Russian Chemical Reviews **79** (1) 31 – 61 (2010) © 2010 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2010v079n01ABEH004048

2-(Het)arylhydrazono-1,3-dicarbonyl compounds in organic synthesis

E V Shchegol'kov, Ya V Burgart, O G Khudina, V I Saloutin, O N Chupakhin

Contents

I.	Introduction	31
II.	Synthesis of 2-(het)arylhydrazono-1,3-dicarbonyl compounds	31
III.	Structure of 2-(het)arylhydrazono-1,3-dicarbonyl compounds	33
IV.	Chemical transformations of 2-(het)arylhydrazono-1,3-dicarbonyl compounds	33
V.	Practical applications of 2-(het)arylhydrazono-1,3-dicarbonyl compounds and their derivatives	47
VI.	Conclusion	48
VII.	Appendix	49

Abstract. The data on the synthesis, structure and chemical transformations of 2-(het)arylhydrazono-1,3-dicarbonyl compounds is surveyed. The synthetic potential and possible applications of the title compounds are analyzed. The bibliography includes 273 references.

I. Introduction

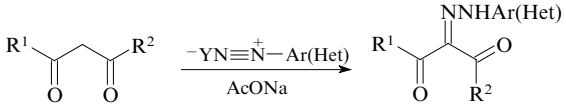
1,3-Dicarbonyl compounds are important 'building blocks' in organic synthesis. They can serve as the basis for preparing diverse open-chain, carbo- and heterocyclic molecules,[1–4] which find extensive practical use in industry and medicine. For example, the known medical drugs amidopyrine, analgin, methyluracil, nifedipine, sulfadimicine, diuciphone and celebrex are heterocyclic derivatives of 1,3-dicarbonyl compounds.[5]

In addition, 1,3-dicarbonyl compounds are the most frequently encountered ligands in metal complexes.[6–9] The high complexing ability of these compounds accounts for diverse aspects of their practical use, in particular, for the separation of mixtures of rare earth elements and extraction-and-photometric determination of metal ions.[1,2,10] Metal chelates of 1,3-dicarbonyl compounds are used as antioxidants and lubricant additives, catalysts for oxidation, addition and polymerization processes, for the production of metallic and oxide coatings, for introducing a metal into high-temperature superconducting films,[10,11] for the manufacture of electroluminescent diodes,[12] *etc*. Today, the development of polydentate ligands able to form coordination clusters and supramolecular structures becomes more and more important, 1,3-dicarbonyl derivatives being rather convenient for this purpose.[9]

Other valuable synthons are 1,3-dicarbonyl derivatives containing additional functional groups able to participate in the chemical transformations or affect the course of the reactions. One of such groups is the (het)arylhydrazone group. No reviews of the chemistry of 2-(het)arylhydrazono-1,3-dicarbonyl compounds have been published, although numerous examples demonstrate the extensive synthetic potential of these derivatives. The prospects of the research along this line are due to the diverse biological action, catalytic activity and complexing properties of their transformation products. This review is meant for considering systematically the published data on the synthesis, structure, and reactions of 2-(het)arylhydrazono-1,3-dicarbonyl compounds and for analyzing the possible routes for their use in organic synthesis and in practice.

II. Synthesis of 2-(het)arylhydrazono-1,3-dicarbonyl compounds

A known method for the synthesis of 2-(het)arylhydrazono-1,3-dicarbonyl compounds is the Japp–Klingemann reaction (1) comprising azo coupling of (het)aryldiazonium salts with 1,3-diketones (R^1, R^2 = Alk, Ar) and 3-oxo esters (R^1 = Alk, Ar; R^2 = OAlk).[13]



(1)

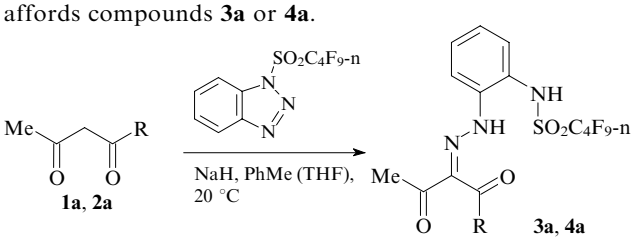
The reaction carried out in water–alcohol or water–acetone medium in the presence of sodium acetate usually provides good yields of coupling products. In some cases, formazans are formed as by-products. Numerous 2-(het)arylhydrazono-1,3-dicarbonyl compounds containing diverse substituents in the 1,3-dicarbonyl residue and the (het)ar-

E V Shchegol'kov, Ya V Burgart, O G Khudina, V I Saloutin, O N Chupakhin I Ya Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, ul. S Kovalevskoi/Akademicheskaya 22/20, 620219 Ekaterinburg, Russian Federation.
Fax (7-343) 374 59 54, tel. (7-343) 362 34 91,
e-mail: schegolkov@ios.uran.ru (E V Shchegol'kov),
tel. (7-343) 362 32 25, e-mail: burgart@ios.uran.ru (Ya V Burgart),
tel. (7-343) 362 34 91, e-mail: kog@ios.uran.ru (O G Khudina),
tel. (7-343) 374 59 54, e-mail: saloutin@ios.uran.ru (V I Saloutin),
tel. (7-343) 374 11 89, e-mail: chupakhin@ios.uran.ru (O N Chupakhin)

Received 28 July 2009
Uspekhi Khimii **79** (1) 33 – 64 (2010); translated by Z P Svitanko

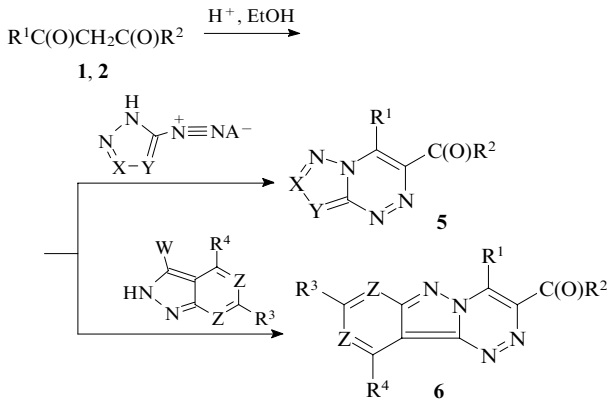
ylhydrazone fragment have been obtained to date (see the Table in the Appendix).[14–74]

An original approach to the synthesis of arylhydrazones has been proposed.[75] The reaction of acetylacetone (**1a**) or ethyl acetoacetate (**2a**) with *N*-nonafluorobutylsulfonylbenzotriazole in the presence of NaH in an inert medium affords compounds **3a** or **4a**.



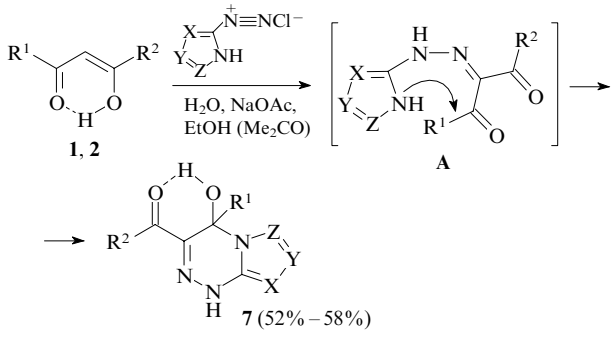
R = Me (**1a**, **3a**), OEt (**2a**, **4a**).

Cases have been described in the literature where acyclic arylhydrazone was not isolated upon azo coupling of 1,3-dicarbonyl compounds with hetaryldiazonium salts, as this product underwent spontaneous cyclization under the reaction conditions to give heterofused triazines. Thus the reaction of compounds **1**, **2** with 1,2,4-triazol-5-yl-,[35] 1,2,3-triazol-5-yl-[76] and pyrazol-3-yldiazonium salts[77–80] gives azolotriazines **5**, while the reactions with indazol-3-yldiazonium[81] and 3-diazopyrazolo[3,4-*d*]pyrimidine[82] yield biannulated triazines **6**.



R^1 = Me, Ph; R^2 = Me, OMe, OEt; X = N, CH, CMe, CPh, CSMe; Y = N, CH, CPh, CN=NPh ; Z = N, CH; R^3 = H, Me; R^4 = H, Ph; W = $N_2^+A^-$, N_2; A = Cl, NO_3, BF_4.

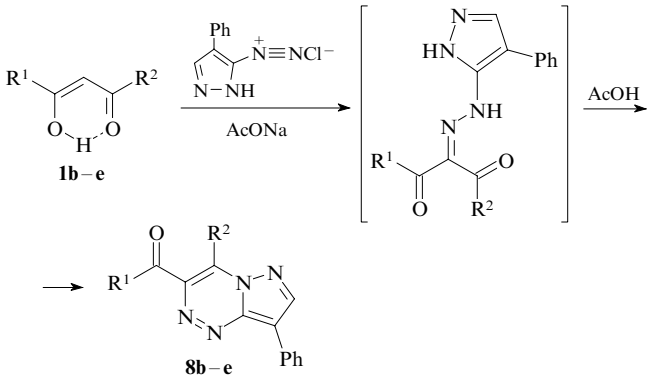
A distinctive feature of fluoroalkylated 1,3-diketones and 3-oxo esters in the azo coupling with hetaryldiazonium chlorides having an α-NH group under standard conditions is the formation of 4-fluoroalkyl-4-hydroxy-1,4-dihydroazolo[5,1-*c*]triazines **7**. These products result from the addition of the NH group of the hetaryl residue to the carbonyl carbon atom at the fluorinated substituent.[83–85]



R^1 = CHF_2, CF_3, $(CF_2)_2H$, C_3F_7, $(CF_2)_4H$, C_4F_9; R^2 = Me, Bu^n, Ph, CF_3, 1-Naph, 2-Fu, OEt, OMe (Naph is naphthyl, Fu is furyl); X = N, CCO_2Et; Y, Z = N, CH.

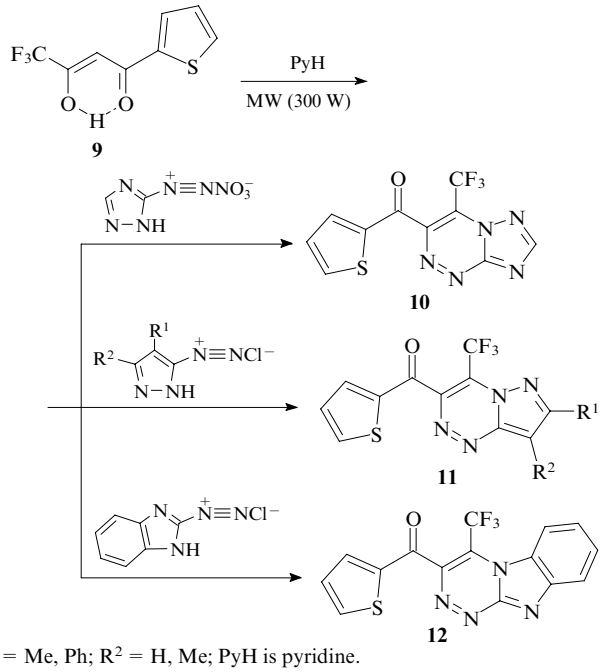
According to NMR spectroscopy data, heterocycles **7** are subject to ring–chain tautomerism through opening of the triazine ring at the C(4)—N(5) bond giving open-chain hetarylhydrazone form **A**. Fluoroalkylated dihydroazolo[5,1-*c*]triazines **7** are stable against dehydration.

