Recent Development in the Chemistry of Arylazoazolones

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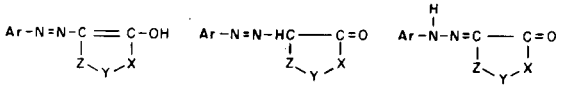
Introduction.

Five membered heterocyclic compounds containing a methylene or methinyl group adjacent to a carbonyl groups couple with aromatic diazonium compounds to give the corresponding azo derivatives [1]. The products may have one of the potentially tautomeric structures **1**, **2** and **3**.



1 **2** **3**

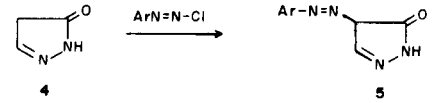
From time to time various workers have produced evidence either in favour of one or more of these forms or the existence of a tautomeric equilibrium involving two or more of them. The formation of a mixture of the methyl derivatives of **1** and **3** upon treatment of a series of the arylazo derivatives of five membered heterocyclic carbonyl compounds with etherial diazomethane [2-6] may indicate that these compounds are present, at least in ether solution, as an equilibrium mixture in which form **1** and **3** predominate. However, it is generally assumed that the hydrazone is the stable form whenever coupling takes place at a methylene carbon atom. Some authors [5,7-11] have presented spectral data in favour of this view. These data indicated the existance of intramolecular bonding between the C=O and NH groups. Also nmr data were interpreted by Jones [8] and Pelz [9] in favour of the hydrazone form **3**. However, Snavely *et al.* [12,13] have interpreted the infrared and nmr data in favour of structure **3**. Polarography has been recently employed to shed further light on this problem and evidence for dependence of the structure of these compounds in solutions on the *p*H of the solution could be obtained [14-17].

When coupling occurs on a methinyl carbon atom, without elimination of a group, only the azo structure is possible [1].

Methods of Preparation.

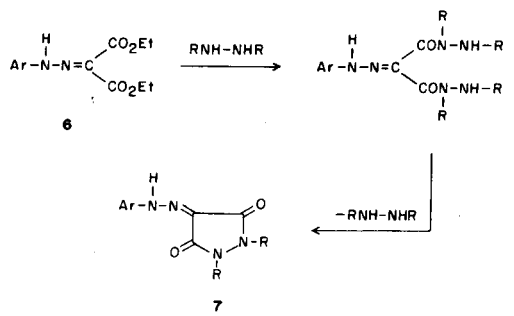
(1) Action of Aromatic Diazonium Salts on Heterocyclic Compounds.

Azoles carrying electron-donating functional substituent at a suitable position couple readily with diazotized amines to yield the corresponding arylazo derivatives. Thus, arylhydrazonoazolones are usually prepared *via* coupling reactions of diazotized amines with active methylene azolones [17-87]. The reaction is usually conducted in the presence of a base like sodium acetate [38-45], sodium carbonate [19-37] sodium hydroxide [19-37] or pyridine [30,54] and usually excellent yields of the hydrazones are formed by this procedure. For example, 4-arylazo-2-pyrazolin-5-one (**5**) is obtained by treatment of 2-pyrazolin-5-one (**4**) in dilute alkali with the appropriate diazonium salts [19,20]. Heterocyclic amines could be also coupled in acid media to yield arylazo derivatives [88].



4 **5**

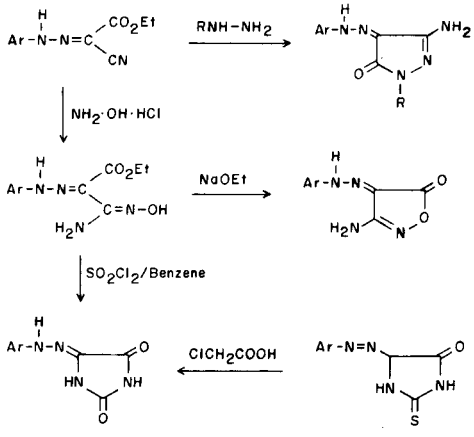
When the heterocyclic azolones are not readily accessible an indirect cyclization procedure of acyclic hydrazones has been utilized [89-143]. For example, 4-arylazo-3,5-pyrazolidenediones **7** are obtained *via* action of hydrazines on arylazo derivatives of diethylmalonate **6** [144-147]. Also, 3-amino-4-arylazo-2-pyrazolin-5-ones are prepared in much better yields *via* cyclization of the arylazo derivatives of ethyl cyanoacetate (*cf.* Chart 1) [122].



6 **7**

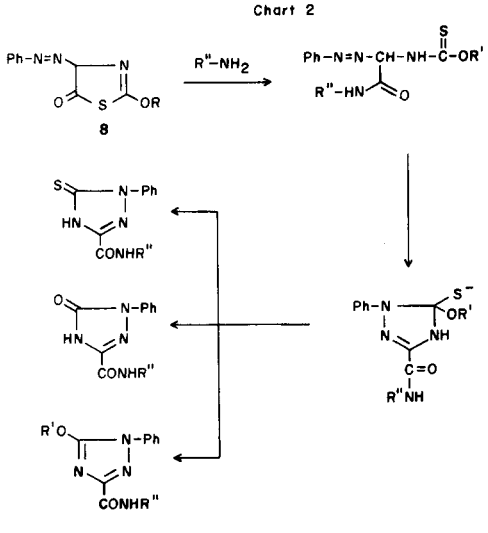
Similarly, 3-amino-4-arylazo-2-isoxazolin-5-one could be synthesised only *via* cyclization of the amidoximes resulting from the reaction of hydroxylamine with the arylazo derivatives of ethyl cyanoacetate [148,149]. These amidoximes could be also rearranged in a Tiemann-like rearrangement reaction into the arylazohydantoins [142]; the latter can be also obtained by the action of chloroacetic acid on arylazo-2-thiohydantoins (*cf.* Chart 1) [150].

