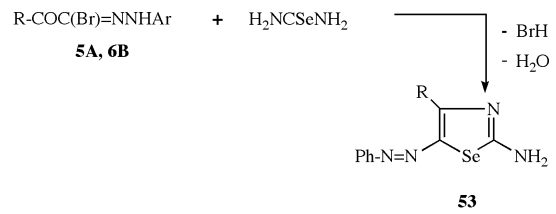
Scheme 19



2.4 Selenazoles.

The reaction of selenourea with *N*-aryl 2-oxoethanehydrazonoyl halides **5A** and **6B** was reported to give 5-arylazoselenazoles **53** [19,46] (Scheme 20).

Scheme 20

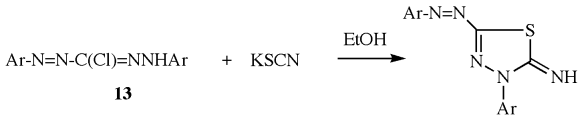


53

2.5 1,3,4-Thiadiazoles.

Reaction of *N*-aryl arylazomethanehydrazonoyl chlorides **13** with potassium thiocyanate in ethanol were reported to yield 2-arylazo-4-aryl-5-imino-1,3,4-thiadiazoles **54** in good yields [12] (Scheme 21).

Scheme 21

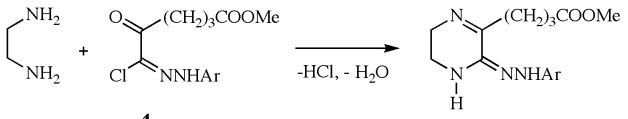


54

2.6 Pyrazines.

The condensation of *N*-aryl 5-methoxycarbonyl-2-oxopentanehydrazonoyl chloride **4** with ethylenediamine afforded products that were identified as the 2-arylazopyrazine derivatives **55** (Scheme 22) [17]. Although, three possible tautomeric forms can be written for these products, they were assigned the tautomeric structure **55** on the basis of their ^{1}H NMR spectra (Scheme 22) [17].

Scheme 22

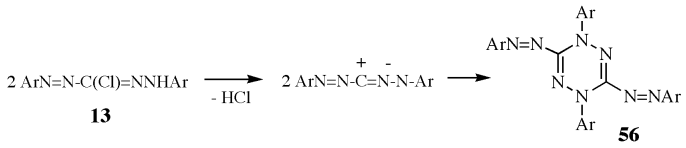


4 **55**

2.7 Tetrazines.

3,6-*Bis*(arylazo)-1,4-diaryl-1,2,4,5-tetrazines **56** were reported [47] to be easily prepared by treatment of *N*-aryl arylazomethanehydrazonoyl chlorides **13** with triethylamine in dioxane at room temperature. The formation of **56** was considered to result from head-to-tail dimerization of the initially formed nitrilium imides (Scheme 23).

Scheme 23



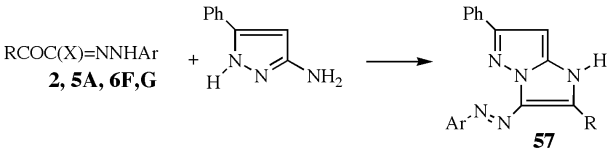
56

3. Arylazo Derivatives of 5,5-Biheterocycles.

3.1 1*H*-imidazo[1,2-*b*]pyrazoles.

3-Amino-5-phenylpyrazole was reported to react readily with various types of 2-oxohydrazonoyl halides namely **2** and **5A** [48, 49] and **6F,G** [31,50-53] in ethanol and yields the respective 3-arylazo-2-substituted-1*H*-imidazo[1,2-*b*]-pyrazoles **57** (Scheme 24).

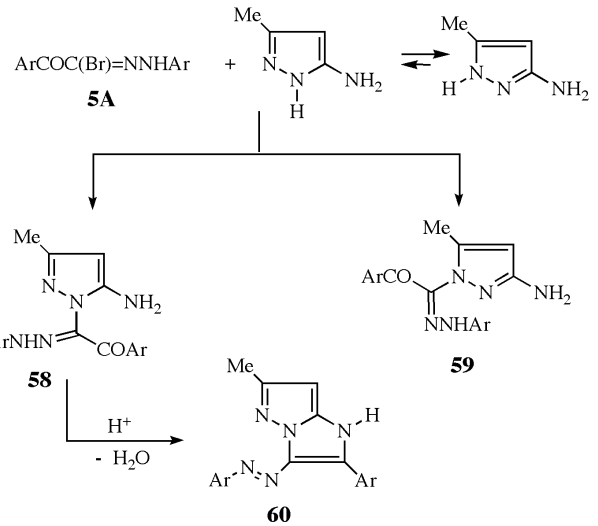
Scheme 24



57

A similar reaction of *N*-aryl 2-oxo-2-phenylethanehydrazonoyl bromides **5A** with 3-amino-5-methylpyrazole was reported, however, to give a mixture of **58** and **59** (Scheme 25) [54]. Treatment of **58** with acid resulted in the elimination of water to give the respective 1*H*-3-arylazoimidazo[1,2-*b*]pyrazole derivative **60** (Scheme 27) [54]. The product **59** was recovered unchanged upon similar treatment with acid.

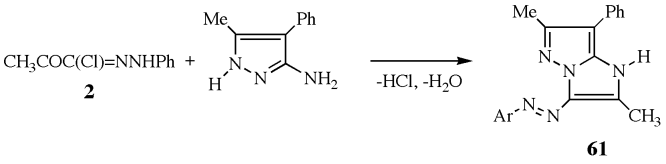
Scheme 25



58 **59** **60**

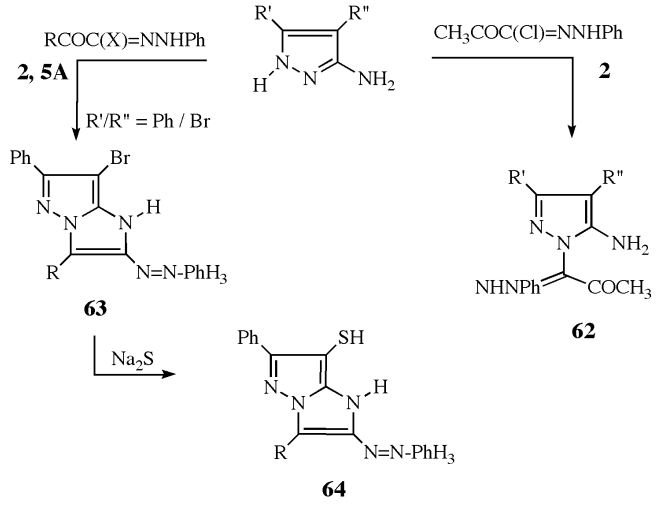
The reaction between 2-oxopropanehydrazonoyl chloride **2** and 3-amino-5-methyl-4-phenylpyrazole leads, as expected, to 1*H*-3-arylazo-imidazo[1,2-*b*]pyrazole derivative **61** (Scheme 26) [55].

Scheme 26



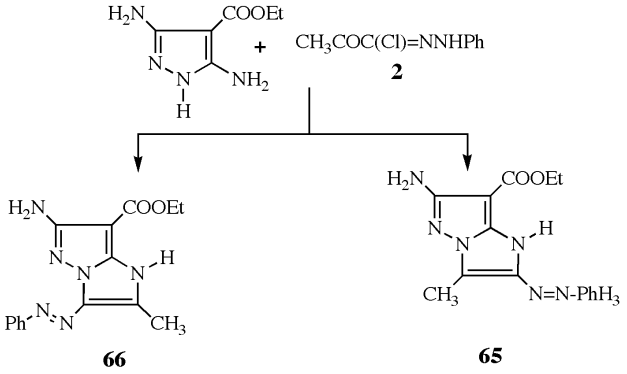
Contrary to the foregoing results, it was reported that reaction of 3-amino-4,5-disubstituted pyrazoles with *N*-phenyl 2-oxopropanehydrazonoyl chloride **2** afforded the amidrazone derivative **62** (Scheme 27) [55]. In another report [14], the reactions of 3-amino-4-bromo-5-phenylpyrazole with the hydrazonoyl halides **2** and **5A** were reported to yield the respective 2-arylazoimidazo[1,2-*b*]-pyrazole derivative **63** which upon treatment with sodium sulfide was converted into **64** (Scheme 27) [56]. No rationalization was offered, however.

Scheme 27



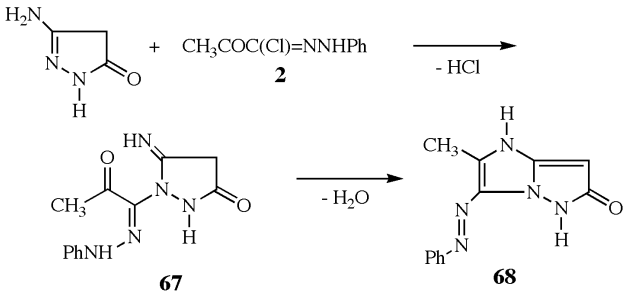
A similar contradiction was also reported. Thus, it was indicated that reaction of ethyl 3,5-diaminopyrazole-4-carboxylate with 2-oxopropanehydrazonoyl chloride **2** yielded the 2-arylazo derivative **65** and not the expected 3-arylazo derivative **66** (Scheme 28) [57]. The latter isomer is the one to be expected as the pyrazole N(1)H is more basic than the exocyclic 5-amino group and thus the structure of the product of this reaction seems to need further investigation.

Scheme 28



Reaction of 3-amino-4,5-dihydropyrazol-5-one with *N*-phenyl 2-oxopropanehydrazonoyl chloride **2** was reported to yield 5,6-dihydro-2-methyl-6-oxo-3-phenylazo-1*H*-imidazo[1,2-*b*]pyrazole **68** *via* dehydrative cyclization of the initially formed amidrazone derivative **67** (Scheme 29) [55].