However, in another publication,[86] the reactions of fluoroalkylated 1,3-diketones **1b–e** with 4-phenylpyrazol-3-yldiazonium chloride were reported to give 3-(fluoroacyl)pyrazolo[5,1-*c*][1,2,4]triazines **8b–e**, resulting from dehydration of intermediate hetarylhydrazones, which were subjected to subsequent cyclization in glacial acetic acid without characterization. However, in our opinion, the data presented by the authors does not suffice to confirm the structure of compounds **8b–e**.



R^2 = 3-F-4-$MeOC_6H_3$: R^1 = CF_3 (**b**), C_2F_5 (**c**);
R^2 = 3-Cl-4-FC_6H_3: R^1 = CF_3 (**d**) , C_2F_5 (**e**).

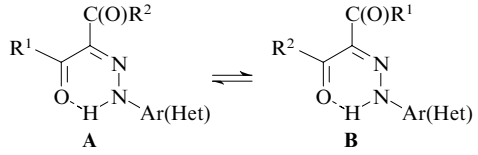
Nevertheless, quite recently more reliable information appeared concerning the azo coupling of 1-(2-thienyl)-4,4,4-trifluorobutanedione (**9**) with hetaryldiazonium salts in pyridine under conditions of microwave (MW) synthesis; this gave dehydration products, fluoroalkyl-containing azolotriazines **10–12**.[87]



R^1 = Me, Ph; R^2 = H, Me; PyH is pyridine.

III. Structure of 2-(het)arylhydrazono-1,3-dicarbonyl compounds

2-(Het)arylhydrazono-1,3-dicarbonyl compounds are subject to *syn*–*anti*-isomerism due to different positions of the substituents relative to the C=N bond. Both isomers are rather stable as they are stabilized by an intramolecular hydrogen bond (IMHB) between the carbonyl oxygen atom and the hydrogen atom of the arylhydrazone amino group.



R^1 = Me, Alk, Alk^F; R^2 = Me, Bu^t, OMe, OEt, Ar.

Mitchell and Nonhebel[33] used IR and ^{1}H NMR spectroscopy data to demonstrate that arylhydrazones obtained from acetylbenzoylmethanes mainly exist as the isomer in which the IMHB involves the acetyl group (form **A**). The preferred binding of the acetyl rather than the benzoyl group was attributed to steric factors. In addition, the authors concluded that the introduction of electron-releasing substituents into the aryl group of the arylhydrazone residue increases the content of isomer **A**, while electron-withdrawing substituents increase the content of isomer **B**.

Bertolasi *et al.*[88] studied the structure of symmetrical 1,2,3-trione 2-arylhydrazones based on dibenzoylmethane using X-ray diffraction. Atta *et al.*[21] determined, by comparing the data of ^{1}H and ^{13}C NMR spectroscopy for 2-arylhydrazone derivatives of ethyl acetoacetate and acetylacetone, that the ester group (form **A**, R^2 = OAlk) rather than the acetyl group (form **B**, R^2 = Me) has a higher tendency to intramolecular hydrogen bonding with the amino group.

However later, on the basis of X-ray diffraction studies of a number of 2-arylhydrazono-3-oxoesters, Bertolasi *et al.*[89] showed that 2-(2-methoxyphenyl)- and 2-(2-cyanophenyl)hydrazono-3-oxoesters tend to form IMHB at the acetyl group, while for 4-cyano-substituted analog the IMHB rather involves the ester group.

It has been reported[34] that the absolute value of the spin–spin coupling constant ^1J (^{15}N^{15}N) of the isomer in which the IMHB involves the ester group is smaller (~10.8 Hz) than that for the isomer with hydrogen-bonded acetyl group (~11.1 Hz).

The spatial structure of the polyfluoroalkylated 2-(het)arylhydrazono-1,3-dicarbonyl compounds has been studied in detail by physicochemical methods.[90,91] It was found by X-ray diffraction and IR spectroscopy that in the solid state these compounds exist as the isomer in which the intramolecular hydrogen bond involves the carbonyl oxygen atom at a non-fluorinated residue (form **B**). According to ^{1}H, ^{13}C and ^{19}F NMR spectroscopy, in solutions in $CDCl_3$ and acetone-d_6, they also exist predominantly as isomer **B**. It was shown by DFT B3LYP/6-31G(d,p) *ab initio* calculations[90,91] that this isomer is energetically more favourable.

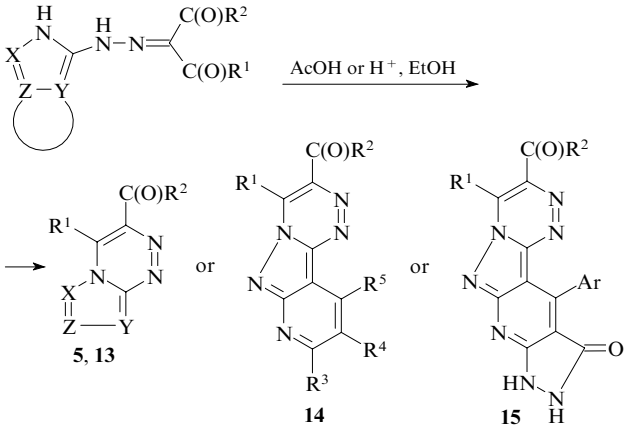
IV. Chemical transformations of 2-(het)arylhydrazono-1,3-dicarbonyl compounds

1. Intramolecular heterocyclization

2-(Het)arylhydrazono-1,3-dicarbonyl compounds can undergo a number of intramolecular cyclizations. The transformations of hetarylhydrazones are especially diverse.

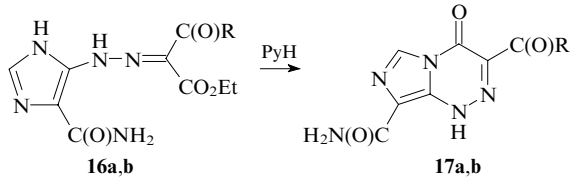
For example, compounds containing an NH group in the azolylhydrazone residue tend to undergo C,N-heterocyclization giving a triazine ring upon condensation of this group with the carbonyl carbon atom of the acyl residue. Thus, 2-(het)arylhydrazono-1,3-dicarbonyl compounds were converted into derivatives of bicyclic triazines (**13**),[35,39,41,92] tricyclic triazines (**14**)[32,36] and tetracyclic triazines (**15**).[55,57,58] Usually the cyclization is carried out on heating the reactants in acetic acid (in acidified ethanol) or in a sealed tube without a solvent.

In the case of cyclization of unsymmetrical 2-hetarylhydrazones of 1,2,3-triones, derivatives of benzoylacetone, the researchers[36,41] do not agree on which acyl group is involved in the reaction. Kočevar *et al.*[36] believe that cyclization involves the acetyl group, while according to Baig and Stevens,[41] the benzoyl group participates in the reaction; however, neither of the authors presented justified proof for this opinion.



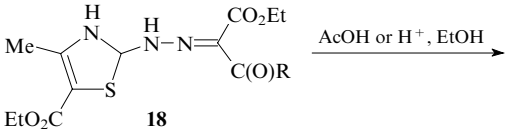
R^1 = Me, Et, Pr^n, Ph; R^2 = Me, Ph, OMe, OEt, OPr^n;
X = N (**5**), CH (**13**): Y = N, CH, CC_6H_4Cl-4, CBr, CCO_2Et, $CC(O)NH_2$; Z = N, CH, CC_6H_4OMe-4, CSBn, CSO_2Bn, CNHMe;
14: R^3 = H, OH; R^4 = H, CN; R^5 = H, Ph;
15: Ar = Ph, C_6H_4Cl-4, 2-Fu.

Baig and Stevens[41,92] found that heterocyclization of 4-carbamoylimidazol-5-ylhydrazono-3-oxoesters **16a**,**b** can be carried out not only in acid medium, but also in a basic medium (in pyridine). In the latter case, the reaction follows an alternative route with participation of the ethoxycarbonyl substituent, resulting in 4-oxo-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxamides **17a**,**b**.

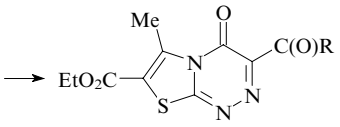


R = Me (**a**), Ph (**b**).

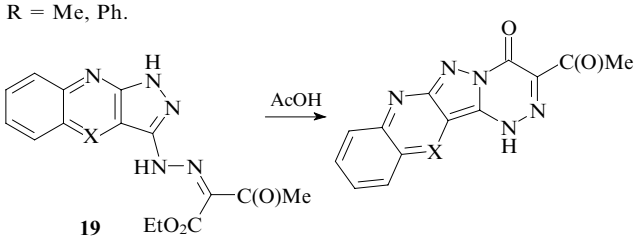
A similar course of cyclization at the ester group was also noted for 2-hetarylhydrazono-3-oxoesters **18**[93] and **19** [X = N (Ref. 55), CH (Ref. 58)] but in an acid medium.



18



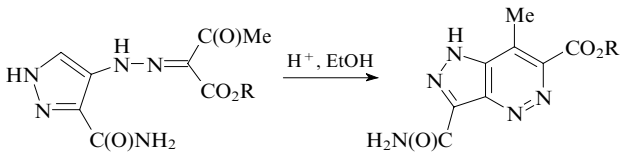
R = Me, Ph.



19

X = CH, N.

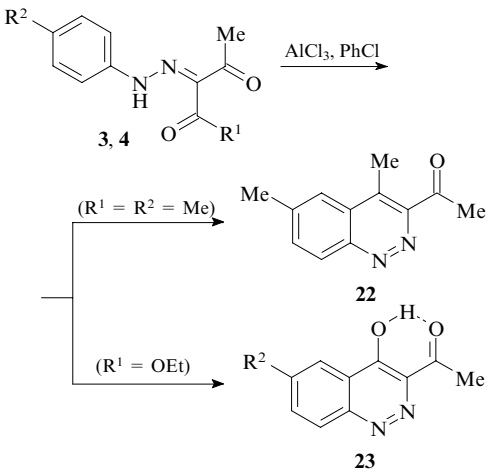
In the case of 2-(het)arylhydrazono-1,3-dicarbonyl compounds with the hetaryl substituent containing a CH group in the α-position to the hydrazone group, in intramolecular C,C-cyclization is possible. Transformations of 2-(3-carbamoylpyrazol-4-yl)hydrazonoacetoacetates **20a**,**b**, resulting in esters of 3-carbamoyl-7-hydroxypyrazolo[4,3-*c*]pyridazine-6-carboxylic acids **21a**,**b** were reported.[41]



20a,**b** **21a**,**b**

R = Me (**a**), Et (**b**).

2-Arylhydrazono-1,3-dicarbonyl compounds can also participate in C,C-cyclization processes. 2-Arylhydrazones **3**, **4** cyclize in the presence of aluminium chloride with participation of the *ortho*-carbon atom of the aryl substituent and the acetyl or ethoxycarbonyl group to give

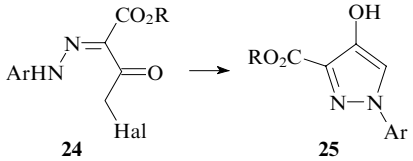


3, **4** **22** **23**

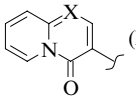
R^1 = Me, OEt; R^2 = H, Me, OMe, Br, $SC_6H_4NO_2$-4, SO_2R^3 [R^3 = OH, NH_2, $N(CH_2)_5$, NHPh, NPy-2].