Chart 1



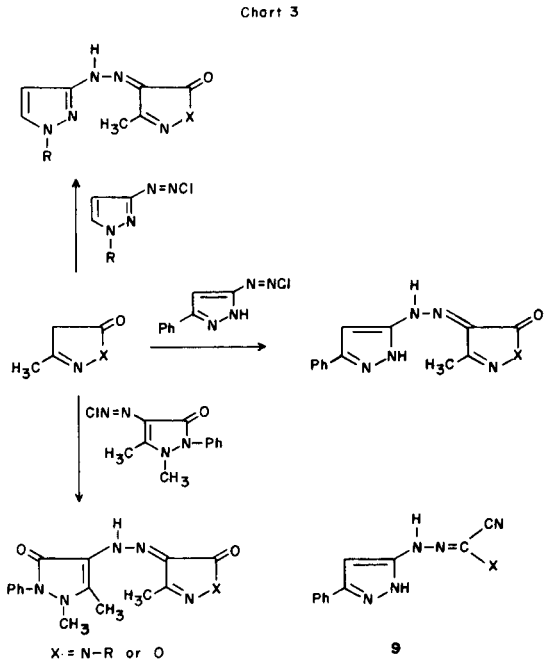
The reaction of amines with 4-phenylazo derivatives **8** results in their rearrangement into triazolines. Depending on the basicity of the amines and the size of the alkoxy group, three different triazolines are obtained. In all cases the first step involves nucleophilic addition of the amine to the carbonyl group followed by ring opening and further ring closure [79,151] (*cf.* Chart 2).

Chart 2

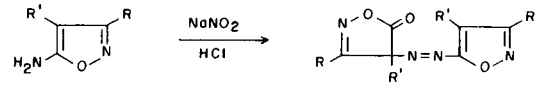


Heterocyclic diazonium salts were utilized for synthesis of arylhydrazonoazolones [26,60-69]. Thus, diazotized 4-aminoantipyrine, 5-aminopyrazoles and 5-amino-3-phenylpyrazole were reported to couple with pyrazolones and isoxazolones to yield the corresponding hydrazones. It is interesting to report here that hydrazones derived from diazotized 5-amino-3-phenylpyrazole and azolones are, in contrast to hydrazones like **9**, resistant to cyclization under a variety of conditions [150,152-162] (*cf.* Chart 3).

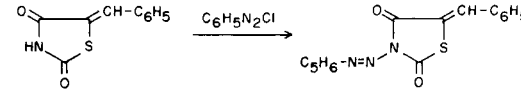
Chart 3



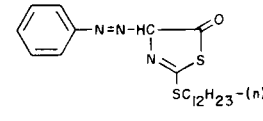
The addition of sodium nitrite to 5-amino-3,4-dialkylisoxazole in aqueous hydrochloric acid effects an oxidative coupling reaction to yield 3,4-dialkyl-4-(3,4-dialkyl-5-isoxazolylazo)-2-isoxazolin-5-one (**10**) [46,60].



Treatment of 5-benzylidene-2,4-thiazolidinedione with benzenediazonium chloride effects *N*-coupling with the formation of 3-phenylazo-5-benzylidene-2,4-thiazolidinedione (**11**) [49].

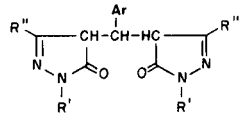


Instead of diazonium salts, diazoamino compounds have been used in the coupling reaction with the active methylene group in the heterocyclic compounds [43,78]. For example, treatment of 2-*n*-dodecylthio-2-thiazolin-5-one hydrobromide with diazoaminobenzene in alcoholic solution gives 2-*n*-dodecylthio-4-phenylazo-2-thiazolin-5-one (**12**) [78].



Although an alkyl substituted methylene group may undergo normal coupling, *e.g.* 3,4-dimethylpyrazolone [9], yet other substituents such as triarylmethyl [80], acyl [42, 81,82], isopropylidine, and halogen [165], have been reported to be cleaved upon coupling with diazonium salts. Similar cleavages have been reported [163]. Upon treatment of arylidenebis(2-pyrazolin-5-ones) (**13**) with diazonium salts 4-arylazo compounds were formed. However, under certain conditions, it has been possible to isolate the intermediate carrying both the acyl group and the azo group (*cf.* **14**) [42].

A variety of heterocyclic compounds and aromatic amines have been coupled together and some of the resulting arylazo derivatives have been reviewed [1,86,87,89,164].



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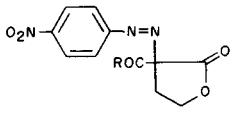

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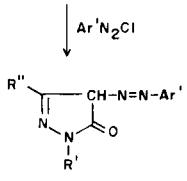
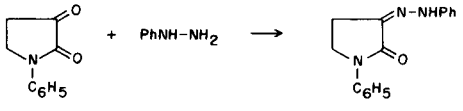


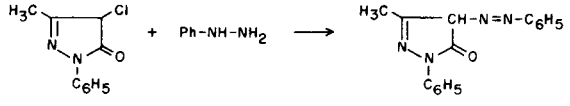
(2) Action of Arylhydrazines on Heterocyclic Compounds.

Phenylhydrazine reacts with 2,3-diketopyrrolidine in acetic acid to give 3-phenylhydrazono-2-ketopyrrolidinone (**15**) [90].

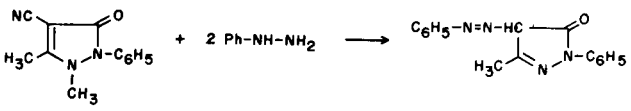


15

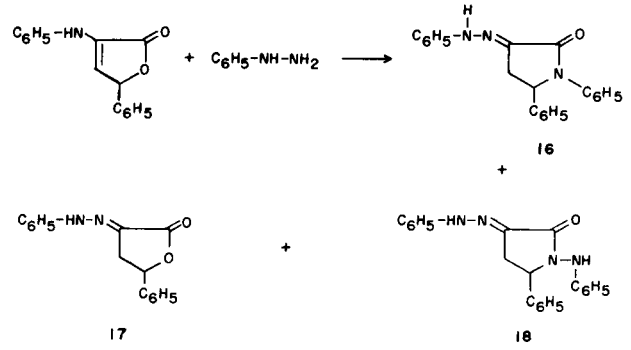
A number of 2-pyrazolin-5-ones having substituents at C-4 react with arylhydrazines by replacement of the substituents to give 4-arylazo derivatives [91-92]. For example, treatment of 4-chloro-3-methyl-1-phenyl-2-pyrazolin-5-one with phenylhydrazine yields the corresponding 4-phenylazo derivative [119].



Ridi [93] has reported that the reaction of 2,3-dimethyl-1-phenyl-4-nitroso-3-pyrazolin-5-one with phenylhydrazine gives 4-phenylazo-3-methyl-1-phenyl-2-pyrazolin-5-one. This may occur by replacement of the methylphenylhydrazine moiety in the 3-pyrazolin-5-one by phenylhydrazine. The 4-oximino-2-pyrazolin-5-one could then react with phenylhydrazine to give the reported product.