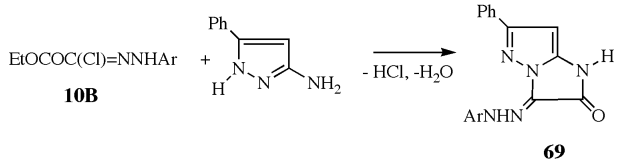
Scheme 29



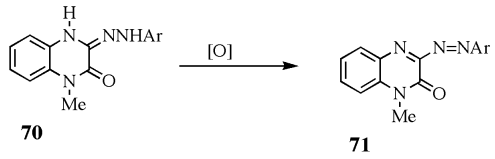
Also, it has been reported that ethyl *N*-arylhydrazonochloroacetate **10B** reacted with 3-amino-4-phenylpyrazole to give a product to which structure **69** was assigned (Scheme 30) [49]. The isomeric 2-arylhydrazono-3-oxo- structure was rejected because the isolated product was recovered unchanged after being subjected to an oxidation treatment. Compounds of the latter type are expected to be oxidized by analogy with 1-methyl-3-phenylhydrazono-1,4-dihydroquinoxalin-2-one **70** which was reported to give the 3-arylazoquinoxaline derivative **71** upon oxidation (Scheme 31) [58].

Ambiguous results were reported concerning the reactions of 3-amino-5-phenylpyrazole with ethyl *N*-(arylhydrazono)chloroacetate **10B**, *N*-(arylhydrazono)chrloroactamide derivatives **12A,B** and *N*-aryl 2-oxopropanehydrazonoyl chloride **2**. These reactions were reported to yield the respective 3-substituted-1,4-diaryl-1*H*,6*H*-pyrazolo[3,4-*c*]pyrazoles **72** *via* elimination of ammonia from the unexpected initially formed 3-amino-4-hydra-

Scheme 30

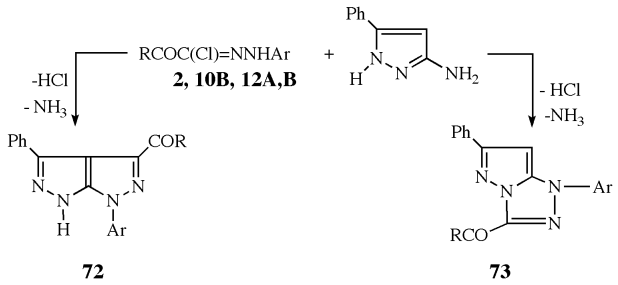


Scheme 31



zonoylpyrazole derivatives (Scheme 32) [59,60]. Neither of the other isomeric products **69** and **73** was formed.

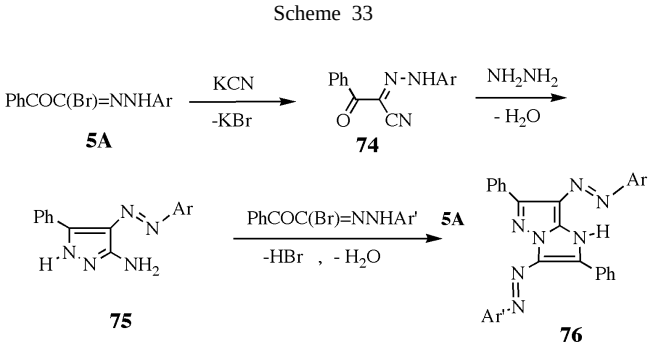
Scheme 32



Treatment of 2-arylhydrazono-3-oxo-3-phenylpropanenitriles **74**, prepared from *N*-aryl 2-oxo-2-phenylethanehydrazonoyl bromides **5A** and potassium cyanide, with hydrazine hydrate in refluxing ethanol afforded the respective 3-amino-4-arylazo-5-phenylpyrazoles **75** in good yields (Scheme 33) [61,62].

Recently, it was reported that when equimolar quantities of *N*-aryl 2-oxo-2-phenylethanehydrazonoyl bromide **5A** (Ar' = Ph) and each of the azo derivatives **75** were refluxed in ethanol in the presence of triethylamine, the respective 3,7-*bis*(arylazo)-2,6-diphenyl-1*H*-imidazo[1,2-*b*]-pyrazoles **76** were formed [63]. Similar reactions of **75** (Ar = Ph) with each of *N*-aryl 2-oxo-2-phenylethanehydrazonoyl bromides **5A-D** also yielded the respective bis-arylazo derivative **76** (Scheme 33). The other regioisomeric structure namely 2,7-bis(arylazo)-3,6-diphenyl-1*H*-imidazo[1,2-*b*]pyrazole was rejected because reaction of 3-amino-5-phenylpyrazole with 2-oxohydrazonoyl halides was reported to afford in all cases examined the respective 3-arylazo-2,6-diaryl-1*H*-imidazo[1,2-*b*]pyrazoles and not the isomeric 2-arylazo-3,6-diaryl-1*H*-imidazo[1,2-*b*]pyrazoles [48,49,54,55,61,62]. Although four possible tautomeric structures can be written for each of the compounds **76**, they were found to exist predominantly in the indicated tautomeric form **76** based on their electronic absorption spectra which were similar to those reported for the azo chromophore [64] and the results of the correlations of their acid dissociation constants with the Hammett equation [63].

Scheme 33

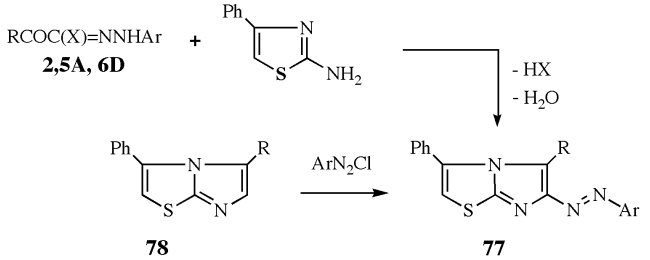


3.2 Imidazo[2,1-*b*]thiazoles.

Reaction of 2-amino-4-phenylthiazole with 2-oxoalkanehydrazonoyl halides **2** and **5A** was reported to give, in each case, a mixture of three products: the hydrohalide salt of the starting 2-aminothiazole, a tetrazine derivative and 6-arylazo-3,5-disubstituted imidazo[2,1-*b*]thiazoles **77** [49]. However, when equivalent amounts of hydrazonoyl halide and 2-amino-4-phenylthiazole were refluxed in ethanol in the presence of triethylamine, only the respective azo-products **77** were obtained in 80% yields. The similar reaction of 2-heteroaryl-2-oxohydrazonoyl bromide **6D** with 2-amino-4-phenylthiazole afforded the respective 6-arylazoimidazo[2,1-*b*]thiazoles **77** (Scheme 34) [21]. The structure **77** w as assigned for the isolated products on the basis of (i) the reaction of 2-aminothiazoles with α-halo ketones to give 5-substituted imidazo[2,1-*b*]thiazoles [65] and (ii) the alternate synthesis of **77** by coupling of diazonium salts with 3,5-diphenyl imidazo[2,1-*b*]thiazoles **78** (Scheme 34) [49].

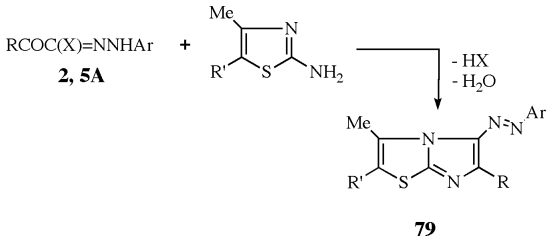
In another report [69], it was indicated that reaction of 2-amino-4-methylthiazole derivatives with the 2-oxohydra-

Scheme 34



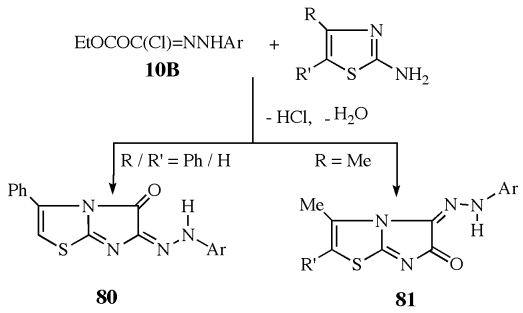
zonoyl halides **2** and **5A** led to the formation of the respective 3-arylazoimidazo[2,1-*b*]thiazoles **79** (Scheme 35). The other expected regioisomers were not formed.

Scheme 35



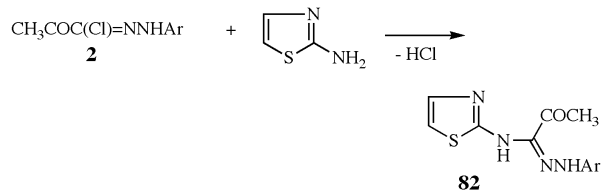
Reaction of 2-amino-4-phenylthiazole with ethyl *N*-(arylhydrazono)chloroacetate **10B** in the presence of triethylamine was reported to give one product that was assigned the structure **80** (Scheme 36) [49]. Although the isolated products **80** can have two tautomeric forms, they were assigned the indicated ketohydrazone tautomeric structure **80** on the basis of their IR spectra. The similar reaction of 2-amino-4-methylthiazole derivatives with ethyl (*N*-arylhydrazono)chloroacetate **10B**, however, was reported to yield, the other isomeric products **81** (Scheme 36) [69].

Scheme 36



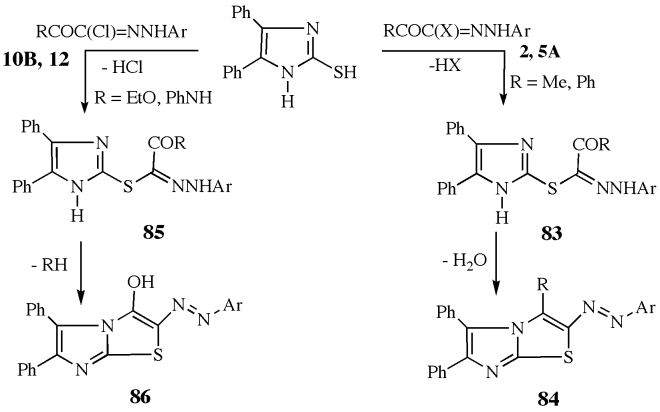
In contrast to the foregoing results, it was reported that reaction of 2-aminothiazole with *N*-aryl 2-oxopropanehydrazonoyl chlorides **2** afforded the amidrazone derivative **82** (Scheme 37) [70].