3-acetylcinnolines **22** and 3-acetyl-4-hydroxycinnolines **23**.[16, 53, 94, 95]

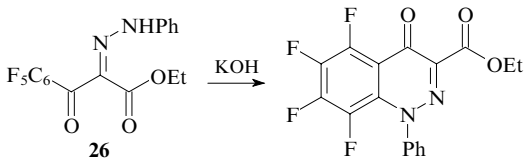
The presence of a reactive substituent in the dicarbonyl fragment of hydrazones provides additional cyclization opportunities: 2-(het)arylhydrazono-4-bromo(chloro)acetoacetates **24** cyclize to 3-alkoxycarbonyl-4-hydroxy-1-(het)arylpyrazoles **25** upon an intramolecular elimination of hydrogen bromide (or chloride).[59]



24 **25**

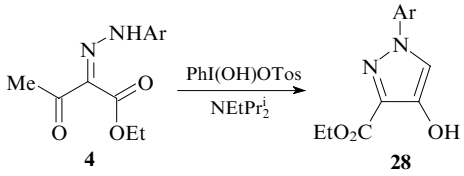
R = Me, Et; Hal = Cl, Br; Ar =  (X = CCN, CCO_2Et, N).

Another illustration is cyclization of 2-phenylhydrazonopentafluorobenzoylacetate (**26**) to ethyl 4-oxo-1-phenyl-5,6,7,8-tetrafluoro-1,4-dihydrocinnoline-3-carboxylate (**27**) upon intramolecular replacement of *ortho*-fluorine by the NH group of the arylhydrazone fragment.[68]



26 **27**

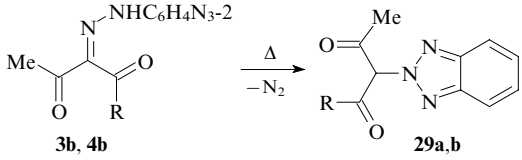
Patel *et al.*[96] showed that 2-arylhydrazonoacetoacetates **4** can also undergo cyclization involving the methyl group under the action of [hydroxy(tosyloxy)iodo]benzene in the presence of diisopropylethylamine. This gives ethyl 1-aryl-4-hydroxy-1*H*-pyrazole-3-carboxylates **28**.†



4 **28**

Tos is *p*-toluenesulfonyl.

2-(2-Azidophenyl)hydrazono-1,3-dicarbonyl compounds **3b**, **4b** can undergo thermal cyclization to give substituted benzotriazoles **29a**,**b**.[23]



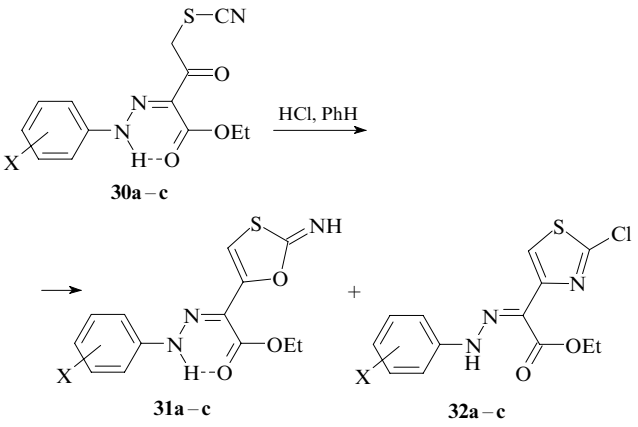
3b, **4b** **29a**,**b**

R^1 = Me (**3b**, **29a**), OEt (**4b**, **29b**).

Cyclization can also take place without participation of the hydrazone NH group. Thus on treatment with hydrogen chloride in benzene, ethyl 2-arylhydrazono-4-thiocyanato-

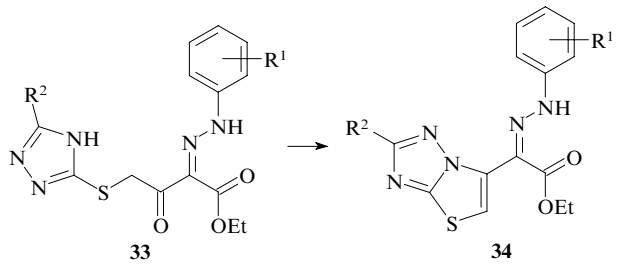
† Hereinafter, unless stated otherwise, Ar stands for phenyl or substituted phenyl.

acetoacetates **30a–c** form a mixture of oxathioles **31a–c** and thiazoles **32a–c**.[18]



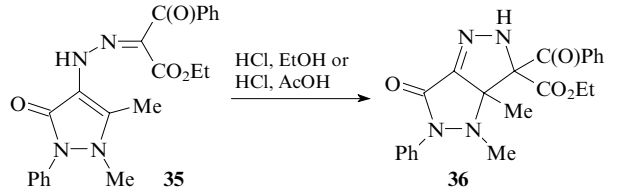
X = 2-Cl (**a**), 4-Cl (**b**), 3-CF_3 (**c**).

Another example of this type of cyclization was reported by Bondar *et al.*,[97] who carried out intramolecular cyclization of ethyl 2-arylhydrazono-4-[(4*H*-1,2,4-triazol-3-yl)-thio]acetoacetates **33** to give ethyl α-arylhydrazono[1,3]thiazolo[3,2-*b*][1,2,4]triazol-5-ylacetates **34**.



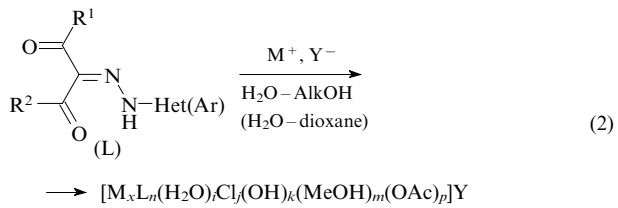
R^1 = H, 3-CF_3, 4-NO_2, 4-Cl, 4-OMe; R^2 = H, Me, Ph.

An unusual cyclization of ethyl 2-[(antipyrin-4-yl)hydrazono]-3-oxo-3-phenylpropanoate (**35**) to ethyl 3-benzoyl-3*a*,4-dimethyl-6-oxo-5-phenyl-2,3,3*a*,4,5,6-hexahydropyrazolo[4,3-*c*]pyrazole-3-carboxylate (**36**) induced by an HCl–EtOH or HCl–AcOH mixture was reported.[30]



2. Complexing properties of 2-(het)arylhydrazono-1,3-dicarbonyl compounds

2-(Het)arylhydrazono-1,3-dicarbonyl compounds are able to form chelates with transition metal cations. Treatment of 1,2,3-trione 2-(het)arylhydrazones[29,63,66,69,70,98–125] and 2-(het)arylhydrazono-3-oxoesters[124–131] with metal salts yielded the corresponding complexes [reaction (2), see the Table in the Appendix]. Studies of the structures of these metal chelates were reported.[63,98,99,114]



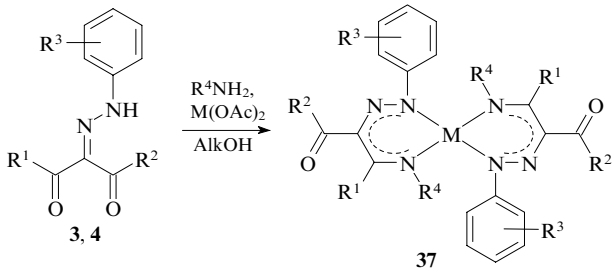
(2)

M = Ni, Cu, Pd and so on; x = 1, 2; n = 1, 2; i = 0, 1, 2, 3, 4, 5; j = 0, 1, 2, 3, 4, 7; k = 0, 1; m = 0, 1, 3; p = 0, 1, 2, 3; Y = Cl, OAc, NO_3, ClO_4.

3. Reactions with mononucleophiles

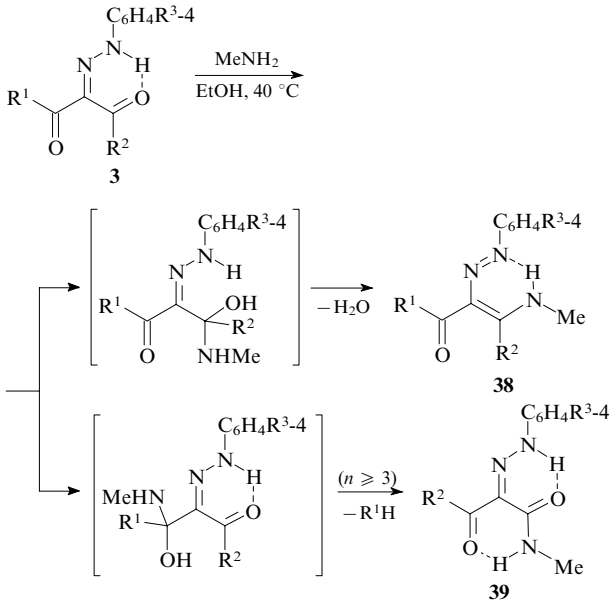
2-(Het)arylhydrazono-1,3-dicarbonyl compounds contain two electrophilic centres, carbonyl groups, which are the sites of attack by nucleophilic reagents. In 3-oxoester and unsymmetrical 1,3-diketone derivatives, these centres are inequivalent, therefore, regioisomers may form.

Template condensations of 1,2,3-trione 2-arylhydrazones **3** (R^1 = Me)[132,133] and 2-arylhydrazono-substituted acetoacetate **4** (R^1 = OEt)[134] with primary amines on a copper(II) and nickel(II) templates, resulting in tetraaza chelate complexes **37** are documented.



R^1 = Me, OEt; R^2 = Me, Ph; R^3 = H, 3-Me, 4-Me, 3-OMe, 4-OMe, 3-NO_2, 4-NO_2; 3-Cl, 4-Cl; R^4 = Me, Et, Pr^n, Bu^n, Ar; M = Cu, Ni.

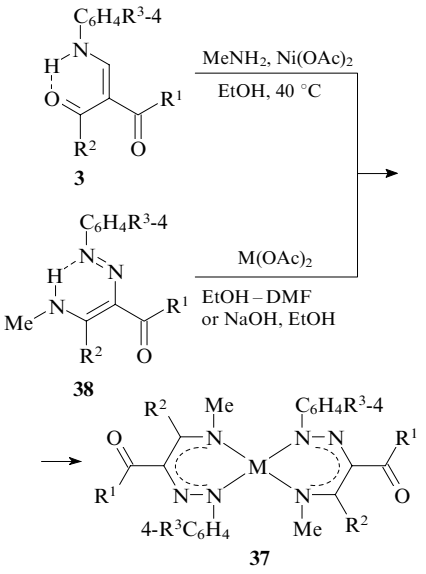
Fluoroalkyl-containing 2-arylhydrazono-1,3-dicarbonyl compounds react ambiguously with methylamine, the reaction route depending on the length of the fluoroalkyl substituent.[135,136] Thus 2-arylhydrazones of 1,2,3-triones **3** with a short-chain fluoroalkyl substituent R^1 ($n \leqslant 2$) are condensed with methylamine at the carbonyl group at the non-fluorinated residue R^2 to give 2-arylazo-3-aminoenones **38**. The transformations of methyl-substituted (R^2 = Me) arylhydrazones **3** containing a long-chain fluorinated substituent ($n \geqslant 3$) are non-selective. In this case, apart from 2-arylazo-3-aminoenones **38**, the reaction gives *N*-methyl-2-arylhydrazono-3-oxobutanamides **39**. The latter are formed



R^1 = $(CF_2)_nX$ (X = F: n = 1, 3, 4; X = H: n = 2, 3); R^2 = Me, Ph, Bu^n, Bu^t; R^3 = H, Me, OMe.