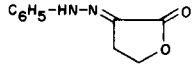


The reaction of 5-phenyl-3-anilino-2(5*H*)-furanone with phenylhydrazine yields a mixture of three products, 1,5-diphenyl-2,3-pyrrolidinedione-3-phenylhydrazone (**16**), 2-phenyl-4-phenylhydrazonobuterolactone (**17**) and 1-anilino-3-phenylhydrazono-2-oxo-5-phenylpyrrolidine (**18**) [94].



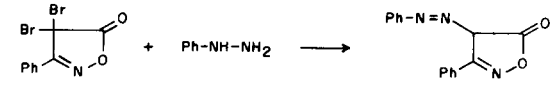
16 17 18

When butyrolactone-4-oxime is boiled with hydrochloric acid for few minutes then treated with phenylhydrazine acetate in alkaline medium, buterolactone 4-phenylhydrazone (**19**) is formed [95].



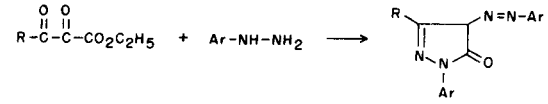
19

Arylazo derivatives can also be obtained by treatment of a *gem*-dibromide with phenylhydrazine [96]. For example, 4,4-dibromo-3-phenyl-5-isoxazolone reacts with phenylhydrazine to give 4-phenylazo-3-phenyl-2-isoxazolin-5-one [96].



(3) Action of Acids and Bases on Arylazo-β-ketoesters.

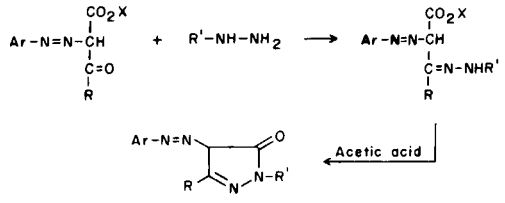
The hydrolysis of arylazo-β-ketoesters with hydrochloric acid affords, among the reaction products, arylazo pyrazolones of general formula **20** probably formed *via* the action of eliminated arylhydrazine on β-keto acid or its ester [97].



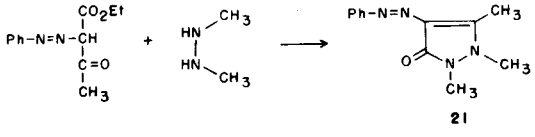
20

Arylazo-β-ketoesters react with hydrazines to give 4-arylazo-5-pyrazolone derivatives [98-112]. The intermediate

phenylhydrazone derivatives have been isolated in some cases and they can be cyclised to the corresponding azo pyrazolones by boiling in acetic acid [113].

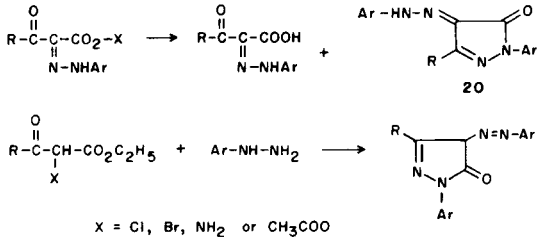


Elguero *et al.* [10] have prepared 1,2,3-trimethyl-4-phenylazo-3-pyrazolin-5-ones **21** by the reaction of *N,N'*-dimethylhydrazine with α-phenylazoacetoacetic ester.

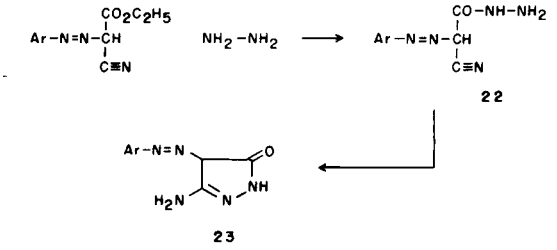


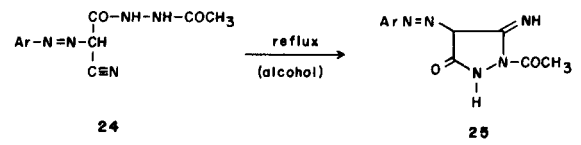
21

Treatment of α,β-diketoesters with hydrazines effects their cyclization into 4-arylazo-2-pyrazolin-5-ones **20**, probably formed *via* the intermediate phenylhydrazones [117]. Instead of the ester, hydrazides of α,β-diketoacids have been used [118]. A very similar synthesis is the use of an α-oximino-β-ketoester and a hydrazine [118]; also quite similar is the cyclisation of α-chloro [119,165], α-amino [120] and/or α-acyloxy [121] β-ketoesters with hydrazines. Apparently an oxidation of a hydrazino to an azo function occurs in the course of the last three reactions.

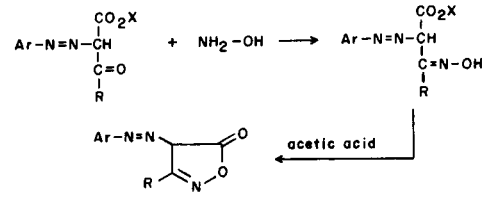


The reaction of ethyl cyanoacetate with hydrazine hydrate leads to the formation of 3-amino-4-arylazo-2-pyrazolin-5-ones (**23**), probably formed *via* the cyclisation of the intermediate hydrazide (**22**) [122]. In support of this view Dubenko and Gorbenko [123] have reported that the cyclisation of phenylazocyanoacetic acid *N*-acetylhydrazide (**24**) leads to the formation of 4-arylazo-1-acetyl-5-iminopyrazolidin-3-one (**25**).

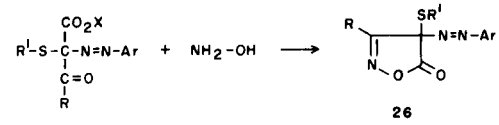




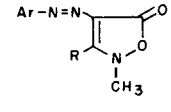
Treatment of arylazo-β-ketoesters with hydroxylamine generally leads to the formation of 4-arylazo-2-isoxazolin-5-ones [111,124-126]. In some cases the intermediate oxime derivative can be isolated and cyclised to the isoxazolone derivative by boiling with acetic acid [125].



α-Ethylthio-α-arylazo-β-ketoesters react with hydroxylamine to give the arylazo derivatives **26** without elimination of the ethylthio group [127].



Treatment of α-arylazo derivatives of β-ketoesters with *N*-methylhydroxylamine yields the corresponding 4-arylazo-3-isoxazolin-5-ones **27** [3,4,128].