Scheme 37



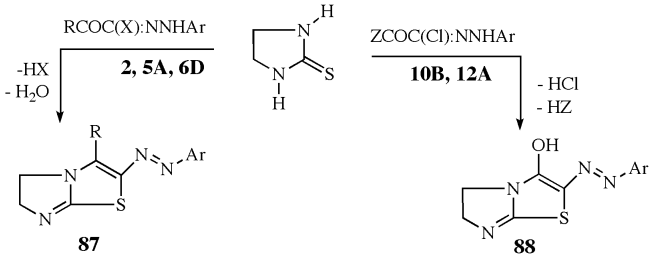
2-Mercapto-4,5-diphenylimidazole was reported to react with *N*-aryl 2-oxoalkanehydrazonoyl halides **2** and **5A** in the presence of triethylamine to give the respective thiohydrazonic esters **83** [60,66,67]. Treatment of the latter with polyphosphoric acid resulted in their cyclization to **84** (Scheme 38) [66].Similar reactions of 2-mercapto-4,5-diphenylimidazole with either ethyl (*N*-arylhydrazono)-chloroacetate **10B** or *N*-(arylhydrazono)chloroacetanilide **12** yielded one and the same product namely **86**. The intermediate thiohydrazonic esters **85** were not isolated (Scheme 38) [67]. However, in one report [60] such intermediates were said to be the end products [60].

Scheme 38



Reactions of 2-mercapto-4,5-dihydroimidazole with each of *N*-aryl 2-oxoalkanehydrazonoyl halides **2, 5A** [68] and **6D** [21] yielded the respective products **87** (Scheme 39). Similar reactions of the 2-mercapto-4,5-dihydroimidazole with either ethyl *N*-(arylhydrazono)chloroacetate **10B** or *N*-phenyl 2-oxo-2-phenylaminoethanehydrazonoyl chloride **12A** afforded the same product namely **88** (Scheme 39) [68].

Scheme 39

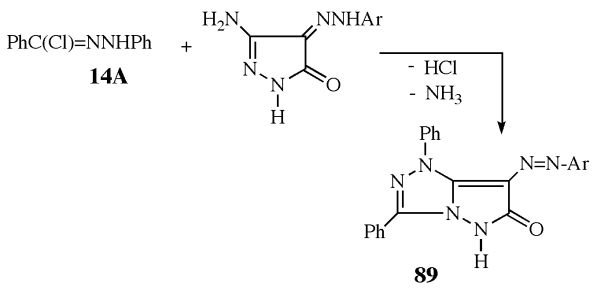


3.3 1*H*-Pyrazolo[5,1-*c*]-1,2,4-triazoles.

N-Phenyl benzenecarbohydrazonoyl chloride **14A** reacted with 3-amino-4-(arylhydrazono)pyrazolin-5-ones

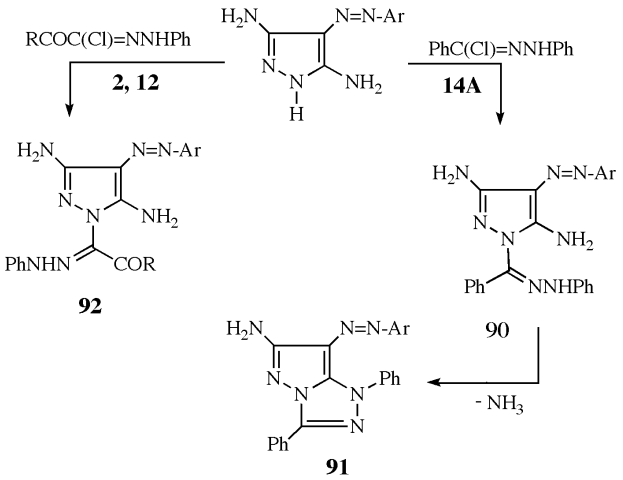
in refluxing ethanol to yield the respective 7-arylazo-1*H*-pyrazolo[5,1-*c*]-1,2,4-triazoles **89** (Scheme 40) [71].

Scheme 40



A similar reaction of *N*-phenyl benzenecarbohydrazonoyl chloride **14A** with 3,5-diamino-4-phenylazopyrazole was reported to yield **91** probably by elimination of ammonia from the intermediate amidrazone **90** (Scheme 41) [72,73]. However, reactions of the same diaminopyrazole with 2-oxohydrazonoyl chlorides **2** and **12** were reported to give the respective amidrazones **92** as end products (Scheme 41) [60,73]. No attempts to cyclize the latter were reported.

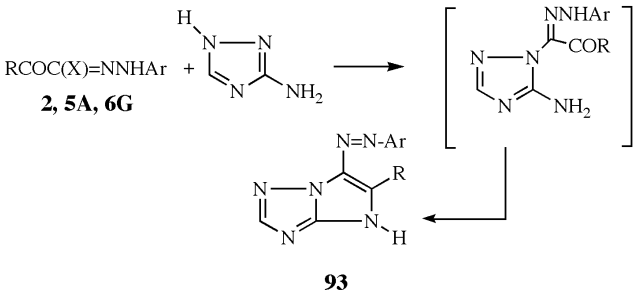
Scheme 41



3.4 Imidazo[1,2-*b*]-1,2,4-triazoles.

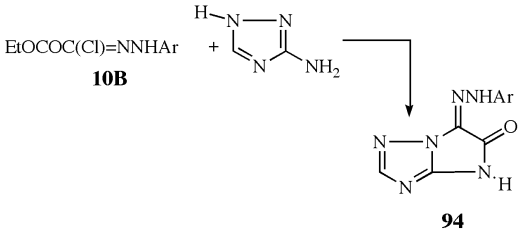
Reaction of 3-amino-1,2,4-triazole with 2-oxohydrazonoyl halides **2** and **5A** in ethanol was first reported [49] to yield the respective 3-arylazo-imidazo[1,2-*b*][1,2,4]triazoles **93** (Scheme 42). The similar reaction of the same aminotriazole with hydrazonoyl bromides **6G** was later reported [53] to afford the respective **93**. The isomeric 2-arylazo derivatives were not produced.

Scheme 42



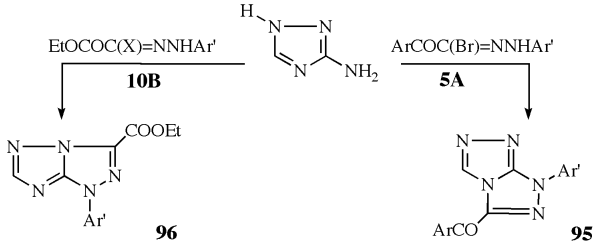
A similar reaction of 3-amino-1,2,4-triazole with ethyl *N*-arylhydrazonochloroacetate **10B** was reported to give **94** (Scheme 43) [49]. The other isomeric structures were rejected on the basis that (i) alkylation of 3-amino-1,2,4-triazole on N-4 is known to be rare and (ii) the isolated product was recovered unchanged upon treatment with oxidizing agents [49].

Scheme 43



In two other reports, it was indicated that reactions of 3-amino[1,2,4]triazole with 2-aryl-2-oxohydrazonoyl bromides **5A** [54] and ethyl *N*-arylhydrazonochoroacetate **10B** [59] in ethanol in the presence of triethylamine, follow different regiochemical pathways and proceed *via* elimination of ammonia from the initially formed amidrazone intermediates to give [1,2,4]triazolo[3,4-*c*][1,2,4]triazoles **95** and [1,2,4]triazolo[5,1-*c*][1,2,4]triazoles **96**, respectively (Scheme 44). In both cases no arylazo derivatives were formed.

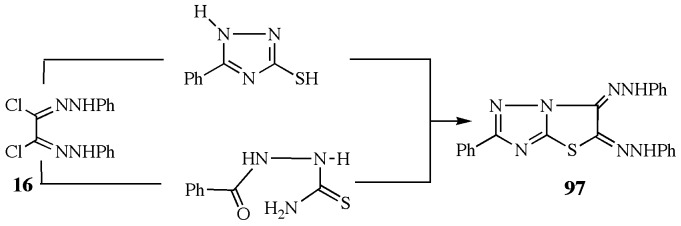
Scheme 44



3.5 Thiazolo[3,2-*b*]-1,2,4-triazoles.

When 5-phenyl-1,2,4-triazole-3-thione was allowed to react with *bis*(hydrazonoyl chloride) **16**, either in ethanol in the presence of sodium ethoxide at room temperature (Method A) or in refluxing chloroform in the presence of triethylamine (Method B), it gave a single crystalline product that was identified as 5,6-*bis*-(phenylhydrazono)-2-phenylthiazolo[3,2-*b*]-1,2,4-triazole **97**. The assigned structure was confirmed by its alternate synthesis by the reaction of the *bis*-halide **16** with 2-benzoylhydrazinethiocarboxamide [74] (Scheme 45). The other regioisomer, namely 5,6-*bis*-(phenylhydrazono)-3-phenylthiazolo[2,3-*c*]-1,2,4-triazole was thus rejected. Formation of **97** is in good agreement with literature reports which indicate that reaction of 5-aryl-3-mercapto-1,2,4-triazoles with haloketones affords 2-arylthiazolo[3,2-*b*]-1,2,4- triazole derivatives [75-78].