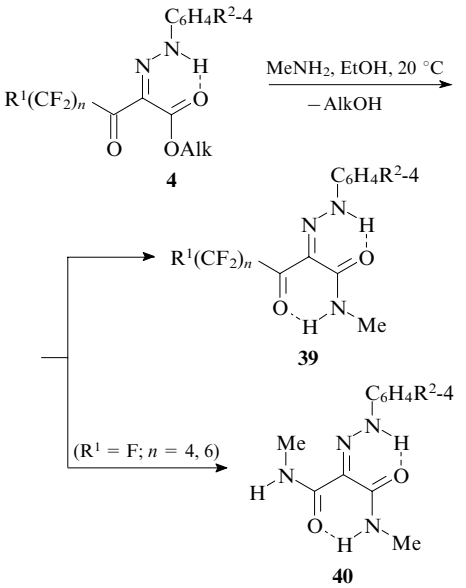
upon the amine addition to the carbonyl group at the fluoroalkyl substituent and the subsequent haloform cleavage of intermediates *via* elimination of fluoroalkane. The reactions of arylhydrazones **3** containing polyfluoroalkyl ($n \geqslant 3$) and bulky *tert*-butyl or phenyl substituents ($R^2 = Bu^t$, Ph) afford only amides **39**.

The template condensation of 1,2,3-trione 2-arylhydrazones **3** with methylamine on a Ni(II) template furnishes metal complexes **37**. An advantage of the template method is the possibility of preparing metal chelates with ligands having a long polyfluoroalkyl group (the number of carbon atoms is $\geqslant 3$) and a bulky hydrocarbon group. An alternative method for the preparation of chelates **37** is treatment of 2-arylazo-3-methylamino-1-(polyfluoroalkyl)enones **38** with metal salts.



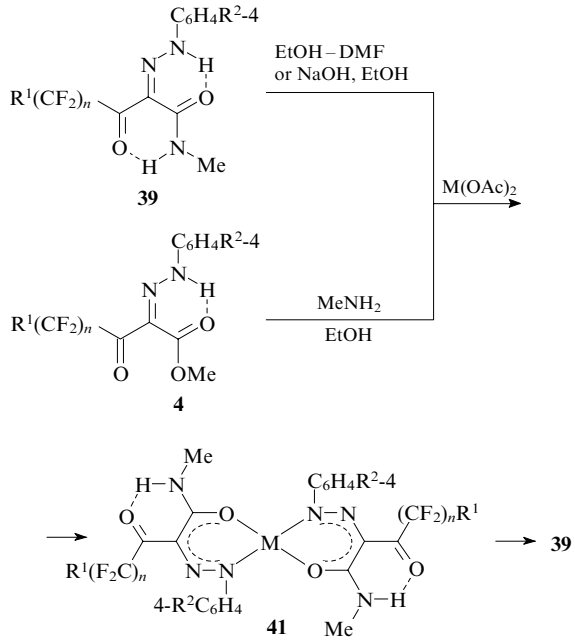
$R^1 = CF_3$, $(CF_2)_2H$, C_3F_7; R^2 = Me, Ph; R^3 = H, Me, OMe; M = Ni, Cu.

The major process in the reaction of 2-arylhydrazono-3-oxoesters **4** with methylamine is amine condensation at the ester group to give amides **39**. However, for esters **4** (n = 4, 6) having nonafluorobutyl and tridecafluorohexyl substituents, this is not the only reaction pathway, as the reaction is accompanied by the addition of amine at the fluoroacyl fragment followed by haloform cleavage to give diamide **40**.[136]



R^1 = H: n = 1, 2, 4; R^1 = F, n = 3, 4, 6; R^2 = H, Me, OMe.

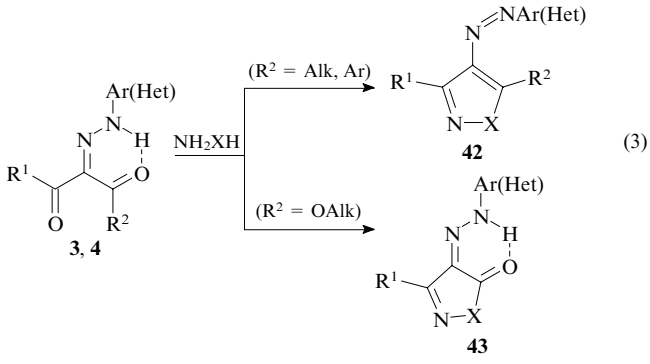
Amides **39** exhibit complexing properties relative to transition metal cations, and they can be used to prepare metal complexes **41**. The same chelates can be synthesized by template condensation of esters **4** with methylamine on nickel(II) template.[136] The template method is used for the synthesis of amides **39** with long polyfluorinated alkyl substituents.



R^1 = H: n = 1, 2; R^1 = F: n = 3, 4; R^2 = H, Me, OMe; M = Ni, Cu.

4. Reactions with dinucleophiles

2-(Het)arylhydrazono-1,3-dicarbonyl compounds tend to undergo cyclocondensation with dinucleophilic reagents. This reaction is widely used by synthetic chemists for the formation of heterocycles of various classes. Published data on the transformations of 2-(het)arylhydrazones induced by α-*N*,*N*′-dinucleophiles (hydrazines, hydrazides, semicarbazides, *etc*.) is most abundant. These reactions result in the corresponding (het)arylazopyrazoles and -pyrazolones [reaction (3)] (see, for example, works [137–179] and other references in the Table in the Appendix). The reactions of unsymmetrical 2-(het)arylhydrazono-1,3-dicarbonyl compounds with substituted hydrazines and hydrazides did not give isomeric pyrazoles. Actually, no strict evidence supporting the structure of the obtained pyrazoles and pyrazolones was presented by the authors. The conclusions about the products were based only on considerations concerning the higher reactivity of the carbonyl group at the methyl substituent of 2-(het)arylhydrazones. This is why the condensation of the free amino group of the dinucleophile involves the acetyl fragment of the substrate, resulting in 4-(het)arylazo-3-methyl-1-R^1-5-R^2-pyrazoles **42** (X = NR^3) and 4-(het)arylhydrazono-3-methyl-1-R^1-pyrazol-5-ones **43** (X = NR^3).

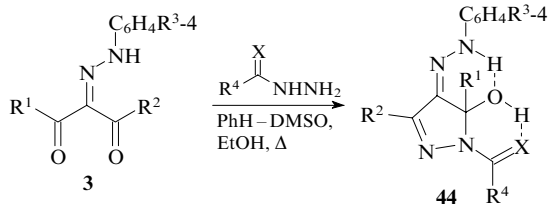


(3)

X = NR^3 [R^3 = H, Alk, C(O)Alk, $NHC(O)NH_2$ *etc.*], O.

The use of hydroxylamine hydrochloride in reactions with 2-(het)arylhydrazono-1,3-dicarbonyl compounds provides a route to isoxazole derivatives **42**, **43** (X = O) containing arylhydrazone residue (see the Table in the Appendix).[16, 21, 24, 25, 44, 67, 71, 72, 172, 180, 181] In all of these studies, the formation of 3-methylisoxazoles is again just postulated.

We found [83, 178] that 3-fluoroalkyl-substituted 4-(het)arylazopyrazoles are the only products formed in the reactions of fluoroalkyl-containing 2-(het)arylhydrazones of 1,2,3-triones with substituted hydrazines. In addition, it was found [179] that unlike reactions with hydrazines, reactions of fluoroalkylated 2-arylhydrazones of 1,2,3-triones **3** with benzoic acid hydrazide and thiosemicarbazide afford 5-fluoroalkyl-substituted 5-hydroxy-4-arylhydrazonopyrazolines **44**.

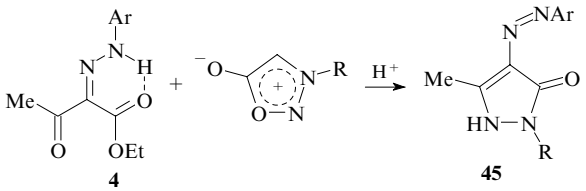


R^1 = CF_3, $(CF_2)_2H$; R^2 = Me, Ph; R^3 = H, Me; X = S, R^4 = NH_2; X = O, R^4 = Ph.

It is evident that in the reactions of fluoroalkylated arylhydrazones **3** with hydrazides, the site of the primary attack of the nucleophile changes, because pyrazoles of a different regioisomeric series are formed. Apparently, this is in line with Pearson's concept [182] according to which the weak nucleophile (hydrazide) first attacks the softer electrophilic centre (acyl group), while in the case of hydrazines, the situation is opposite. In the reactions of non-fluorinated 1,2,3-trione 2-arylhydrazones [see reaction (3)] with hydrazines and hydrazides, the cyclocondensation route does not change.

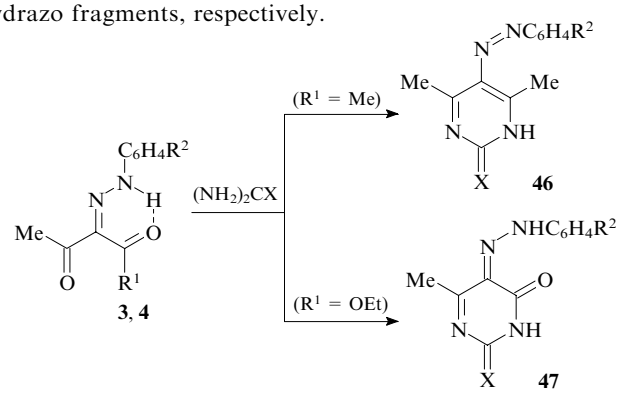
Note also that no hydroxy-substituted pyrazolines are formed in reactions of non-fluorinated 1,2,3-trione 2-(het)arylhydrazones with hydrazides. Apparently, the electron-withdrawing effect of the polyfluoroalkyl group prevents elimination of the water molecule.

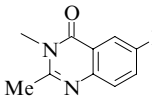
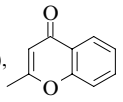
2-Arylazopyrazolones **45** can be prepared by the reaction of 2-arylhydrazonoacetoacetate **4** with 3-(het)arylsydnones. The latter represent a latent form of hydrazines, as they decompose to hydrazines in acid media.[183]



R = Ar, 2-oxochromen-8-ylmethyl.

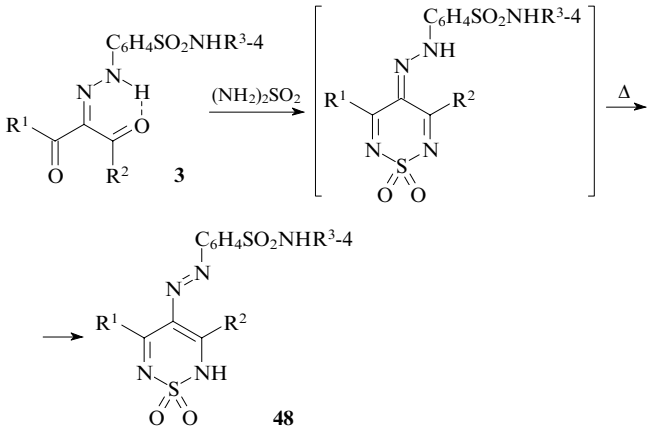
2-Arylhydrazono-1,3-dicarbonyl compounds **3** [60, 184] and **4** [16, 24, 185] react with urea, thiourea and guanidine to hive pyrimidine derivatives **46**, **47** containing azo and hydrazo fragments, respectively.



R^1 = Me (**3**), OEt (**4**); R^2 = H, 2-Me, 4-Me, 2-OMe, 4-OMe, $4\text{-}O_2SNH_2$, $4\text{-}(SC_6H_4NO_2\text{-}4)$,  (R^3 = H, Br), ;

X = O, S, NH.