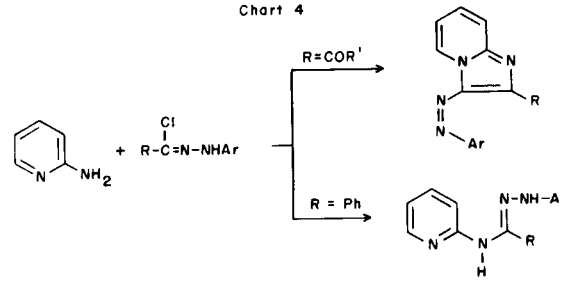


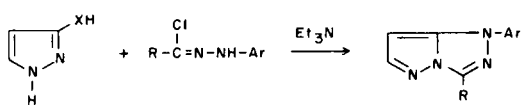
27

(4) Reactions of Heterocyclic Amines with Hydrazidic Halides.

Recently, a variety of arylazo fused heterocycles have been prepared *via* reaction of the hydrazonyl chloride derivatives with aminoazoles and aminoazines [166,167]. However, in some cases the reaction resulted in a novel 2 + 3 cycloaddition yielding fused 1,2,4-triazoles, examples are shown in Chart 4.

Chart 4

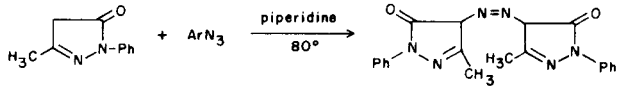




(5) Miscellaneous Methods.

No attempt is made here to include all those methods described for the preparation of individual arylazo heterocyclic compounds. Only some of these are reported here.

3-Methyl-1-phenyl-2-pyrazolin-5-one reacts with aryl or arylsulphonyl azides to yield azopyrazolones **28** [129].



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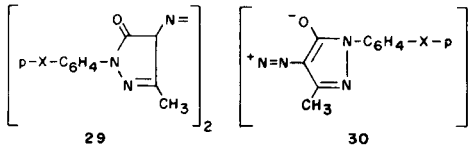
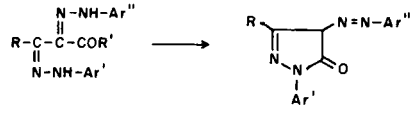
A number of azopyrazolone dyes **29** have been synthesized by an azo group transfer of heterocyclic diazonium salts to 1-substituted-3-methyl-5-pyrazolones. 2-Azido-3-ethylbenzothiazolium fluoroborate or 2-azido-3-ethyl-4,5-dimethylthiazolium fluoroborate may be used as the heterocyclic diazonium salt. Kinetic investigation of the dye synthesis point to a multiple stage mechanism with intermediate formation of 4-diazo-3-methylpyrazolones **30** [130].



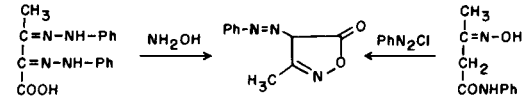
29 **30**

Cyclisation of a variety of bishydrazones of α,β-diketoacids [131-133], α,β-diketoesters [134,135], and α,β-diketoamides [136], using either acid, base or heat has been reported to give 4-arylazo-2-pyrazolin-5-ones. In this reaction the aryl groups have usually been the same, although Kleene [135] has used different aryl groups. Chargaff and Magasanik [137] have reported that the oxidation of the 1,2-bisphenylhydrazone of mesoxaldehyde gave rise to 4-phenylazo-1-phenyl-2-pyrazolin-5-one.

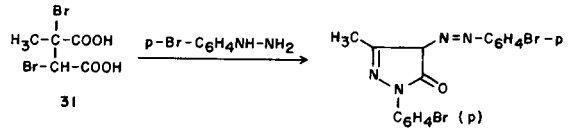


Similarly ozazones could be converted into arylazopyrazolone derivatives [132,133,16].

When acetoacetanilide oxime is treated with benzenediazonium chloride, both coupling and cyclisation *via* the loss of aniline, take place with the formation of 3-methyl-4-phenylazo-2-isoxazolin-5-one [140]. The latter compound can also be obtained by the action of hydroxylamine on α,β-diketobutyric acid ozazone [133].

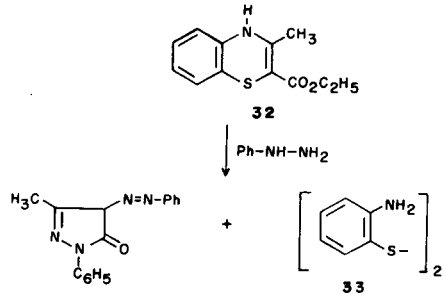


Fichter [141] has reported an arylazo-2-pyrazolin-5-one as one of the products from the reaction of α,α'-dibromo-α-methylsuccinic acid (**31**) with *p*-bromophenylhydrazine.



31

When ethyl 3-methyl-4*H*-benzo-1,4-thiazine-2-carboxylate (**32**) is heated with phenylhydrazine in ethanol, the thiazine ring is ruptured and 3-methyl-1-phenyl-4-phenylazopyrazolone is formed together with the disulphide, **33** [168].

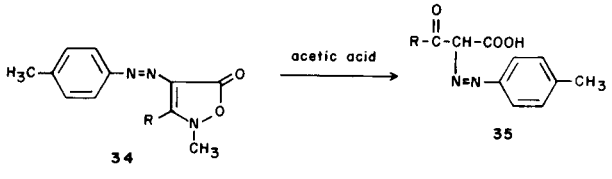


32 **33**

Chemical Properties.

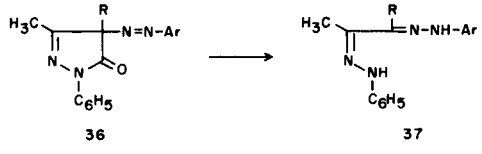
(1) Action of Acids and Alkalies.

The introduction of the arylazo function makes the heterocyclic ring less aromatic. Consequently, arylazoazoles undergo ring cleavage more readily than the corresponding parent compounds. Thus, 3-substituted-2-methyl-4-arylazo-3-isoxazolin-5-ones **34** readily undergo heterocyclic ring cleavage by the action of hot acetic acid with the formation of α-arylazoacetoacetic acid (**35**). Under similar conditions 3-isoxazolin-5-ones are not cleaved [3].