Scheme 45

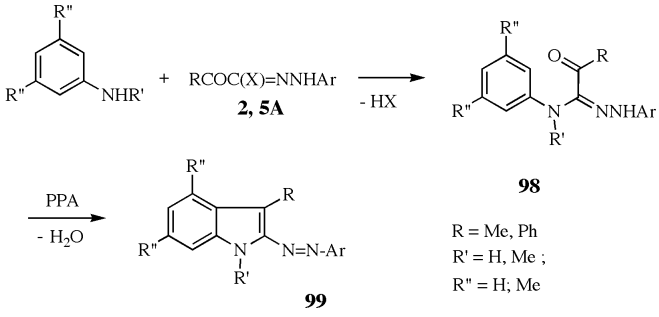


4. Arylazo Derivatives of 5,6-Biheterocycles.

4.1 Indoles.

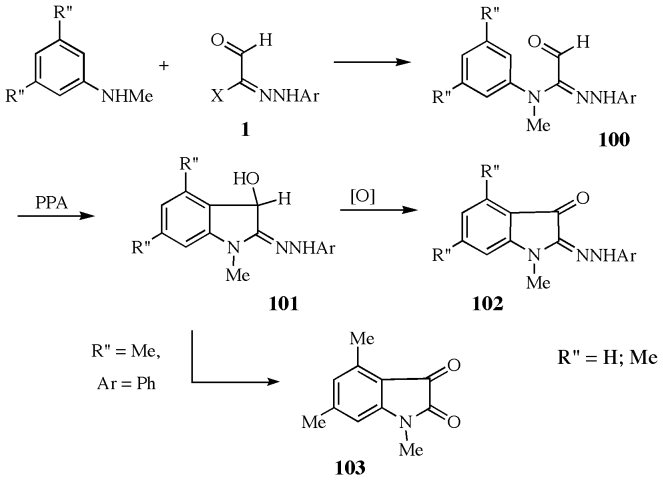
The reaction of *N*-aryl 2-oxoalkanehydrazonoyl halides **2** and **5A** each with aniline or *N*-methylaniline in ethanol in the presence of triethylamine afforded the respective amidrazone derivatives **98**. Addition of the latter to polyphosphoric acid preheated at 80 °C yielded the corresponding 2-arylazoindoles **99** (Scheme 46) [79,80].

Scheme 46



A similar treatment of the amidrazones **100** (R" = H or Me), prepared from the hydrazonoyl chloride **1** and *N*-methylaniline, with polyphosphoric acid was reported to yield the isatin derivatives **102** and **103** (Scheme 47) [80]. The formation of these products was considered to result from atmospheric oxidation of the cyclized intermediates **101**, followed by hydrolysis in the case of **103**. This process was said to be peculiar to aldehydic aminohydrazones which give systems bearing a hydrogen atom in position 3 of the indole ring: removal of this hydrogen by oxidation prevents water loss and leads to isatin derivatives.

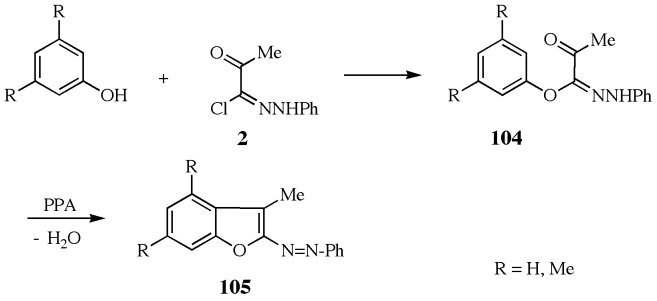
Scheme 47



4.2 Benzofurans.

3-Substituted 2-arylazobenzofurans **105** were synthesized by the reaction of 2-oxohydrazonoyl halide **2** with phenols in the presence of a base as catalyst such as triethylamine or ethoxide anion and cyclization of the resulting aryl hydrazonic esters **104** by treatment with polyphosphric acid (Scheme 48) [79].

Scheme 48



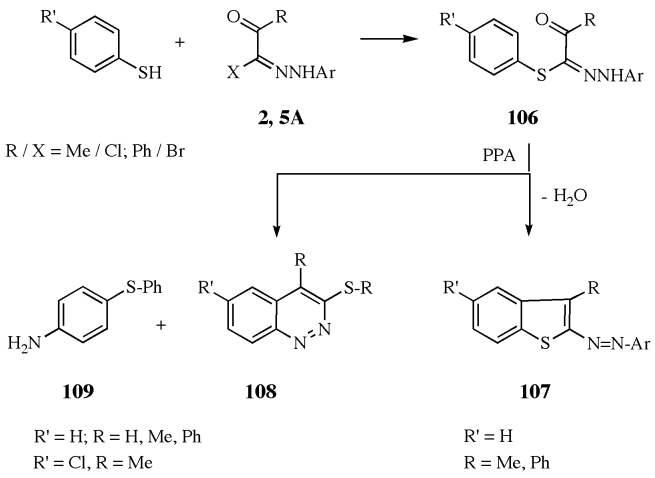
4.3 Benzothiophenes.

2-Arylazo-3-substituted-benzothiophenes **107** were obtained from the reactions of thiophenol with 2-oxohydrazonoyl halides **2** and **5A** in the presence of a base as

catalyst and treatment of the resulting aryl thiohydrazonic esters **106** with polyphosphric acid (Scheme 49) [79].

A similar treatment of some other thiohydrazonic esters, prepared from the hydrazonoyl halides **1**, **2**, **5A** and thiophenol, was reported to give the 3-(arylthio)cinnolines **108** and 4-aminophenyl phenyl sulfide **109**, formation of the latter was attributed to [3,5]-rearrangement of **106** (Scheme 49) [79,80].

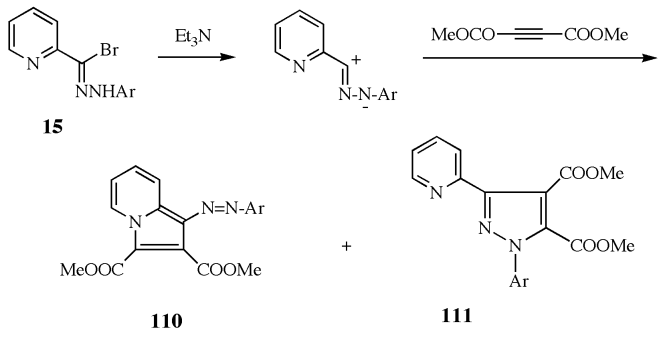
Scheme 49



4.4 Pyrrolo[1,2-*a*]pyridines.

Reaction of *N*-aryl 2-pyridinecarbohydrazonoyl bromide **15** with dimethyl acetylenedicarboxylate in the presence of triethylamine was reported to afford a mixture of the 1-arylazopyrrolo[1,2-*a*]pyridine **110** and the 1,3-dipolar cycloadduct **111** (Scheme 50) [81].

Scheme 50

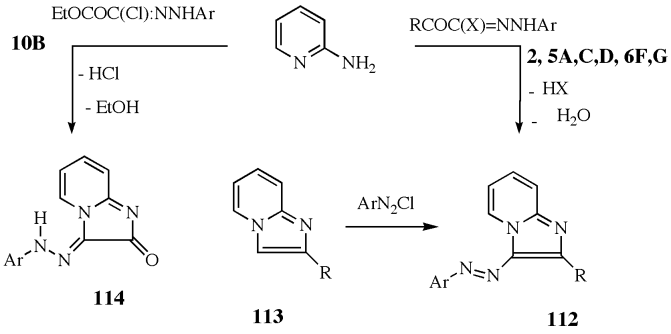


4.5 Imidazo[1,2-*a*]pyridines.

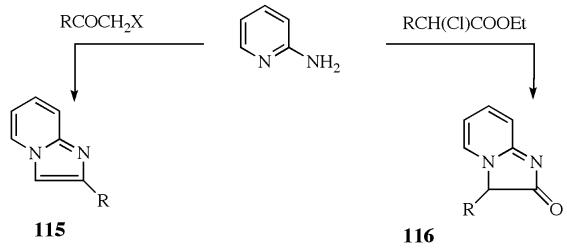
Reactions of 2-oxohydrazonoyl halides **2** and **5A** with 2-aminopyridine in ethanol at reflux gave the respective 3-arylazo-2-methylimidazo[1,2-*a*]pyridine **112** (Scheme 51) [49]. The assigned structure **112** was confirmed by the fact that coupling of 2-methylimidazo[1,2-*a*]pyridine **113** with *N*-nitrosoacetanilide or diazotized aniline in ethanol was found to yield a product identical in all respects with **112** (Ar = Ph) [49]. The isomeric 2-arylazo structure was rejected based on the fact that 2-aminopyridine has been known to react with α-haloketones to give **115** (Scheme 52) [58,82]. Later, similar reactions of 2-aminopyridine with other 2-oxohydrazonoyl halides (**5C,D** and **6F,G**) were reported to give the respective 3-arylazo derivatives of imidazo[1,2-*a*]pyridine **112** (Scheme 51) [31,48, 52,53,83,84]. In no such cases, were the isomeric 2-arylazo derivatives isolated. As before, the structures of the products were in some cases suggested by their synthesis from the respective 2-substituted imidazo[1,2-*a*]pyridines **113** and diazotized anilines (Scheme 51) [52].

Ethyl *N*-arylhydrazonochloroacetates **10B** reacted similarly with 2-aminopyridine and afforded **114** (Scheme 52) [49]. The other possible 2-arylhydrazono structure was rejected because reactions of 2-aminopyridine with α-haloesters are known to give **116** (Scheme 52) [49,58,82].

Scheme 51



Scheme 52

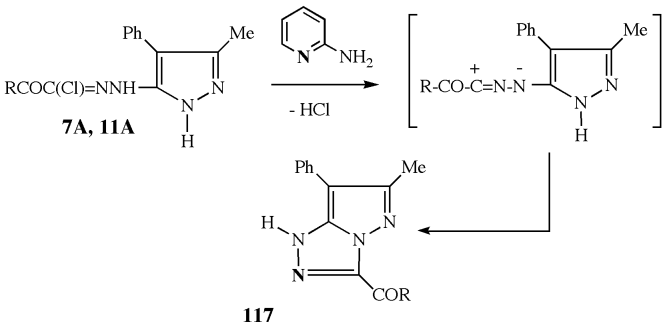


Similar reactions of 2-aminopyridine with *N*-(pyrazol-5-yl) 2-oxohydrazonoyl halides **7A** and **11A** in refluxing ethanol, in the presence of triethylamine or piperidine, were reported to give pyrazolotriazoles **117** probably by cyclization of the nitrilimine intermediates (Scheme 53) [27,85]. In this case it seems that 2-aminopyridine acted as a base catalyst.