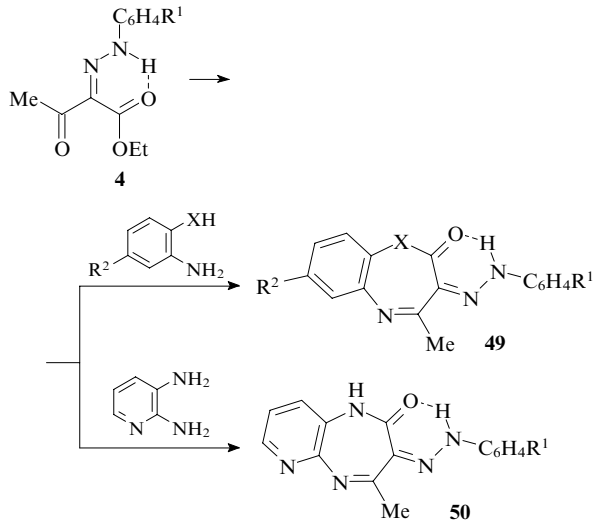
2-Arylhydrazones of 1,2,3-triones **3** undergo cyclocondensation with sulfamides at the 1,3-dicarbonyl fragment to give 4-arylazo-1,2,6-thiadiazine 1,1-dioxides **48**.[20]



R^1, R^2 = Me, Ph; R^3 = H, C(=NH)NH_2, $CH_2C(O)NH_2$, $C(O)C_6H_4OPr^i\text{-}4$, 2-Py, 1,3-thiazol-2-yl, 4-methylpyrimidin-2-yl, 5-methylisoxazol-3-yl.

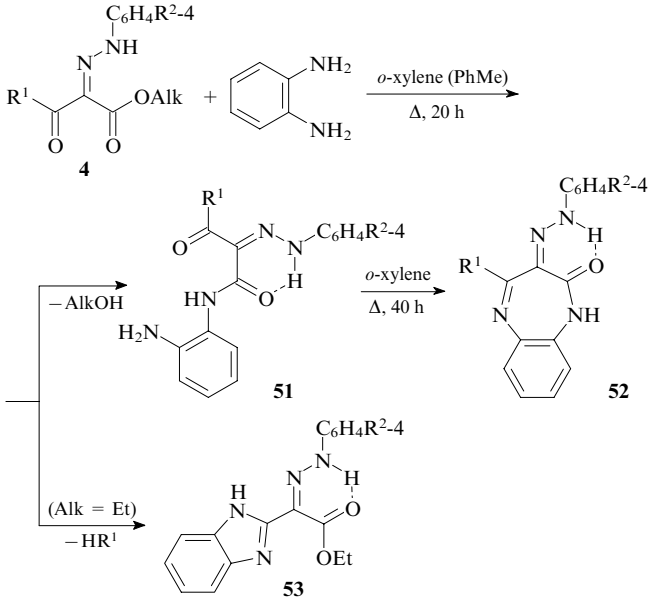
2-Arylhydrazonoacetoacetates **4** react with *o*-phenylenediamines, *o*-aminophenols, *o*-aminobenzenethiol and 2,3-diaminopyridine to give 3-arylhydrazones of 4-methyl-1*H*-1,5-benzodiazepine-2,3-diones,[186, 187] 4-methyl-1,5-benzoxazepine-2,3-diones and 4-methyl-1,5-benzothiazepine-2,3-diones [187, 188] (**49**) and 4-methyl-1*H*-pyrido[2,3-*b*]-[1,4]diazepine-2,3-diones **50**.[186] The amino group of unsymmetrical dinucleophiles adds first, apparently, to the acetyl

fragment of ester **4**, because authors report in all cases isolation of single regioisomers.



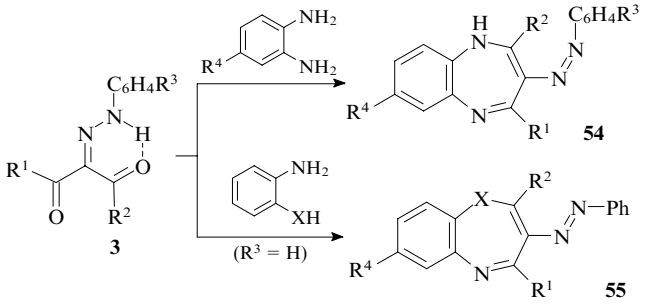
R^1 = H, 2-Cl, 4-Cl, 2-F, 2,4-F_2, 4-Br, 3-CF_3, 3,5-$(CF_3)_2$, 2-SMe, 3-SMe; X = NH: R^2 = H, Me; X = O: R^2 = H, NO_2; X = S, R^2 = H.

We showed[189,190] that 2-arylhydrazono-3-oxoesters **4** bearing a 3-fluoroalkyl substituent react first with *o*-phenylenediamine at the alkoxycarbonyl fragment giving rise to 2-arylhydrazono-3-oxoacid *o*-aminoanilides **51**, which can further cyclize on long-term refluxing in *o*-xylene to 3-arylhydrazono-4-fluoroalkyl-1*H*-1,5-benzodiazepine-2,3-diones **52**. The regioselectivity of these transformations decreases with reduction of the length of the fluoroalkyl fragment, because esters **4** with short difluoro- or trifluoromethyl substituents form not only *o*-aminoanilides **51**, but also ethyl 2-(benzimidazol-2-yl)-2-(arylhydrazono)acetates **53**. These are products of diamine cyclocondensation at the oxo group at the fluoroalkyl substituent followed by aromatization of the intermediate through elimination of the fluoroalkane molecule.



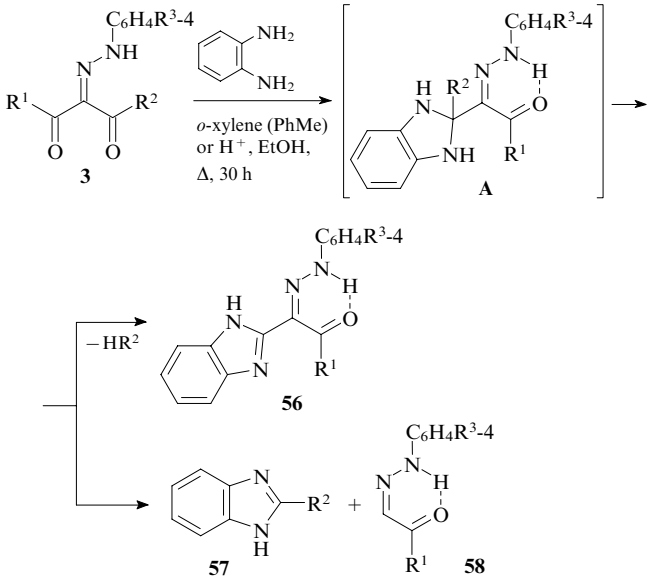
R^1 = CHF_2, CF_3, $(CF_2)_2H$, n-C_4F_9, n-C_6F_{13}; R^2 = H, Me, OMe; Alk = Me, Et.

1,2,3-Trione 2-arylhydrazones **3** react with substituted *o*-phenylenediamines, *o*-aminophenol and *o*-aminobenzenethiol in acid media to yield arylazo-1,5-benzodiazepines **54**,[187,191] -1,5-benzoxazepines and -1,5-benzothiazepines (**55**).[187]



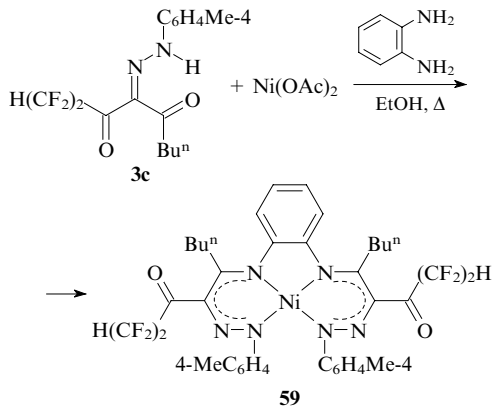
R^1 = Me, Ph; R^2 = Me, Ph, C_6H_4Cl-4, C_6H_4Br-4; R^3 = 2-Cl, 3-Cl, 4-Cl, 4-Br, 4-I, 4-F, 2-OMe, 4-OMe; R^4 = H, Cl; X = O, S.

Our study of the reaction of the 2-arylhydrazones of fluoroalkyl-1,2,3-triones **3** with *o*-phenylenediamine has demonstrated[189,192] that in boiling toluene (or *o*-xylene), these reactions may follow two pathways depending on the nature of non-fluorinated substituent. Indeed, compounds **3** having alkyl substituents (R^2 = Alk) are converted to 1-(benzimidazol-2-yl)-1,2-dioxoalkane arylhydrazones **56**, whereas phenyl-substituted analogues **3** (R^2 = Ph) yield only cleavage products, namely, benzimidazole **57** and arylhydrazone **58**. Probably, the reaction starts with cyclocondensation of *o*-phenylenediamine at the carbonyl group at the non-fluorinated substituent of 1,2,3-trione 2-arylhydrazones **3** with intermediate formation of benzimidazoline **A**, which may follow alternative aromatization pathways.



R^1 = CHF_2, CF_3, $(CF_2)_2H$, $(CF_2)_4H$, C_4F_9; R^2 = Me, Bu^n, Bu^t, CF_3, Ph; R^3 = H, Me, OMe.

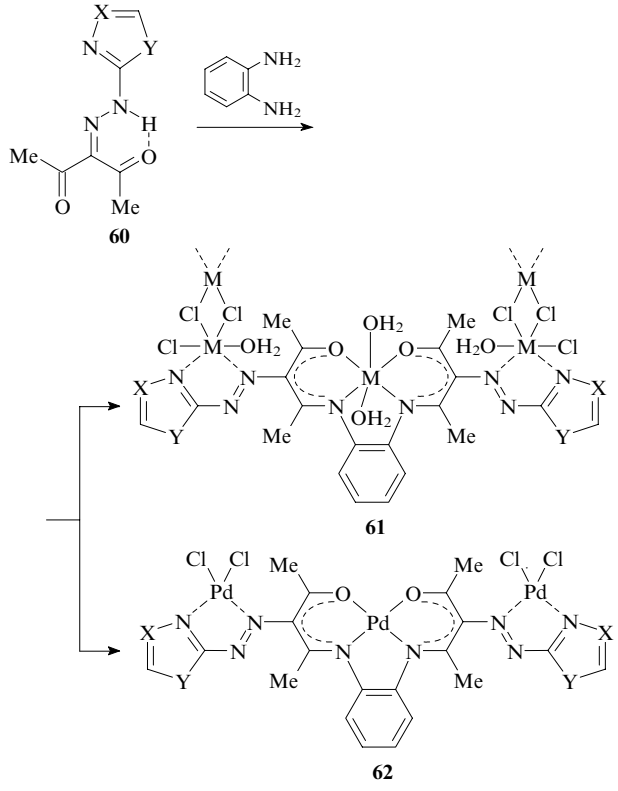
In the template reaction of 1,2,3-trione 2-arylhydrazone **3c** with *o*-phenylenediamine on a Ni(II) template, nickel(II) *N,N′*-phenylenebisiminate **59** is formed.[193]



3c **59**

The nickel complexes erroneously described[189] as *N,N′*-phenylenebis(2-arylazo-1,3-aminovinylketonates) have actually a similar structure.

The template condensation of 1,2,3-trione 2-azolylhydrazones **60** with *o*-phenylenediamine in the presence of nickel(II), copper(II) and palladium(II)[194] salts results in polynuclear complexes **61**, **62**.