34 **35**

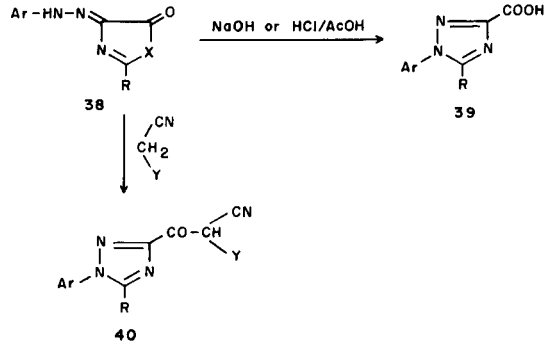
When 4-alkyl(or aryl)-4-arylazopyrazolones **36** are treated with concentrated alkali the pyrazolone ring is cleaved with the formation of the ozazone **37** [9].



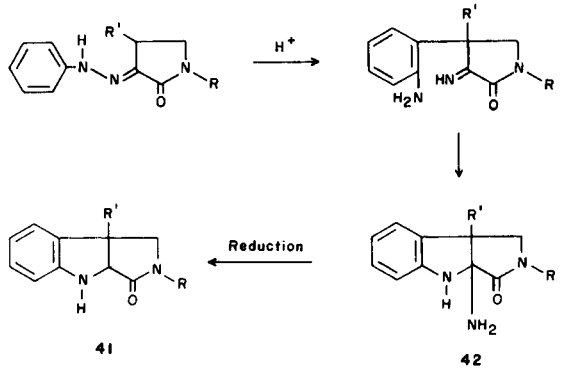
36 **37**

When 4-arylazo-2-phenyl(or alkyl)-2-oxazolin-5-ones **38** (X = O) are treated with alcoholic alkali [169-172], or with hydrochloric acetic acid mixture [173], heterocyclic ring opening, followed by recyclization *via* loss of water, takes place with the formation of 1-aryl-5-phenyl-1*H*-1,2,4-triazole-3-carboxylic acid **39**. Similar rearrangement was reported when 4-arylazo-2-phenyl(or alkyl)-2-imidazolin-5-ones **38** (X = N) were treated with alkali to yield the triazole acids **39** [174,175].

Reactions with 2-thiazolin-5-ones have been reviewed by Metzger. Recently [151,176] azolylacetonitriles **40** have been obtained *via* rearrangement of **38** with active methylenenitriles.

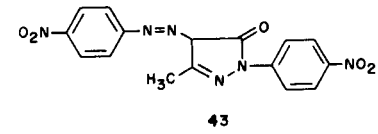


Another type of rearrangement has been reported upon heating 4-arylazopyrrolidinones with hydrochloric acid in methanol to yield the pyrroloindolone derivatives **41** [177]. The intermediate 3-amino-8b-alkyl[1,3-*a*,4,8-*b*]tetrahydropyrrolo[3,4-*b*]indol-3(2*H*)-ones **42** were separated and converted into **41** by long reflux with aqueous acetic acid.



This type of transformation represents a normal Fisher indole synthesis in which intermediates of type **42** were isolated.

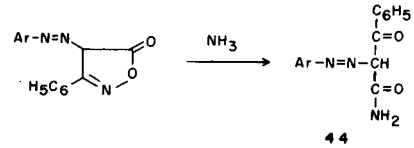
Nitration of 1-phenyl-3-methyl-4-*p*-nitrophenylazo-5-pyrazolone with concentrated nitric acid gives 1-*p*-nitrophenyl-3-methyl-4-*p*-nitrophenylazo-5-pyrazolone (**43**) [178]. On the other hand, treatment of 4-(2,4-dichlorophenylazo)-1-phenyl-3-methyl-5-pyrazolone with concentrated nitric acid results in the formation of 4-nitro-3-methyl-1-phenyl-5-pyrazolone [90].



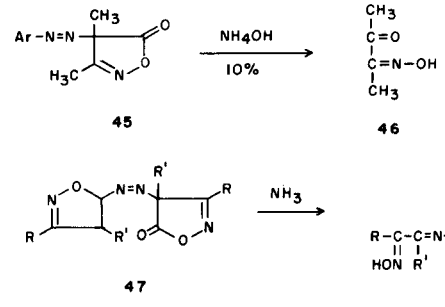
Arylazoaminopyrazoles have been reported to react with nitrous acid to yield the corresponding diazo derivatives. The reactions of these diazo derivatives have been recently reviewed [164]. Chemical reactions of 4-arylazo-5-aminopyrazoles have also been very recently reported [179] and will not be described here further.

(2) Action of Ammonia, Amines and Hydrazines.

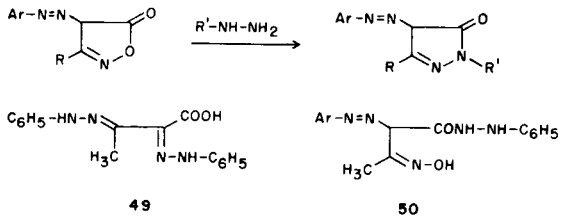
4-Arylazo-3-phenyl-2-isoxazolin-5-ones react with alcoholic aqueous ammonia to yield α-arylazobenzoylacetamide **44** [43] whereas the reaction of 4-arylazo-3,4-dimethyl-2-isoxazolin-5-one (**45**) with hot ammonia affords dimethylglyoxal monoxime (**46**) [46].



Similarly, 4-(3,4-dialkylisoxazolylazo)-2-isoxazolin-5-ones **47** react with hot ammonia to give **48** [46].

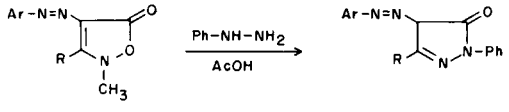


4-Arylazo-2-isoxazolin-5-ones react with hydrazine hydrate in absence of acetic acid to yield 4-arylazo-2-pyrazolin-5-ones [180]. Similar treatment with hydrazines also effects the conversion of the isoxazolone ring into the pyrazolone nucleus [180-182]. However, Knorr and Reuter [140] have reported the isolation of acetylglyoxalic acid diphenylhydrazone (**49**) as an intermediate in this reaction and the dihydrazone was readily converted into the pyrazolone on heating with glacial acetic acid. Mustafa *et al.* [180] have found that when the reaction between 4-arylazo-2-isoxazolin-5-ones and phenylhydrazine was conducted at room temperature, the phenylhydrazide of arylazoacetoacetic acid oximes **50** were isolated. The latter phenylhydrazides underwent cyclisation to the arylazopyrazolone derivatives when refluxed with glacial acetic acid.