4.6 Imidazo[1,2-*a*]pyrimidines.

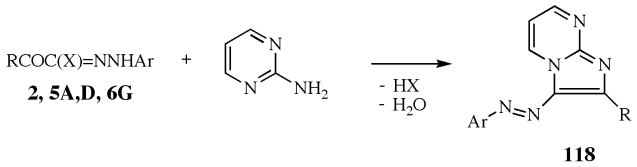
Reactions of 2-aminopyrimidine with 2-oxohydrazonoyl halides **2** and **5A** were first reported to yield the respective

Scheme 53

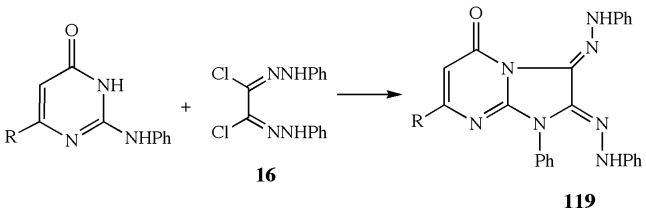


3-arylazoimidazo[1,2-*a*]pyrimidines **118** (Scheme 54) [49]. The other 2-arylazo regioisomeric structure was rejected based on the fact that reactions of 2-aminopyrimidine with α-haloketones are known to give 2-substituted imidazo[1,2-*a*]pyrimidines [49]. Other 2-oxohydrazonoyl halides, namely **5D** and **6G**, were reported later to react similarly with 2-aminopyrimidine and give the respective **118** (Scheme 54) [53,84].

Scheme 54



Scheme 55



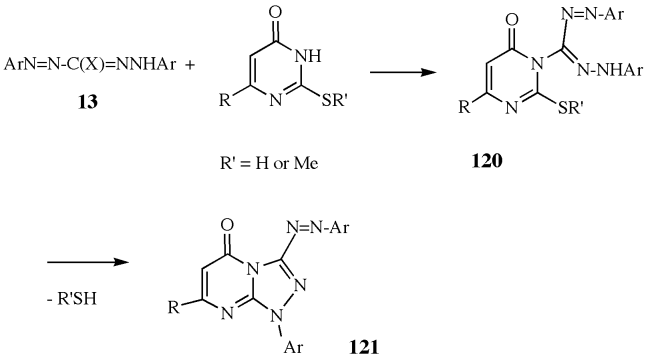
The reactions of the *bis*-hydrazonoyl chloride **16** with 2-phenylamino-6-substituted-pyrimidin-4-ones furnished 2,3-dihydro-7-substituted-2,3-di(phenylhydrazono)imidazo[1,2-*a*]pyrimidin-5(1*H*)-ones **119** (Scheme 55) [86]. The other regioisomers namely 2,3-dihydro-5-substituted-2,3-di(phenylhydrazono)imidazo[1,2-*a*]pyrimidin-7(1*H*)-ones were not produced. The assigned structure **119** for the isolated products was based on their ^{13}C NMR and IR spectral data. This regiochemical assignment is analogous to that reported for the formation of 2,3-dihydroimidazo[1,2-*a*]pyrimidin-5(1*H*)-ones from 1,2-dibromoethane with 2-arylamino-4(3*H*)-pyrimidinone derivatives [87].

4.7 [1,2,4]Triazolo[4,3-*a*]pyrimidines.

Recently, a one-pot synthesis of a series of 3-arylazo-[1,2,4]triazolo[4,3-*a*]pyrimid-5(1*H*)-ones **121** by the reactions of 2-thiouracil derivatives with *N*-aryl arylazomethanehydrazonoyl chlorides **13** in chloroform, in the presence of triethylamine at reflux, was reported (Scheme 56) [88]. The assignment of structure **121** was based on ^{13}C NMR and IR spectral data [89-91].

3-Chloroformazans **13** were also reported [88] to react similarly with 2-methylthiouracils to afford the same products **121**. This finding was considered to indicate that such reactions involve the respective amidrazones **120** as intermediates (Scheme 56) [88].

Scheme 56



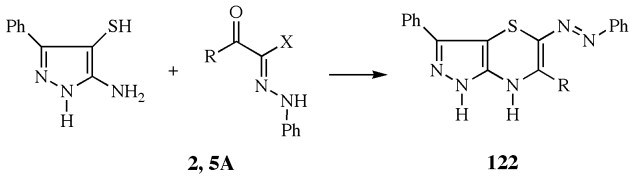
4.8 7*H*-Pyrazolo[4,3-*b*]-1,4-thiazines.

Reaction of 5-amino-4-mercapto-3-phenylpyrazole with *N*-aryl 2-oxohydrazonoyl halides **2** and **5A** in ethanol in the presence of triethylamine was reported to yield 2-(phenylazo)-3-substituted-7-phenylpyrazolo[4,3-*b*]-1,4-thiazines **122** (Scheme 57). In no case the other possible regioisomeric products namely 7-phenylazopyrazolo[4,3-*a*]-1,4-thiazine and 2-phenylazoimidazo[1,2-*b*]pyrazoles were formed [68].

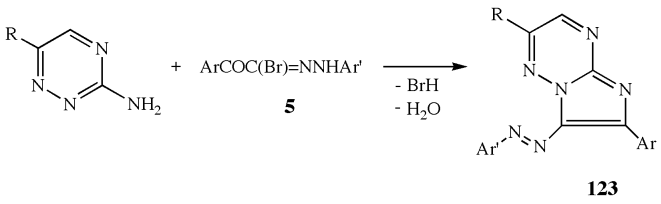
4.9 Imidazo[1,2-*b*]-1,2,4-triazines.

N-Aryl 2-aryl-2-oxoethanehydrazonoyl bromides **5** were reported to react with 3-amino-1,2,4-triazine to afford 3-arylazoimidazo[1,2-*b*]-1,2,4-triazines **123** *via* dehydrative cyclization of the initially formed amidrazones (Scheme 58) [92].

Scheme 57



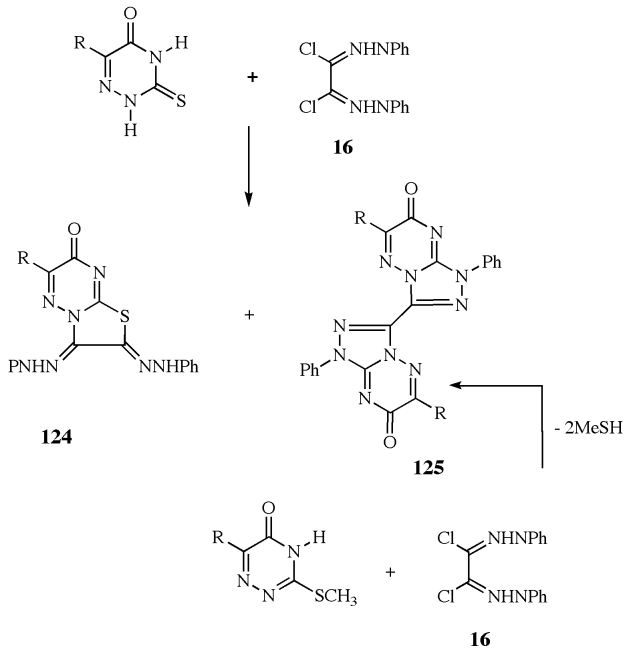
Scheme 58



4.10 Thiazolo[3,2-*b*]-1,2,4-triazines.

Reaction of the *bis*-hydrazonoyl chloride **16** with 6-benzyl-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4*H*)-one in ethanol in the presence of sodium ethoxide at room temperature gave a mixture of two products namely 2,3-bis(phenylhydrazono)thiazolo[3,2-*b*]-1,2,4-triazin-7-one **124** and 3,3'-bis-(1,2,4-triazolo[4,3-*b*]-1,2,4-triazin-7(1*H*)-one) **125**, in 72% and 10% yields, respectively (Scheme 59) [86]. The product **125** was obtained as the sole product by the reaction of the *bis*-hydrazonoyl chloride **16** with 6-benzyl-3-methylthio-5(4*H*)-1,2,4-triazinone (Scheme 59) [86]. The assigned structures **124** and **125** were assigned on the basis of their IR spectra [86,93,94].

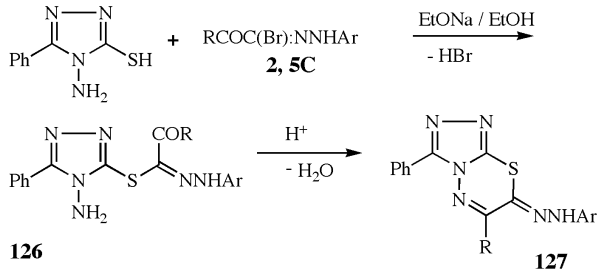
Scheme 59



4.11 [1,2,4]Triazolo[3,4-*b*]-1,3,4-thiadiazines.

Recently, it was reported that reaction of 4-amino-5-phenyl-4*H*-1,2,4-triazole-3-thiol with 2-aryl-2-oxoethanehydrazonoyl bromides **5A,C** in ethanol in the presence of sodium ethoxide afforded the respective thiohydrazonates **126** [95,96]. The isolated thiohydrazonates **126** were converted into the corresponding triazolothiadiazines **127** by treatment with acetic acid (Scheme 60) [95,96]. Similar reactions of the same 4-amino-1,2,4-triazole with hydrazonoyl bromides having electron-withdrawing substituents in the *N*-aryl group directly afforded, however, the respective 7-arylhydrazono-3,6-diaryl-1,2,4-triazolo[3,4-*b*]-1,3,4-thiadiazines **127**, probably *via in situ* dehydrative cyclization of the respective thiohydrazonates **126** [95].