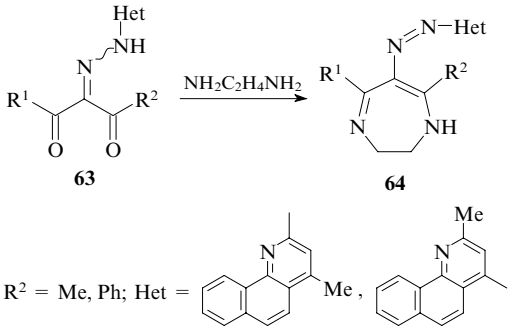


60 **61** **62**

61: M = Ni, Cu; X = CH, Y = S; X = N, Y = NH;
62: X = CH, Y = S; X = N, Y = NH.

Singh *et al.*[45] described heterocyclization of 1,2,3-trione 2-hetarylhydrazones **63** with ethylenediamine, resulting in 1,4-diazepine derivatives **64**.

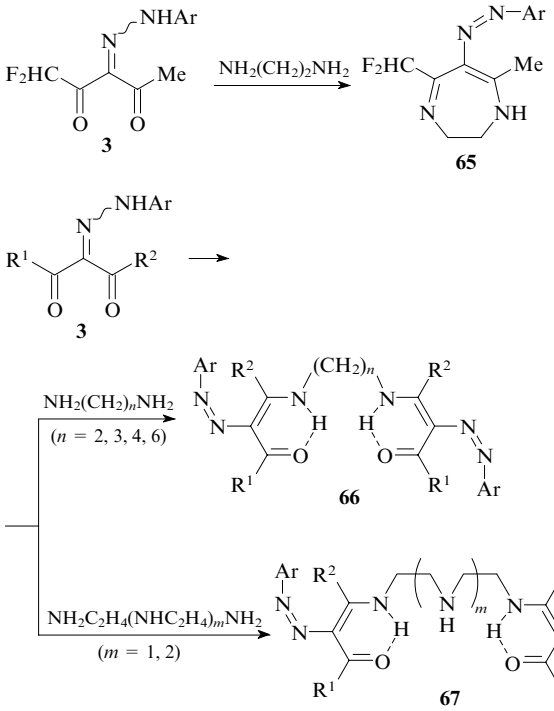
However, our studies[195,196] of the reactions of 1,2,3-trione 2-arylhydrazones with ethylenediamine revealed only one case of formation of a 1,4-diazepine derivative, 6-arylazo-7-methyl-5-difluoromethyl-2,3-dihydro-1*H*-1,4-diazepine (**65**), in particular, when 3-arylhydrazones of 1,1-difluoropentane-2,3,4-trione were used.



63 **64**

R^1, R^2 = Me, Ph; Het =

Arylhydrazones of other 1,2,3-triones with either fluoroalkyl or non-fluorinated substituents reacted with ethylenediamine giving rise to open-chain *N,N′*-ethylenebis(2-arylazo-3-amino-1-R^1-3-R^2-prop-2-en-1-ones) **66** (n = 2). Analogous *N,N′*-oligomethylenebis(arylazoaminovinyl ketones) **66** (n = 3, 4, 6) were obtained[195–203] by reactions of compounds **3** with ethylenediamine, trimethylenediamine and tetramethylenediamine. Note that all of these transformations are regioselective. 1,2,3-Trione 2-arylhydrazones also react with diethylenetriamine and triethylenetetramine in a similar way to yield compounds **67**.[196]



3 **65**

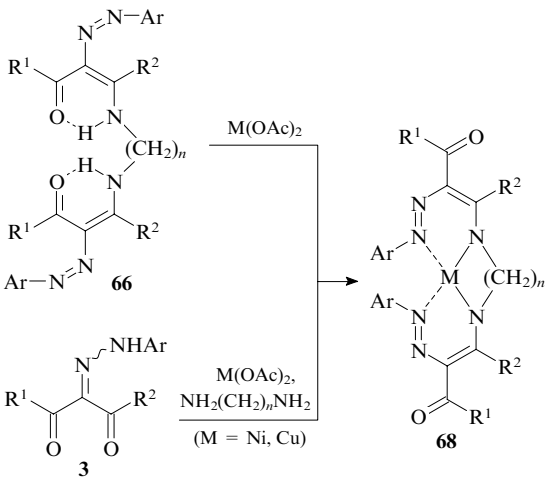
3

66

67

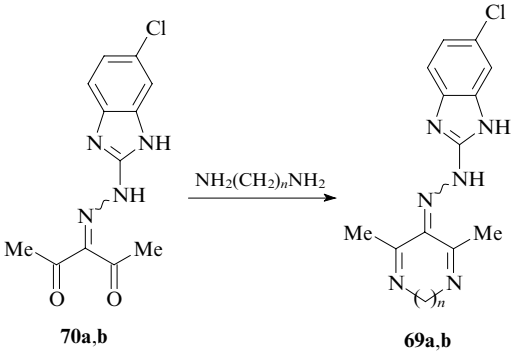
R^1 = Me, Ph, CF_3, $(CF_2)_2H$, $(CF_2)_4H$; R^2 = Me, Ph.

Podands **66** show complexing properties[195–205] being converted to metal chelates **68** on treatment with nickel(II) and copper(II) acetates. The same complexes can be obtained by the template method directly from 1,2,3-trione 2-arylhydrazones **3**.[195–198]



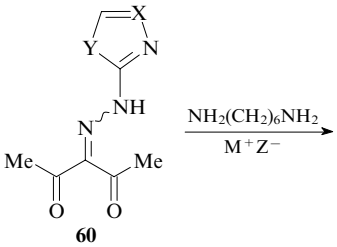
R^1 = Me, CF_3, $(CF_2)_4H$, C_4F_9; R^2 = Me, Ph; n = 2, 3, 4; M = Ni, Cu, Pd.

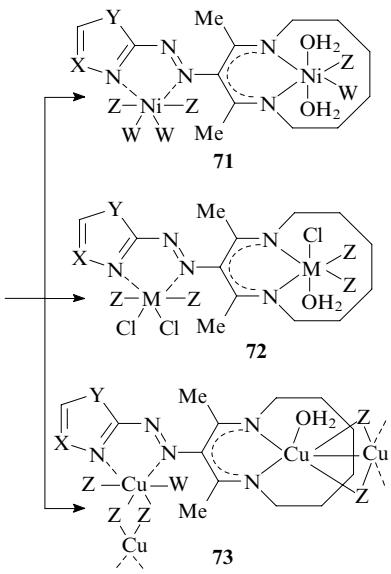
In view of the above data, the reported [206] formation of cyclization products **69a**,**b** in the reactions of pentane-2,3,4-trione 2-hetarylhydrazones **70a**,**b** with hexamethylenediamine and octamethylenediamine raises doubts, because the authors cite no data supporting the cyclic structure. Probably, these reactions yield the products of linking of two molecules of trione hydrazone **70** with one diamine molecule, the more so, as the authors report the formation of Pd(II) and Pt(II) complexes of these compounds.



n = 6 (**a**), 8 (**b**).

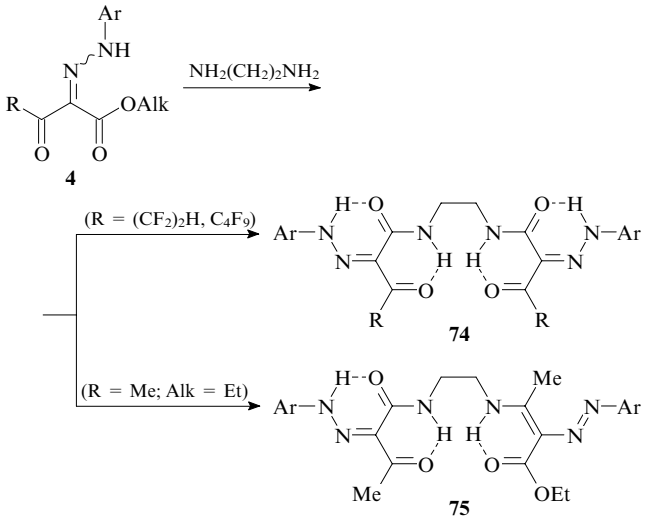
The same researchers describe [207] the template cyclization of pentane-2,3,4-trione 2-triazolyl- and 2-thiazolylhydrazones **60** with 1,6-diaminohexane in the presence of Ni(II), Cu(II), Pt(II), Pt(IV) and Pd(II) salts, resulting in polynuclear complexes **71**–**73**. Note that the structure of these complexes was not confirmed by X-ray diffraction.



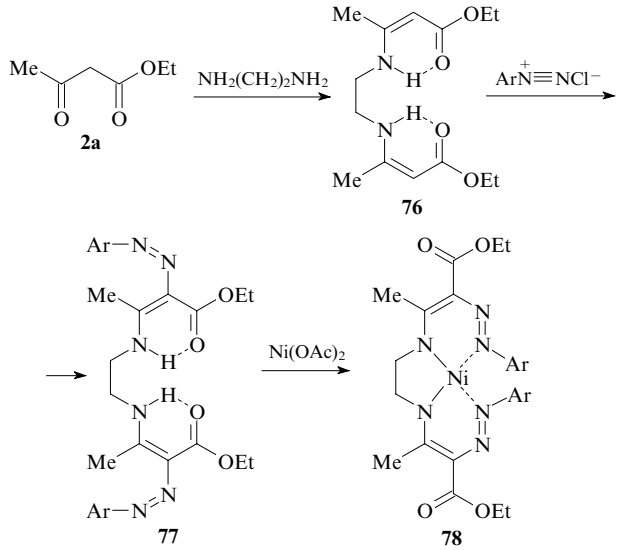


X = N, Y = NH; X = CH, Y = S; **71**, **73**: Z = OAc, W = H_2O; Z = Cl, W is absent; **72**: Z = Cl: M = Pd(II), Pt(II); Z is absent, M = Pt(IV).

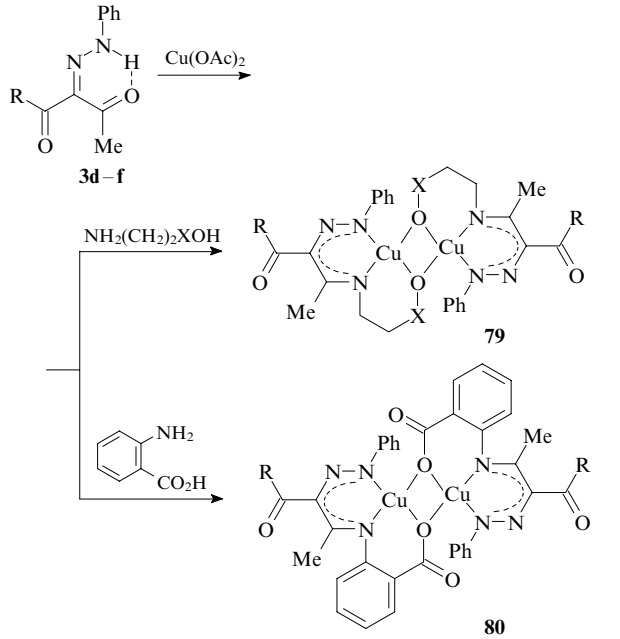
2-Arylhydrazono(fluoro)-3-oxoesters **4** react with ethylenediamine at the alkoxycarbonyl group giving the corresponding *N*,*N*′-ethylenediamides **74**.[196] However, 2-arylhydrazonoacetoacetate **4** (R = Me, Alk = Et) were converted under these conditions only to 'mixed type' addition products, compounds **75**. In the formation of these products, one molecule of ester **4** (R = Me, Alk = Et) adds ethylenediamine at the ester fragment, while the other molecule reacts at the keto group. A similar template reaction [in the presence of $Ni(OAc)_2$] resulted in symmetrical diamide of type **74**.