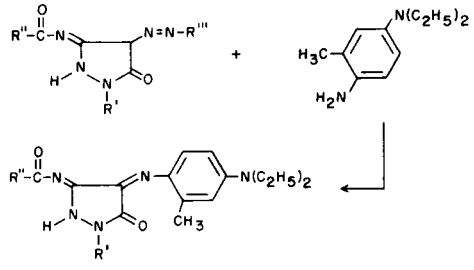
49 50

The reaction of 2-methyl-3-substituted-4-arylazo-3-isoxazolin-5-ones with phenylhydrazine in presence of acetic acid leads to cleavage of the hetero-ring and recyclisation to 3-substituted-1-phenyl-4-arylazo-2-pyrazolin-5-ones [3].



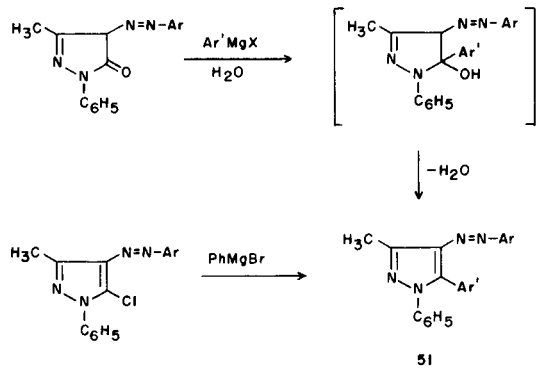
4-Arylazo derivatives of 2-phenyl-2-oxazolin-5-ones rearrange under the influence of ammonia [169,170], amines [169-171], or hydrazines [169,170,172] *via* heterocyclic ring opening followed by cyclization with the loss of water to yield the corresponding 1,2,4-triazole derivatives.

The arylazo group in 4-arylazo-3-acylimino-5-pyrazolidone is replaced by an arylimino group by the action of amines [163].



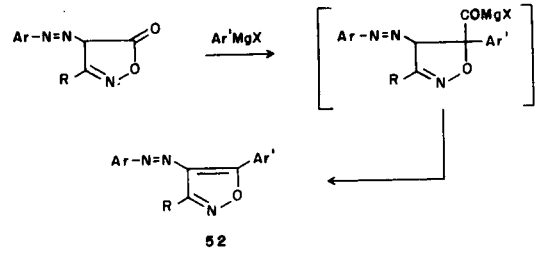
(3) Action of Grignard Reagents.

The introduction of an arylazo group in the α-position with respect to the heterocyclic carbonyl groups seems to activate the latter toward organomagnesium compounds. Thus, whereas 1,4-addition of the reagent takes place upon treatment of 4-arylidene-1-phenyl-3-methyl-5-pyrazolone with Grignard reagents to yield 4-diarylmethyl-3-methyl-1-phenyl-5-pyrazolone [183], 1,2-addition of the reagent to the carbonyl group in 4-arylazo-3-methyl-1-phenyl-2-pyrazolin-5-ones has been reported by Mustafa and co-workers [184] with the formation of 1-phenyl-3-methyl-4-arylazo-5-arylpyrazoles **51**.



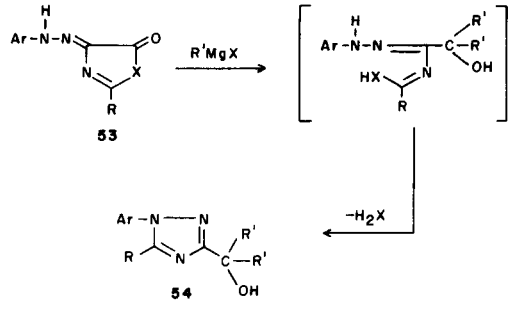
51

1,5-Diphenyl-3-methyl-4-phenylazo-5-pyrazole **51** (Ar' = C_6H_5) has also been obtained by the action of phenylmagnesium bromide on 1-phenyl-3-methyl-4-phenylazo-5-chloropyrazole followed by hydrolysis. Similarly, 4-arylazo-3-substituted-2-isoxazolin-5-ones on treatment with Grignard reagents yield the corresponding 4-arylazo-5-arylisoxazoles **52** [185].



52

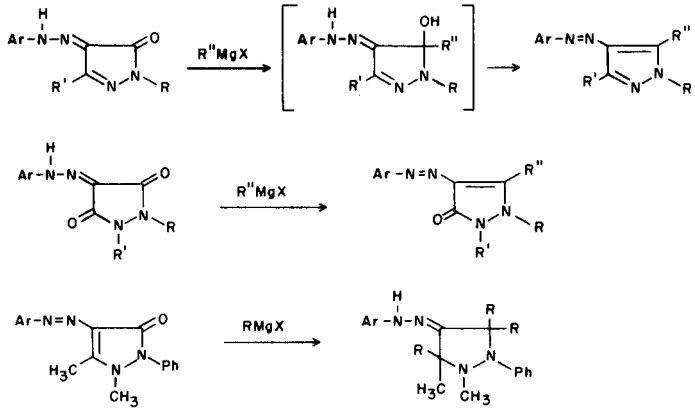
On the other hand, the reaction of the Grignard reagent with 4-arylhydrazono-2-oxazolin-5-ones **53** (X = O) and 4-arylhydrazono-2-thiazolin-5-ones **53** (X = S) has been reported to effect their rearrangement into 1,2,4-triazole derivatives **54** [170-172].



53 54

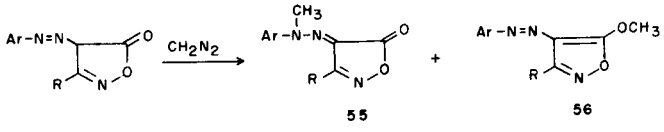
Arylazopyrazoles react quite readily with the Grignard reagent affording arylazopyrazole derivatives [186]. Similar behaviour has been reported for arylhydrazono-3,5-pyrazolidinediones [187]. Antipyrene itself does not react with Grignard reagents, but the arylazo antipyrene adds three molecules of the reagent to give arylhydrazonopyrazolidine derivatives (*cf.* Chart 5) [188].

Chart 5

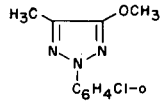


(4) Alkylation.