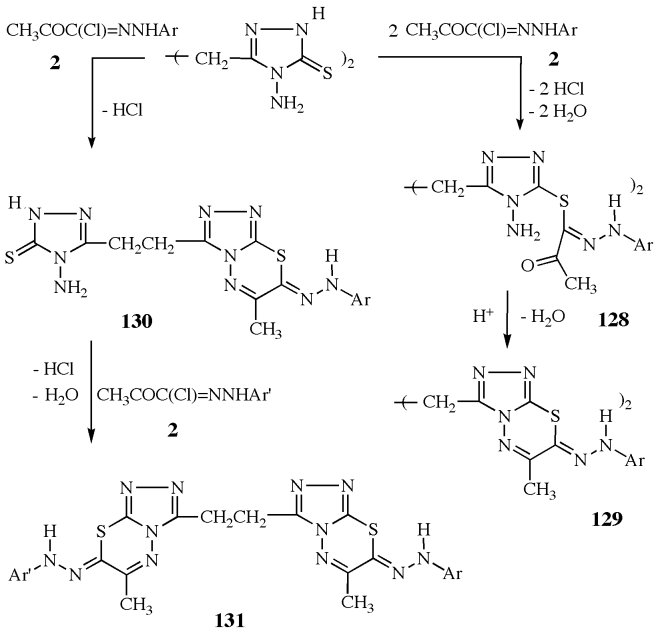
Scheme 60



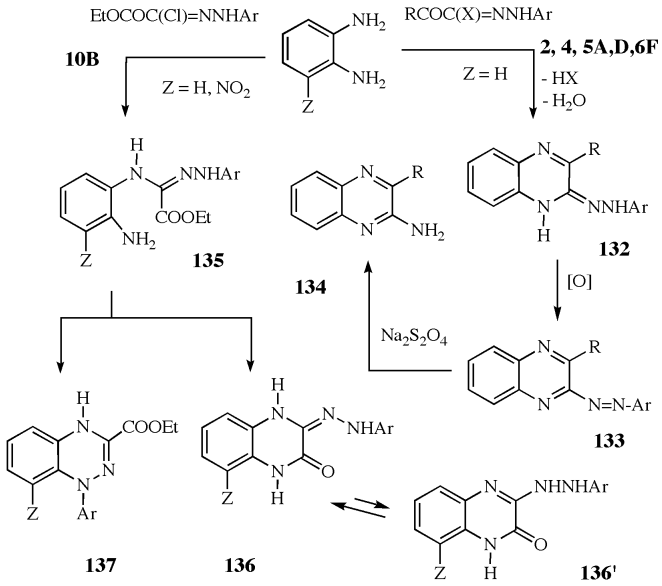
Also, reaction of 1,2-*bis*(4-amino-5-mercapto-4*H*-1,2,4-triazol-3-yl)ethane with two molar equivalents of an *N*-aryl 2-oxopropanehydrazonoyl chloride **2** in ethanol, in the presence of sodium ethoxide, at room temperature gave the respective 1,2-*bis*(7-arylhydrazono-7*H*-1,2,4-triazolo[3,4-*b*]-1,3,4-thiadiazin-3-yl)ethane **129** [97]. Formation of **129** indicates that the initially formed bis-thiohydrazonates **128** undergo *in situ* dehydrative cyclization to give **129** as end products (Scheme 61) [97]. The intermediacy of **128** was confirmed by their isolation and conversion into **129**. For example, reaction of **2** (Ar = Ph), with two molar equivalents of 1,2-bis(4-amino-5-mercapto-4*H*-1,2,4-triazol-3-yl)ethane in benzene in the presence of triethylamine at room temperature afforded **128** (Ar = Ph) in 92% yield. When this ester **128** was refluxed in acetic acid for 1 h, it yielded the corresponding **129** (Ar = Ph) in 90% yield (Scheme 61) [97].

Reaction of the same *bis*-triazolethione as above with one molar equivalent of *N*-(*p*-chlorophenyl) 2-oxoethanehydrazonoyl chloride **2** (Ar = 4-ClC_6H_4) in ethanol, in the presence of sodium ethoxide, yielded one product which was identified as **130** (Scheme 61) [97]. This product was used as precursor for the synthesis of a series of 1-(7-*p*-chlorophenylhydrazono-7*H*-[1,2,4]triazolo[3,4-*b*]-1,3,4-thiadiazin-3-yl)-2-(7-arylhydrazono-7*H*-1,2,4-triazolo[3,4-*b*]-1,3,4-thiadiazin-3-yl)ethanes **131** (Scheme 61) [97].

Scheme 61

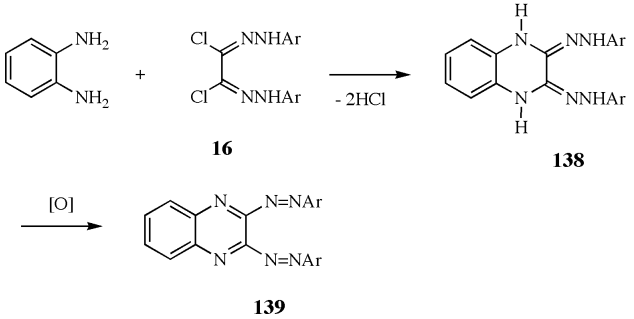


Scheme 62



138 that was converted into 2,3-*bis*-(arylazo)-quinoxaline **139** upon treatment with iodobenzene bis(trifluoroacetate) (Scheme 63) [102].

Scheme 63



5. Arylazo Derivatives of 6,6-Biheterocycles.

5.1 1,2-Dihydroquinoxalines.

Reactions of *o*-phenylenediamine with various hydrazonoyl chlorides *e.g.*, **2**, **4**, **5A,D** and **6F**, were reported to yield the respective 2-arylhydrazono-1,2-dihydroquinoxaline derivatives **132** [17,52,98,99]. The salts of the latter are deep colored substances similar to compounds described as dyes [17], whereas the free bases **132** were reported to be unstable in contact with air oxygen and to easily undergo oxidation to the red quinoxaline derivatives **133** [17]. Reduction of the azo derivative **133** with sodium dithionite, afforded the aminoquinoxaline derivative **134** (Scheme 62) [17].

The reaction of *o*-phenylenediamine with ethyl *N*-(arylhydrazono)chloroacetates **10B** was reported by several authors to yield 3-arylhydrazono-1,2,3,4-tetrahydroquinoxalin-2-ones **136** [98-101] (Scheme 62). Such products were said to exist as a mixture of two tautomeric forms **136** and **136'** as their ^{1}H NMR spectra revealed the presence of six protons that exchange with deuterium oxide [98]. In contrast to the foregoing findings, it was reported that reactions of *o*-phenylenediamine with ethyl *N*-(arylhydrazono)chloroacetates **10B** afforded ethyl 1-aryl-4*H*-benzo[*c*]-1,2,4-triazine-3-carboxylates **137** *via* elimination of the aromatic amino group as ammonia from the initially formed amidrazone intermediate **135** (Scheme 62) [59]. This unexpected result needs further investigation.

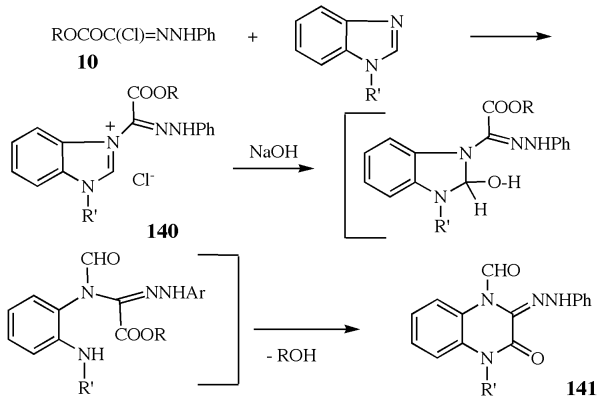
Reaction of the *bis*-(hydrazonoyl chloride) **16** with *o*-phenylenediamine gives the *bis*-hydrazone derivative

1-Alkylbenzimidazoles reacted with hydrazonoyl chlorides **10** and gave the corresponding salts **140**. Treatment of the latter salts with aqueous sodium hydroxide in ethanol yielded the 3,4-dihydroquinoxalin-2-one derivatives **141** *via* cleavage of the imidazole ring followed by cyclization (Scheme 64) [103].

5.2 4*H*-Benzo-1,4-oxazines.

2-Aminophenol was reported to react with each of the hydrazonoyl halides **2**, **5A,D** and **6F,H** in ethanol in the presence of sodium ethoxide to yield the respective 2-arylhydrazonobenzo-1,4-oxazine **142** or their 2-arylazo-tautomers (Scheme 65) [52,84,100,104,105]. Treatment of some of these products with ammonium acetate or phosporous pentasulfide yielded the corresponding arylazo derivatives of quinoxaline **132** or 1,4-thiazine **143**,

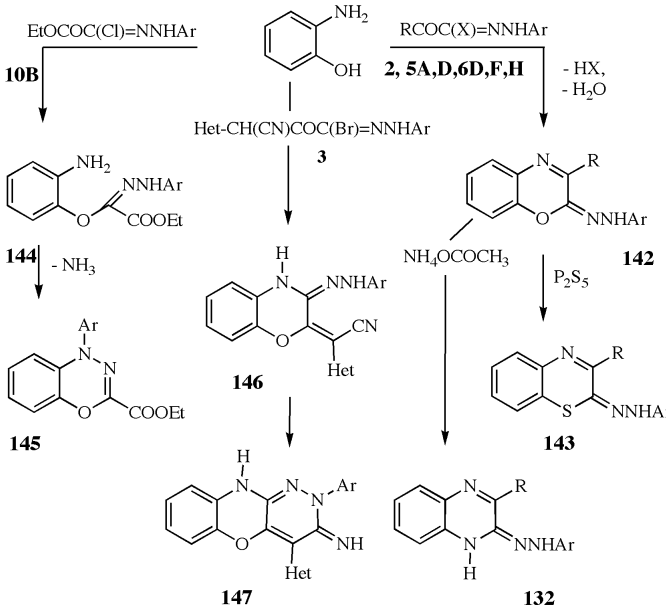
Scheme 64



respectively (Scheme 65) [104,105]. In contrast to these reports, it was indicated that reaction of 2-aminophenol with ethyl *N*-(arylhydrazono)chloroacetates **10B** afforded 2,4-disubstituted 1,3,4-oxadiazines **145** *via* the unexpected elimination of the aromatic amino group from the initially formed hydrazonic ester **144** (Scheme 64) [59]. This reaction requires further confirmation.