Arylhydrazonoacetoacetate can also be used to prepare nickel(II) tetraaza chelates similar to the complexes based on 2-arylhydrazones of 1,2,3-triones, but Balakrishnan [208] proposed quite a different synthetic routes to these products. First, the condensation of acetoacetate **2a** with ethylenediamine afforded diimine **76**, which was then subjected to azo coupling. The subsequent treatment of ligand **77** with nickel(II) acetate gave complex **78**.

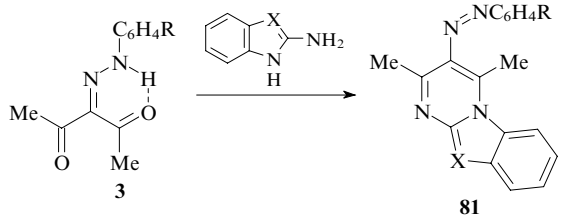


A three-component template condensation of 1,2,3-trione 2-arylhydrazones **3d**–**f** with 3-aminopropan-1-ol,[209] β-alanine or anthranilic acid on the copper(II) ion template,[210] resulting in binuclear metal complexes **79**, **80**, is known.



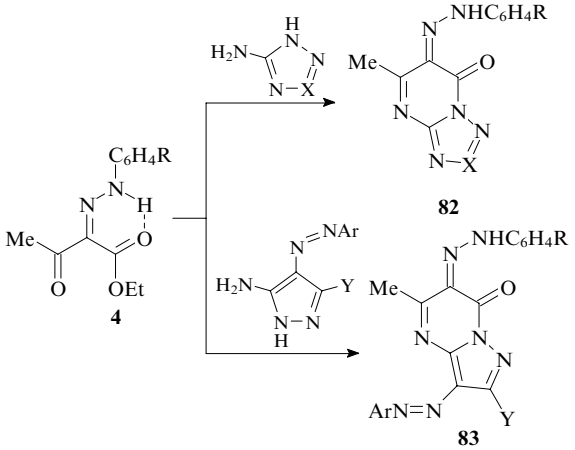
R = Me (**d**), Ph (**e**), CF_3 (**f**); X = CH_2, C(O).

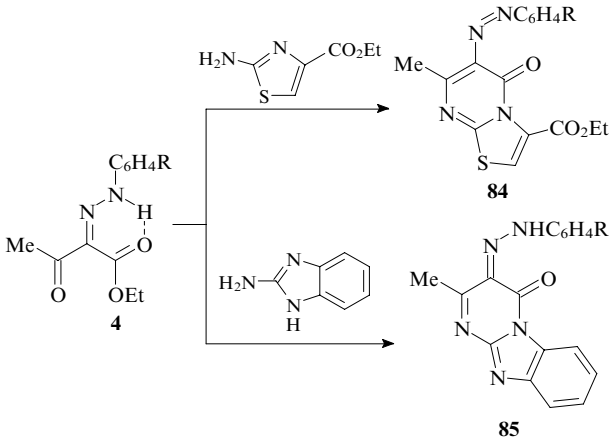
The presence of the 1,3-dicarbonyl fragment in 2-arylhydrazono-1,3-dicarbonyl compounds **3** and **4** accounts for their possible cyclocondensation with hetarylamines, which yields heterannelated pyrimidines **81**,[211,212] **82**,[184,211,213,214] **83**,[212] **84**,[211] **85**.[214]



R = H, 2-Me, 4-Me, 2-Cl, 2-Br, 4-Br, 2-I, 3-NO_2, 4-CO_2Et;
X = CH, N.

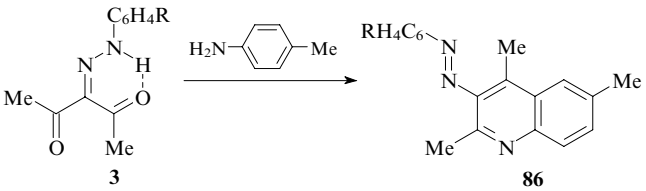
In the case of 2-arylhydrazonoacetoacetates **4**, cyclization is regioselective, because the pyrimidine ring is formed upon condensation of the free amino group of hetarylamine with the acetyl substituent of ester **4** and condensation of the α-NH group of the heterocycle with the ethoxycarbonyl.[215]





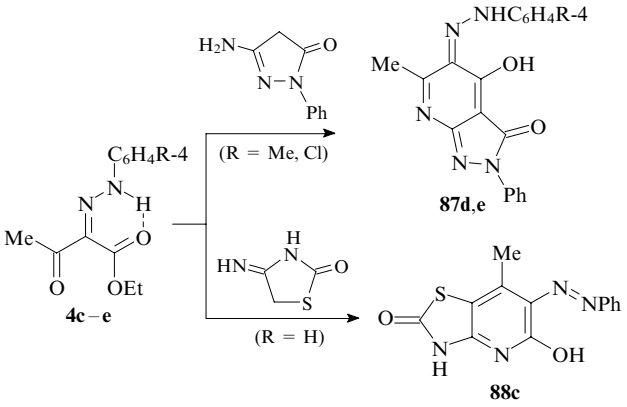
R = H, 3-Me, 4-Me, 4-Cl, 4-Br, 4-OH, 2-NO_2, 4-NO_2 , 4-OMe;
X = CH, N.

A regioselective cyclization of pentane-2,3,4-trione 2-arylhydrazones **3** with 4-aminotoluene, giving rise to 3-arylazo-2,4,6-trimethylquinolines **86**, has been reported.[216]



R = H, 3-Me, 4-Me, 2-OMe, 4-OMe, 2-Cl, 3-Cl, 4-Cl, 4-Br, 3-OH, 4-CO_2H.

Examples are known of heterocyclization of 2-arylhydrazone-substituted acetoacetates **4c**–**e** with hetarylamines functioning as N,C-dinucleophiles to give fused pyridines **87d**,**e** [214] and **88c**.[217]



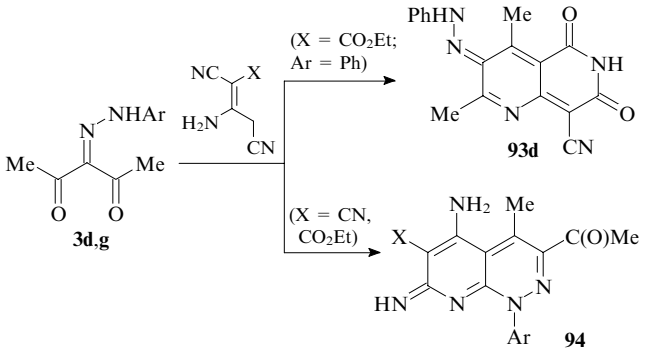
R = H (**c**), Me (**d**), Cl (**e**).

5. Reactions with ambident bifunctional reagents

2-Arylhydrazono-1,3-dicarbonyl compounds react with bifunctional reagents, for example, with amino compounds having an activated methylene group. These reactions involve not only the 1,3-dicarbonyl fragment, but also the arylhydrazone substituent. According to Elnagdi *et al.*,[218,219] cyclization of ethyl 2-arylhydrazono-3-oxobutanoates **4c**,**d** with 2-amino-1,1,3-tricyanopropene involves the 1,3-dicarbonyl fragment and gives pyridin-2-ones **89**. In addition to this product, these reactions give pyridopyridazines **90**, resulting from the competing cyclization involving the arylhydrazone group.[220] However, El-Sakka [221] obtained, along with monocyclic pyridin-2-one **89**, the product of its subsequent cyclization, pyridopyridine **91** (Scheme 1).

The reactions of compounds **4c**,**d** with diethyl 2-amino-1-cyanopropene-1,3-dicarboxylate affords only pyridopyridazines **92**.[220]

Alternative reaction pathway was also found for analogous transformations of 2-arylhydrazones of pentane-2,3,4-triones **3d**,**g**. The authors believe that 2-arylhydrazono-1,3-dicarbonyl compounds are first condensed by the acetyl group with the activated methylene group of the reagent. This yields initially the Knoevenagel intermediates, and finally results in heterocycles **93d**,[219] **94**.[220]

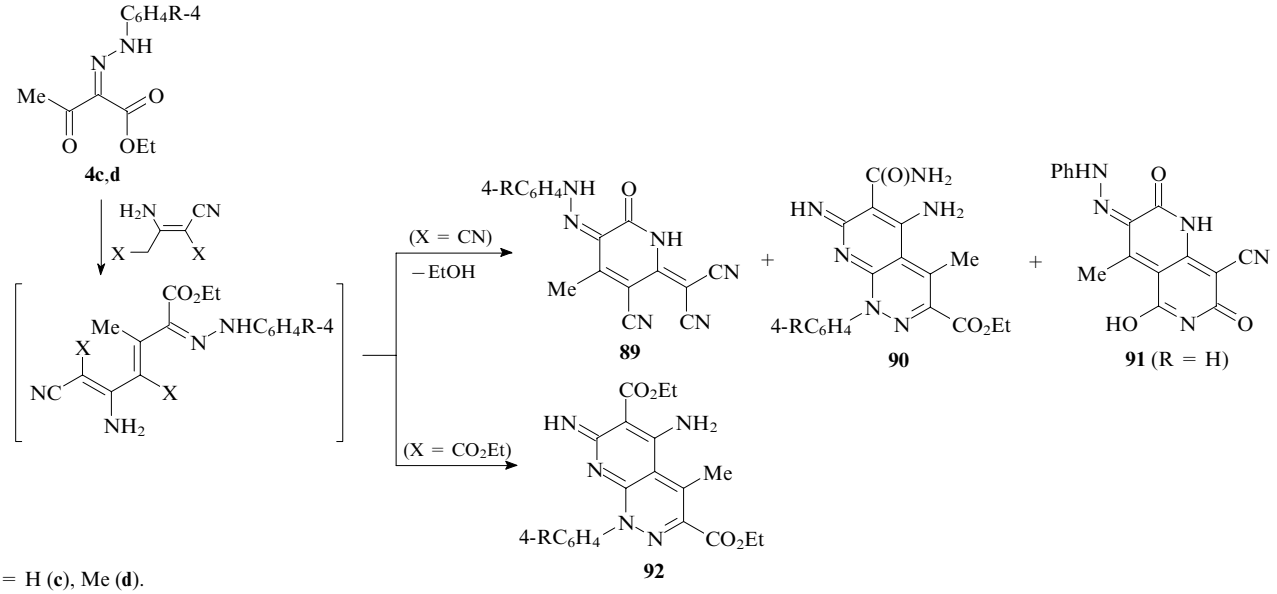


Ar = Ph (**d**), 4-MeC$_6$H$_4$ (**g**).

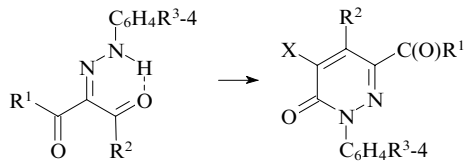
The presence of the HN group in the molecules of 2-arylhydrazono-1,3-dicarbonyl compounds provides the possibility of cyclizations with various esters containing an activated methylene group to give pyridazinone derivatives. Thus compounds **3**, **4** are condensed with ethyl cyanoacetate,[222–224] triethyl phosphonoacetate anion,[225] and ethyl trimethylsilylacetate [226] giving rise to substituted pyridazin-3-ones **95**.

The pyridazine nucleus is formed through condensation of the ester methylene group with the acyl fragment of 2-arylhydrazono-1,3-dicarbonyl compounds and the ethoxycarbonyl residue with the HN group of the arylhydrazone fragment. Similar pyridazin-3-ones **95** (X = H) can be synthesized by the reactions of compounds **3**, **4** and the Wittig reagents.[227]

Scheme 1



R = H (**c**), Me (**d**).