Meyer [2] reported that when 3-phenyl-4-phenylazo-2-isoxazolin-5-one was treated wtih diazomethane, 3-phenyl-4-β-methylphenylhydrazono-2-isoxazolin-5-one (**55**, Ar = R = C_6H_5) was formed together with an unidentified product, which was proved by Mustafa *et al.* [3] to be 5-methoxy-3-phenyl-4-phenylazoisoxazole (**56**). Summers *et al.* [4,5] obtained the triazole derivative **57** from the reaction

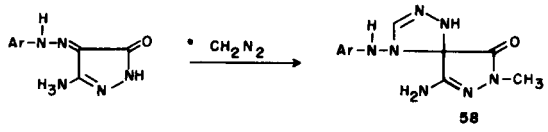


of 4-*o*-chlorophenylazo-3-methyl-2-isoxazolin-5-one with diazomethane, in addition to the *N*-methyl (**55**, R = CH_3, Ar = C_6H_4-Cl-*o*) and *O*-methyl (**56**, R = CH_3, Ar = C_6H_4Cl-*o*) derivatives.



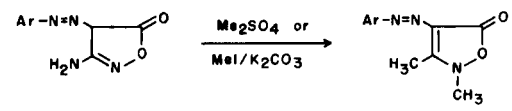
57

The reaction of arylhydrazones with diazomethane usually does not involve the azomethine linkage [37]. Only addition of the reagent to the double bond in 4-arylhydrazono-3-amino-2-pyrazolin-5-one affording the spiropyrazolyl-1,2,4-triazole derivative **58** has been recently reported [189].

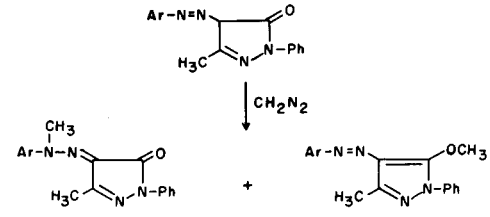


58

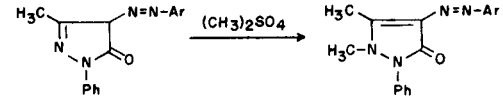
4-Arylazo-3-methyl-2-isoxazolin-5-ones react with dimethyl sulphate to give 2,3-dimethyl-4-arylazo-3-isoxazolin-5-ones [3]. The latter can also be obtained by treatment of 3-methyl-4-arylazo-2-isoxazolin-5-ones with methyl iodide in presence of potassium carbonate [4].



Methylation of 4-arylazo-3-methyl-1-phenyl-2-pyrazolin-5-ones with diazomethane [3] or dimethyl sulphate in presence of alkali gives a mixture of *N*-methyl and *O*-methyl derivatives [190].

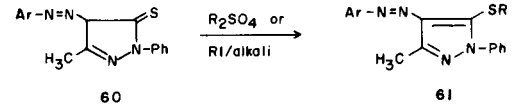


On the other hand, treatment of 4-arylazo-3-methyl-1-phenyl-2-pyrazolin-5-ones with dimethyl sulphate results in the formation of arylazo derivatives of antipyrine **59** [191].



59

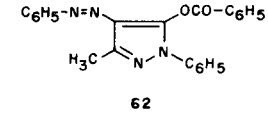
When 4-arylazo-3-methyl-1-phenyl-2-pyrazolin-5-thiones **60** were treated with alkyl sulphates or iodides in presence of alkali, 4-arylazo-3-methyl-1-phenyl-5-thioalkylpyrazoles **61** [192] were obtained. Similar *S*-alkylation has been reported with chloroacetic acid [192].



60 **61**

(5) Acylation.

Auwers [190] reported that treatment of 3-methyl-1-phenyl-4-phenylazo-2-pyrazolin-5-one with benzoyl chloride under the influence of sodium hydroxide leads to the formation of the corresponding *O*-benzoyl derivative **62** which was also obtained from condensation of 3-methyl-1-phenyl-5-pyrazolone with *S*-phenylbenzoylhydrazine [190].

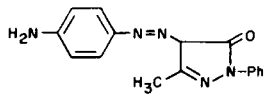


62

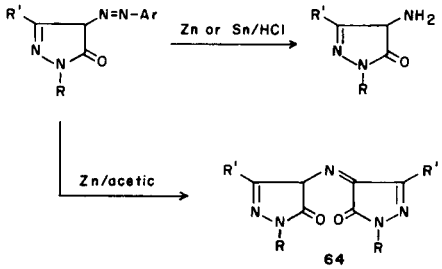
(6) Reduction.

Reduction usually affords the corresponding amino compound [48,193,194]. However, other products were isolated depending on the catalyst used and the reaction con-

ditions. Thus, treatment of 3-methyl-4-(*p*-nitrophenylazo)-1-phenyl-2-pyrazolin-5-one with sodium hydrogen sulphide effects only reduction of the nitro group with the formation of 1-phenyl-3-methyl-4-(*p*-aminophenylazo)-2-pyrazolin-5-one (**63**) [195], whereas, 4-amino-2-pyrazolin-5-ones were obtained by reduction with zinc and hydrochloric acid [194] or with tin and hydrochloric acid of 4-arylazo-2-pyrazolin-5-ones [29].



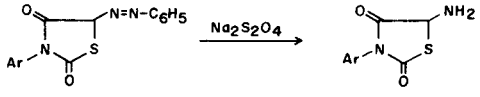
63



64

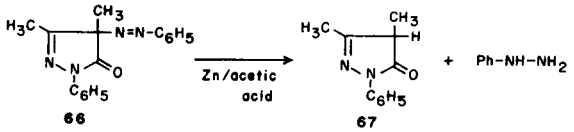
Reduction with zinc and acetic acid generally leads to rubazonic acid (**64**) although Knorr [196] reported the isolation of aniline and 4-amino-3-methyl-1-phenyl-2-pyrazolin-5-one from the reduction of 4-phenylazo-3-methyl-1-phenyl-2-pyrazolin-5-one with the same reagents.

Alcoholic solutions of sodium hydrosulphite [29,47,48, 193] were also used to effect reduction. For example, treatment of 3-aryl-5-phenylazo-2,4-thiazolidinedione with sodium hydrosulphite effects the reduction of the azo group with the formation of the corresponding 3-aryl-5-amino-2,4-thiazolidinediones **65** [47,48]. Ammonia and aniline were identified among the reduction products of phenylazorhodanine with zinc and sodium hydroxide [32].



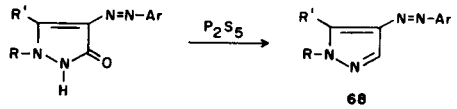
65

Reduction of 4-phenylazo-3,4-dimethyl-1-phenyl-2-pyrazolin-5-one (**66**) with zinc and acetic acid effects the elimination of the azo group with the formation of 3,4-dimethyl-1-phenyl-2-pyrazolin-5-one (**67**) [9].