The reaction of 2-aminophenol with 2-oxohydrazonoyl bromide **3** was reported to afford tricyclic compounds **147** as sole end products *via* cyclization of the initially formed 3-arylhydrazono-1,4-benzoxazine derivatives **146** (Scheme 65) [106].

Scheme 65



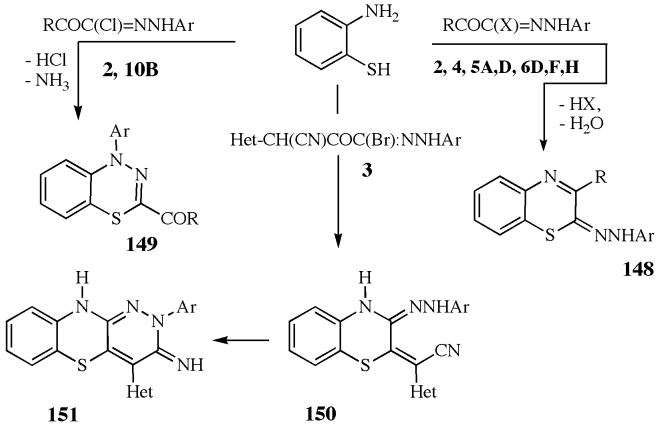
5.3 4*H*-1,4-Benzothiazines.

Reactions of 2-aminothiophenol with the hydrazonoyl halides **2, 4, 5A,D, 6D,F,H** and **10B** in ethanol in the presence of base catalyst were studied by several groups and in all cases they were reported to give the respective 2-arylazo-1,4-benzothiazine **148** (Scheme 66) [17,21,28,52, 84,100,104,107-109].

In contrast to these results, it was reported that reactions of 2-aminothiophenol with *N*-aryl 2-oxopropanehydrazonoyl chloride **2** and ethyl *N*-(arylhydrazono)chloroacetate **10B** afforded the respective 2-substituted 1,3,4-thiadiazines **149** (Scheme 66) [59,60]. Such reactions need further investigation to confirm the ambiguous elimination of an aromatic amino group.

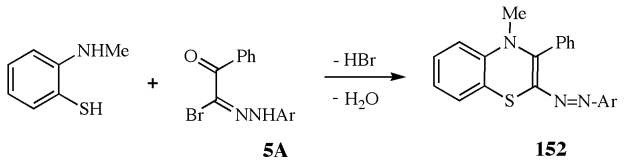
A similar reaction of 2-aminothiophenol with hydrazonoyl bromides **3** afforded tricyclic compounds **151** as sole products *via* cyclization of the initially formed 3-arylhydrazono-1,4-benzothiazine derivatives **150** (Scheme 66) [106].

Scheme 66



2-Methylaminothiophenol reacted similarly with *N*-aryl 2-oxo-2-phenylethanehydrazonoyl bromides **5A** and gave the corresponding 2-arylazo-3-phenyl-4-methyl-1,4-benzothiazines **152** (Scheme 67) [107].

Scheme 67



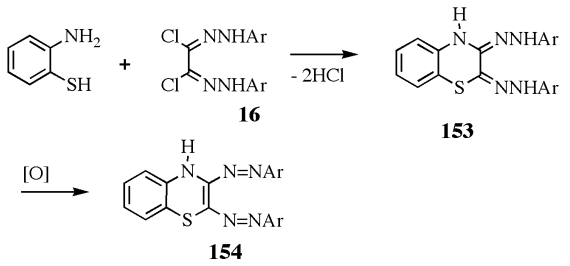
Bis-(hydrazonoyl chlorides) **16** were reported to react with 2-aminothiophenol and give the *bis*-hydrazone derivatives **153** that were readily oxidized to 2,3-*bis*-(arylazo)-1,4-benzothiazines **154** (Scheme 68) [110].

6. Arylazo Derivatives of 5,5,6-Triheterocycles.

6.1 Pyrrolo[2,1-*b*]benzothiazoles.

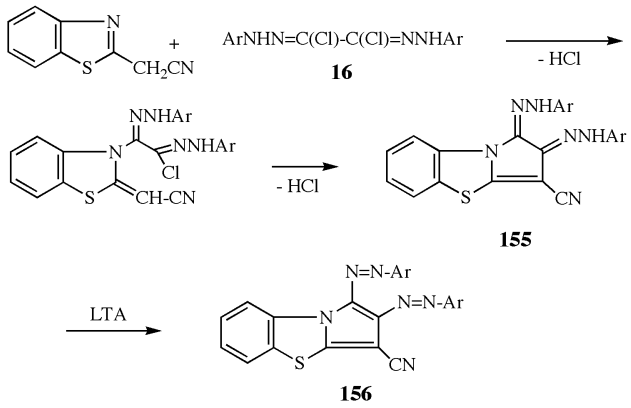
2-Cyanomethylbenzothiazole reacted with the *bis*-hydrazonoyl chlorides **16** in ethanol, in the presence of sodium ethoxide, and gave the respective bis-hydrazone

Scheme 68



derivatives **155**. Oxidation of the latter with lead tetraacetate afforded 1,2-*bis*-(arylazo)-3-cyanopyrrolo[2,1-*b*]-benzothiazoles **156** (Scheme 69) [111].

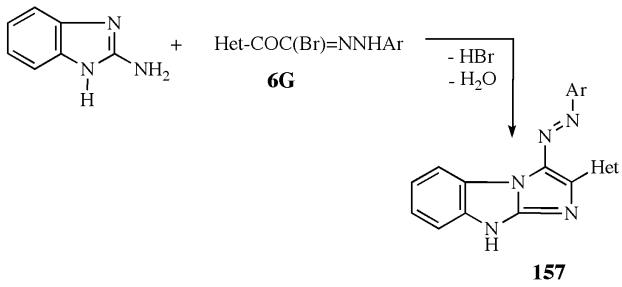
Scheme 69



6.2 Imidazo[1,2-*a*]benzimidazoles.

When the hydrazonoyl bromide **6G** was refluxed with 2-aminobenzimidazole in ethanol, it furnished 3-arylazo-2-(benzothiazol-2-yl)-1*H*-imidazo[1,2-*a*]benzimidazoles **157** [53] (Scheme 70).

Scheme 70



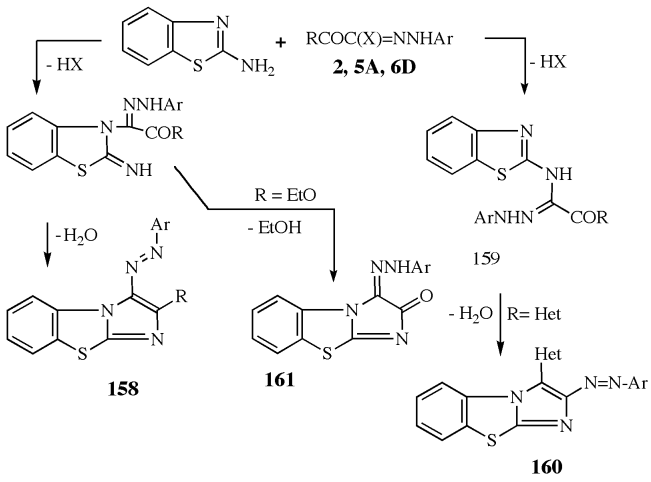
6.3 Imidazo[2,1-*b*]benzothiazoles.

Reactions of 2-aminobenzothiazole with *N*-aryl 2-oxopropanehydrazonoyl chloride **2** and *N*-aryl 2-oxo-2-phenylethanehydrazonoyl bromide **5A** were reported to give the respective 3-arylazoimidazolo[2,1-*b*]benzothiazoles **158** (Scheme 71) [69]. In another report, however, it was indicated, that reaction of the chloride **2** with 2-aminobenzothiazole yielded the unexpected amidrazone derivative **159** as end product which was not cyclized [55] (Scheme 71). No rationalization was given for this unexpected result.

When *N*-phenyl 2-oxo-2-(pyrazol-3-yl)ethanehydrazonoyl bromide **6D** was used in reaction with 2-aminobenzothiazole, it was reported that the product was 2-phenylazoimidazolo[2,1-*b*]benzothiazoles **160** (Scheme 71) [21]. No rationalization was given to account for this different regiochemical result.

A similar reaction of 2-aminobenzothiazole with ethyl *N*-(arylhydrazono)chloroacetates **10B** afforded **161** *via* cyclization of the initially formed respective amidrazones (Scheme 71) [69].

Scheme 71



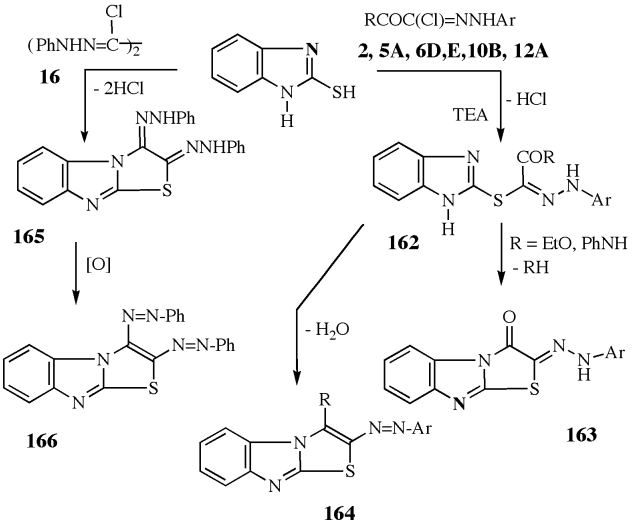
6.4 Thiazolo[3,2-*a*]benzimidazoles.

2-Mercaptobenzimidazole was reported to react with ethyl (*N*-arylhydrazono)chloroacetates **10B** and 2-phenylamino-2-oxoethanehydrazonoyl chlorides **12A** in the presence of base catalyst to yield the corresponding thiohydrazonic esters **162** (Scheme 72) [68]. Acid treatment of these products resulted in their cyclization to thiazolo[3,2-*a*]-benzimidazol-3-ones **163** (Scheme 72) [68].

Similar reactions of 2-oxopropanehydrazonoyl chloride **2**, 2-oxo-2-phenylethanehydrazonoyl bromide **5A** [68], 2-oxo-2-(pyrazol-3-yl)ethane-hydrazonoyl bromide **6D** [21,28] and *N*-phenyl 2-(2-phenyl-4-methylthiazol-5-yl)-2-oxoethanehydrazonoyl bromide **6E** [30] each with 2-mercaptobenzimidazole afforded the respective thiohydrazonic esters **162** that cyclized upon heating to the corresponding 2-arylazo- thiazolobenzimidazoles **164** (Scheme 72).

Very recently, it was reported that reaction of *bis*-(hydrazonoyl chloride) **16** with 2-mercaptobenzimidazole in chloroform in the presence of triethylamine at room temperature yielded 2,3-bis(phenylhydrazono)thiazolo[3,2-*a*]benzimidazole **165** (Scheme 72) [86]. Oxidation of **165** with lead(IV) acetate in glacial acetic acid yielded the corresponding bis-(phenylazo) derivative **166** (Scheme 72) [68],.

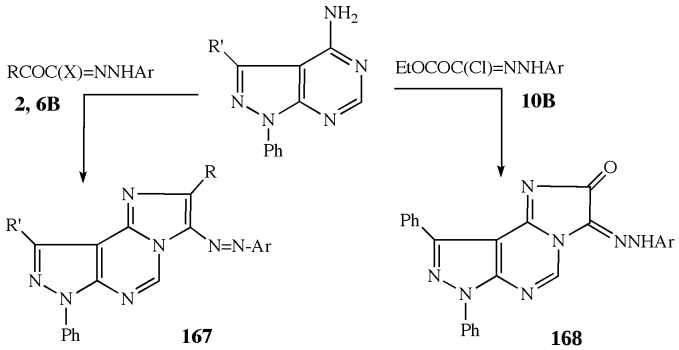
Scheme 72



6.5 1*H*-Imidazo[1,2-*c*]pyrazolo[4,3-*e*]pyrimidines.

4-Aminopyrazolo[3,4-*d*]pyrimidine was reported to react readily with 2-oxoalkanehydrazonoyl halides **2** and **6B** to give the respective 3-arylazo-1*H*-imidazo[1,2-*c*]pyrazolo[4,3-*e*]pyrimidines **167** (Scheme 73) [112,113]. When ethyl *N*-(arylhydrazono)chloroacetates **10B** were employed instead of **2** or **6B**, the reaction gave **168** (Scheme 73) [112,113].

Scheme 73

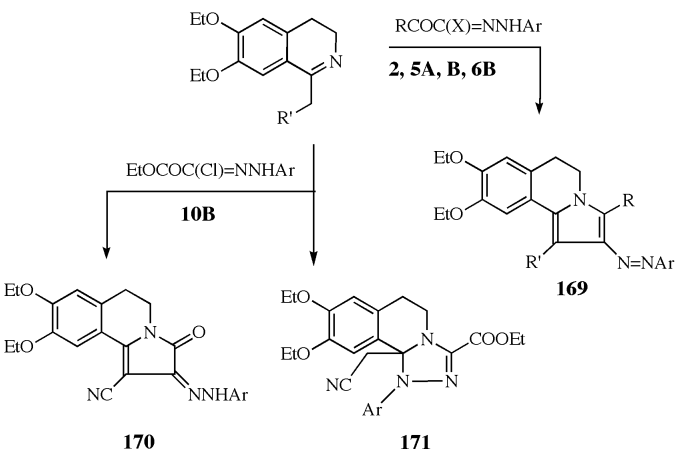


7. Arylazo Derivatives of 5,6,6-Triheterocycles.

7.1 Pyrrolo[2,1-*a*]isoquinolines.

Recently, reactions of 1-cyanomethyl and 1-ethoxycarbonylmethyl derivatives of 6,7-dialkoxy-3,4-dihydroisoquinoline each with 2-oxohydrazonoyl halides **2** and **5** in tetrahydrofuran, in the presence of triethylamine under reflux, has been studied and found to result in the formation of the respective 2-(arylazo)pyrrolo[2,1-*a*]isoquinoline derivatives **169** (Scheme 74) [114a]. A similar reaction of the same 1-cyanomethyl derivative with ethyl *N*-arylhydrazonochloroacetate **10B** afforded 2-arylhydrazono)pyrrolo[2,1-*a*]isoquinolin-1-carbonitrile **170** (Scheme 74) [114a]. The latter reaction was reported to give, however, the cycloadduct **171** when it was carried out in dichloromethane at room temperature (Scheme 74) [114b].

Scheme 74



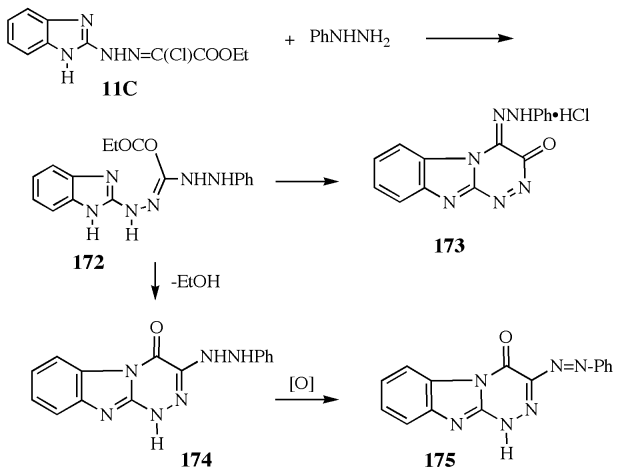
7.2 1,2,4-Triazino[4,3-*a*]benzimidazoles.

Reaction of phenylhydrazine with ethyl *N*-(benzimidazol-2-yl)hydrazonochloroacetate **11C** was reported to give the hydrochloride salt of 4-phenylhydrazono-3-oxo-[1,2,4]triazino[4,3-*a*]benzimidazole **173** (Scheme 75) [115]. This result requires further investigation as the expected product from cyclization of the initially formed intermediate **172** is expected to have the isomeric structure **174** or its oxidation product **175** (Scheme 75).

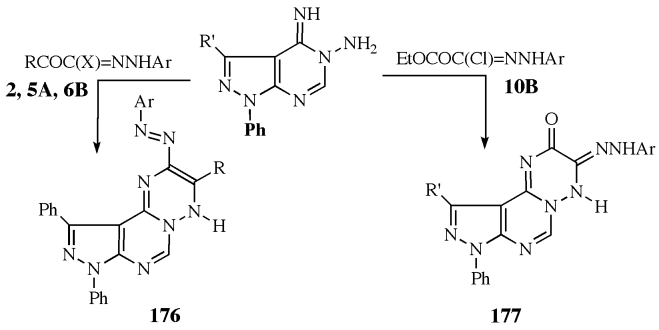
7.3 1*H*-Pyrazolo[3,4-*d*]pyrimido[3,4-*b*]-1,2,4-triazines.

5-Amino-1,3-diphenyl-4-imino-1*H*-pyrazolo[3,4-*d*]pyrimidine was reported to react with *N*-aryl-2-oxoalkanehydrazonoyl halides **2, 5A** and **6B** to give the respective 6-arylazopyrazolo[3,4-*d*]pyrimido[3,4-*b*]-1,2,4-triazines **176**. When ethyl *N*-(arylhydrazono)chloroacetate **10B** was used in this reaction, it gave **177** (Scheme 76) [116,117].

Scheme 75



Scheme 76

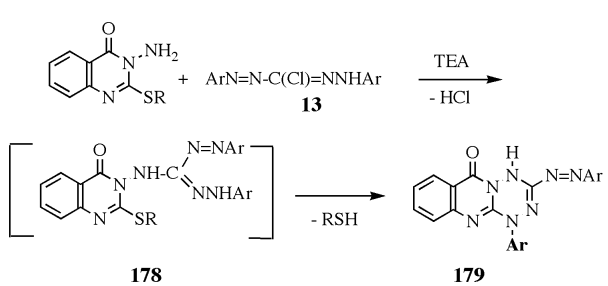


8. Arylazo Derivatives of 6,6,6-Triheterocycles.

8.1 1,2,4,5-Tetrazino[3,2-*b*]quinazolines.

N-Aryl arylazomethanehydrazonoyl chlorides **13** have been reported to react with 3-amino-2-thioxo-4(1*H*)quinazolinone or its methylthio derivative in refluxing ethanol in the presence of triethylamine to afford the respective 3-arylazo-6*H*-1,2,4,5-tetrazino[3,2-*b*]quinazolin-6-ones **179** *via* elimination of hydrogen sulphide or methanethiol, respectively, from the initially formed amidrazone intermediates **178** (Scheme 77) [118].

Scheme 77



9. Arylazoheterocycles of Industrial Interest.

An increasing understanding of the fundamental chemistry of arylazo derivatives of various heterocyclic ring systems has enabled chemists to explore their utilities in various industrial fields. For example, many of such derivatives are continuously evaluated and patented for potential use in various sectors of industry including hair dyeing [119], thermal transfer printing [120], nonlinear optics [121], disperse dyes [122], pigments [123], dyeing and printing polyesters [124] and ink-jet inks [125].

10. Conclusion.

Taking the number of references as a measure of how extensively a given subject has been studied, one may conclude, on the basis of the literature reports cited herein, that the synthesis of arylazoheterocycles *via* hydrazonoyl halides has been studied by a large number of investigators. The results indicate that hydrazonoyl halides are useful and versatile building blocks for the synthesis of arylazo derivatives of a wide variety of heterocyclic systems. Studies have been focused hitherto on the synthesis of mono- and di-arylazo derivatives. Nevertheless, synthesis of other arylazo derivatives should also be of interest. We hope that this review will further stimulate interest in exploring other utilities of hydrazonoyl halides for the synthesis of fluorescent arylazoheterocycles and their applications in fields such as phototherapy, laser chemistry, high performance sensors, fluorescence probes or electro-luminescence devices.

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