66 67

An abnormal reduction has been reported by Michaelis, Kotelmann and Drews [197] who found that phosphorous pentasulphide effects the conversion of 4-arylazo-3-pyrazolidin-5-ones, having no 1-substituent, to 4-arylazopyrazol derivatives **68**.

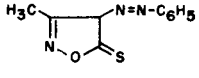


68

The polarographic behaviour of arylhydrazonoazolones has been recently investigated [16]. The 4-e reduction waves in both acidic and basic media have been observed. Mechanisms to account for the reduction waves were suggested. Some preliminary reduction schemes suggesting formation of aminoazolones and diaminoazoles have been suggested. However, CPE experiments were not conducted. Thus, the proposed mechanism needs further confirmation.

(7) Reaction with Phosphorus Pentasulphide.

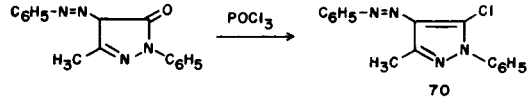
Arylazo heterocyclic compounds having a carbonyl function can be converted into the corresponding thione compounds by the action of phosphorus pentasulphide in the proper solvent [5,198-201]. For example, when 3-methyl-4-phenylazo-2-isoxazolin-5-one was treated with phosphorus pentasulphide in xylene or toluene, 3-methyl-4-phenylazo-2-isoxazolin-5-thione (**69**) was obtained [198, 199].



69

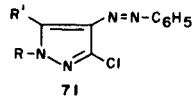
(8) Reaction with Phosphorus Oxychloride.

Treatment of 4-arylazo-3-methyl-1-phenyl-2-pyrazolin-5-ones with phosphorus oxychloride under pressure yields 1-phenyl-3-methyl-4-arylazo-5-chloropyrazoles (**70**) [203]. In the same way, 4-arylazo-3-pyrazolin-5-ones having no



70

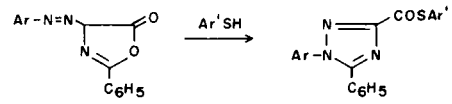
substituent in the 1-position react with phosphorus oxychloride to give the corresponding 3-chloro derivatives **71** [202].



71

(9) Reaction with Aromatic Thiols.

The reaction between 4-arylazo-2-phenyl-2-oxazolin-5-ones and aromatic thiols effects rearrangement *via* heterocyclic ring opening and cyclisation with the loss of water to yield 3-aryl-5-thiocarboxy-1*H*-2-aryl-1,2,4-triazoles **72** [171].

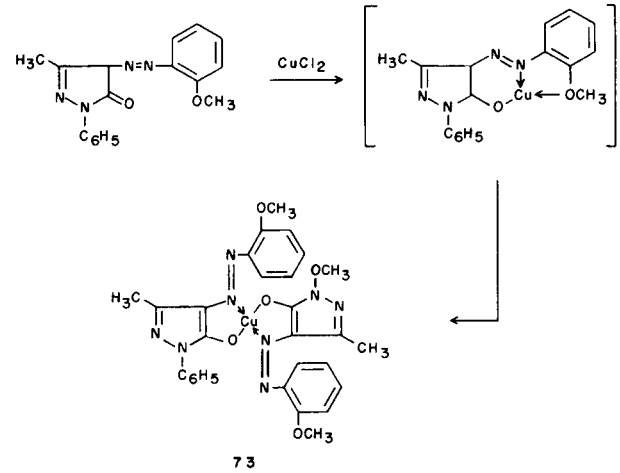


72

(10) Metal Complexes.

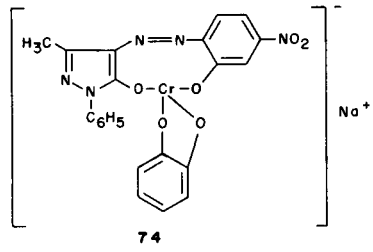
The most important reactions of arylazo heterocyclic compounds are those with various salts to form metal complexes [204-240]. These products are of great importance, since they have been extensively used as dye-stuffs. Of these metal complexes those of pyrazolone find wide application due to their excellent dyeing characteristics. Chromium complexes are prepared by reaction of arylazo derivatives with inorganic compounds [204-207] including chromium sulphate [208], chromium trifluoride [209] with organic chromium compounds such as chromium formate [210], ammonium oxalochromate, and chromium complexes with salicylic acid [210]. Copper [211-219], nickel [204, 213], lead [212], zinc [221], and cobalt [223,224] have also been used. The aromatic moiety of the arylazo group usually has a hydroxyl or carboxyl group ortho to the azo linkage. Usually these complexes contain a number of pyrazolinone residues corresponding to the valence of the metal atom. The metal atom reacts with the C-5 oxygen of the ring in its enol form and with the hydroxyl group of the aromatic ring to form more or less covalent bonds. There is also electron donation by other oxygen atoms and by the azo group [239].

Although a large number of metal dye-complexes have been used in dyeing, only a few of such compounds have been characterised and reported in the literature. The reaction with copper salts is shown in the following equation together with the structure of the final product **73**. In some cases the formation of intermediates have been reported [217-219].

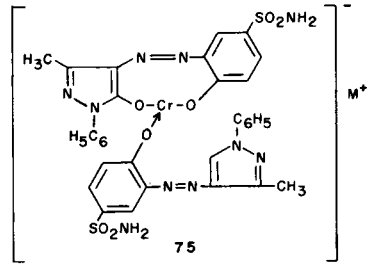


73

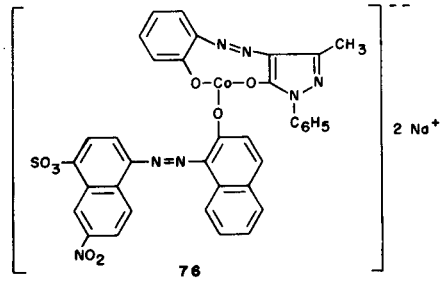
Structure **74** has been proposed for the 1:1 chromium complexes [232] and **75** for the 2:1 complexes, while structure **76** was proposed for the cobalt complexes [227].



74



75



76

Studies of the formation constants of arylazo pyrazolone and arylazo thiopyrazolone metal derivatives have shown decreasing order of stability of bivalent derivatives in the order Cu > Ni > Cd > Zn. It was also shown that arylazo thiopyrazolones have a strong affinity for metal ions than the oxygen analogue [228].

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