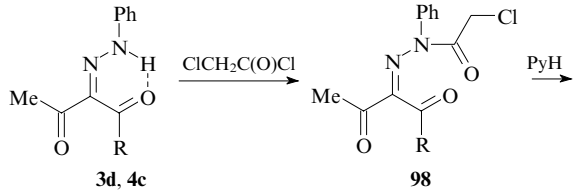


3, **4** **95**

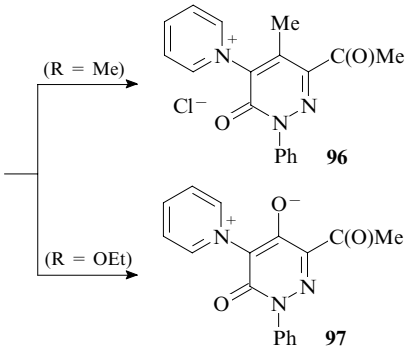
R^1 = Me, OMe, OEt, NHPh, NMe_2, Ph; R^2 = Me, Ph;
R^3 = H, Me, Cl, NO_2.

Reactant	X	Reaction conditions	Yield (%)
$NCCH_2CO_2Et$	CN	NH_4OAc (AcOH), Δ	60–97
$Me_3SiCH_2CO_2Et$	H	1) Bu^nLi, THF, −78 °C; 2) 40–45 °C	20–74
$(EtO)_2P(O)CH_2CO_2Et$	H	NaH, THF, 25–65 °C	25–71
$Ph_3P{=}CHCO_2R^4$ (R^4 = Me, Et, Ph)	H	–	–

For the preparation of pyridazin-3-ones **96**, **97**, Gewald *et al.*[228] propose N-acylation of 2-phenylhydrazones **3d**, **4c** with chloroacetyl chloride followed by cyclization of intermediates **98** with pyridine.

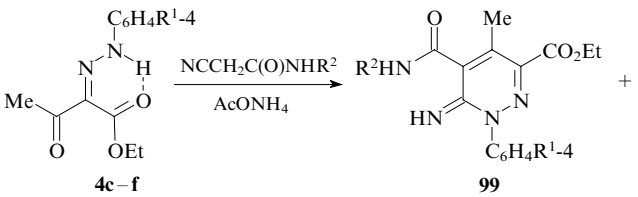


3d, **4c** **98**

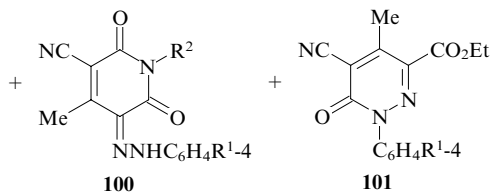


96 **97**

Ethyl 2-arylhydrazono-3-oxobutanoates **4c**–**f** react with cyanoacetamide in the presence of ammonium acetate to give a mixture of ethyl 1-aryl-6-imino-5-carbamoyl-4-methyl-1,6-dihydropyridazine-3-carboxylate **99** with 5-arylhydrazono-4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitriles **100** in 1 : 1.3 ratio;[229] only upon refluxing the reactants in a benzene–acetic acid mixture, ethyl 1-aryl-5-cyano-4-methyl-6-oxo-1,6-dihydropyridazine-3-carboxylates **101** were formed along with heterocycles **99**, **100** (0.5 : 1 : 1 ratio).



4c–**f** **99**

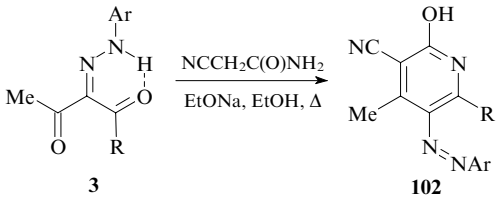


100 **101**

R^1 = H (**c**), Me (**d**), Cl (**e**), OMe (**f**);
R^2 = H, 4-MeC_6H_4, thiazol-2-yl.

When *N*-substituted cyanoacetamides were used in this reaction[230] and the reaction was carried out in a mixture of boiling benzene and acetic acid in the presence of ammonium acetate, heterocycles **99** and **100** were produced in 1 : 3 ratio. Evidently, in all cases, the primary step of formation of heterocycles **99**–**101** is the condensation of the acetyl fragment of ester **4** with the methylene group of cyanoacetamide.

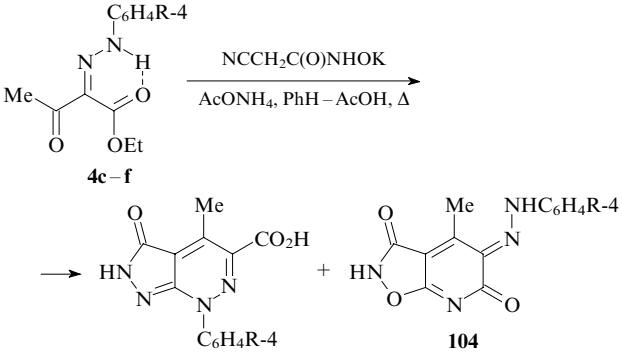
The 2-arylhydrazones of 1,2,3-triones **3** are react with cyanoacetamide more selectively yielding pyridines **102**.[231]



3 **102**

R = Me, Ph; Ar = 2-OH-5-ClC_6H_3, 2-OHC_6H_4, 4-OHC_6H_4, 2-ClC_6H_4,4-BrC_6H_4, 2-$MeOC_6H_4$, 3-$NO_2C_6H_4$, 2,4-$(MeO)_2C_6H_3$.

The reactions of 2-arylhydrazono-3-oxoesters **4c**–**f** with the potassium salt of cyanoacetohydroxamate afford mixtures of fused heterocycles, in particular, pyrazolo[3,4-*c*]-pyridazines **103** and isoxazolo[5,4-*b*]pyridines **104** in 1 : 1 yield.[232]



4c–**f**

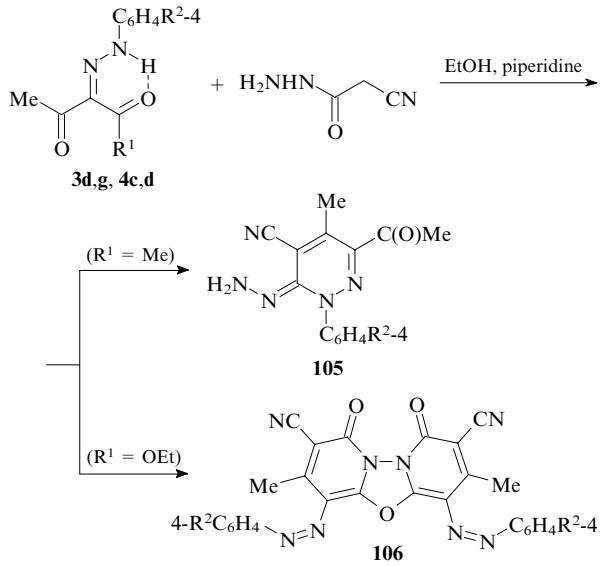
103 **104**

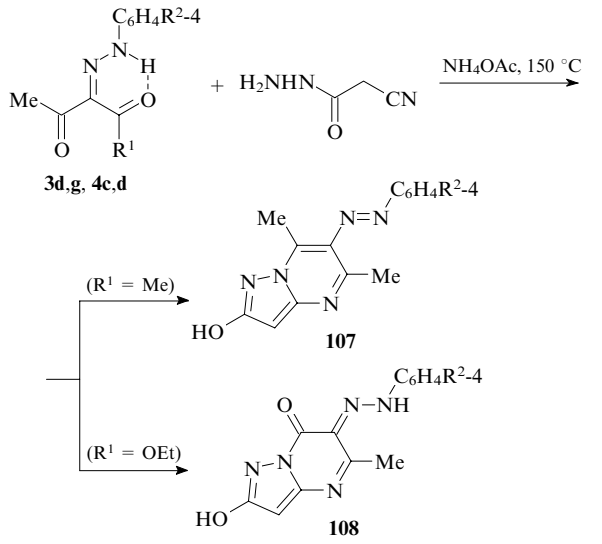
R = H (**c**), Me (**d**), Cl (**e**), OMe (**f**).

Unlike the classical reactions of 2-(het)arylhydrazono-1,3-dicarbonyl compounds **3**, **4** with hydrazides, which lead to pyrazole derivatives **43**, their cyclization with cyanoacetohydrazide, which combines a hydrazine fragment and an activated methylene group in the molecule, furnish different heterocyclic systems depending on the reaction conditions.[233] When these reactions were carried out in ethanol in the presence of piperidine, 2-arylhydrazones of pentane-2,3,4-trione **3d**,**g** were converted to 6-acetyl-2-aryl-3-hydrazono-5-methyl-2,3-dihydropyridazine-4-carbonitriles **105**, while ethyl 2-arylhydrazono-3-oxobutanoates **4c**,**d** were converted to pyrido[1′,2′:4,5][1,3,4]oxadiazolo[3,2-*a*]pyridines **106**. Under these conditions, apparently, an intermediate is

formed initially upon condensation of the acetyl residue of arylhydrazones **3**, **4** with the activated methylene group of the hydrazide. Then the acetylacetone derivatives undergo intramolecular heterocyclization by condensation of the HN group of the arylhydrazone fragment with the carbonyl group of the hydrazide residue, while acetoacetate derivatives undergo more complex transformations. Most probably, first, two intermediate molecules are linked through the condensation at the hydrazine group with elimination of hydrazine, then two pyridine rings are formed upon condensation of the hydrazide HN group with the ethoxycarbonyl residues, and finally two pyridine nuclei are linked by condensation of two hydroxyl substituents in pyridines. This gives rise to the central oxadiazole ring of product **106**.

The same researchers [233] found that short-term heating of compounds **3d**,**g**, **4c**,**d** with cyanoacetohydrazide at 150°C in the presence of ammonium acetate affords 6-arylazo-5,7-dimethylpyrazolo[1,5-*a*]pyrimidin-2-ols **107** and 6-arylhydrazones of 2-hydroxy-5-methylpyrazolo[1,5-*a*]-pyrimidine-6,7-dione **108**. The formation of these heterocycles is due to the initial condensation of the free amino group of the hydrazide fragment of the nucleophile with the acetyl (in the case of arylhydrazones **3**) or ethoxycarbonyl (in the case of esters **4**) group. The researchers assumed that

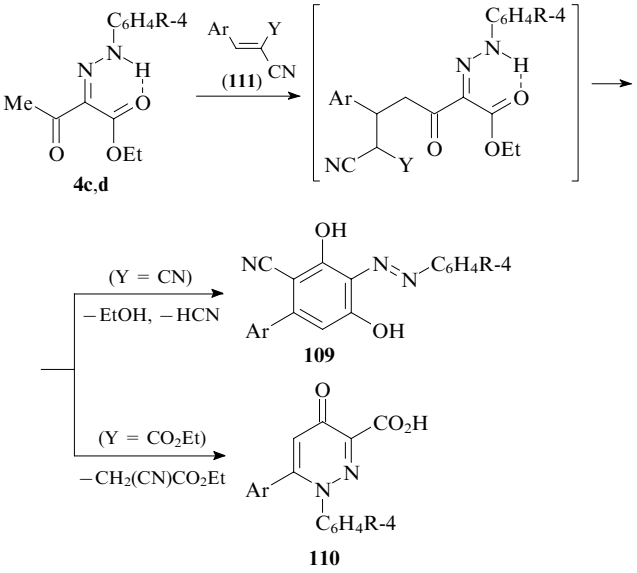




R^2 = H (**3d**, **4c**), Me (**3g**, **4d**).

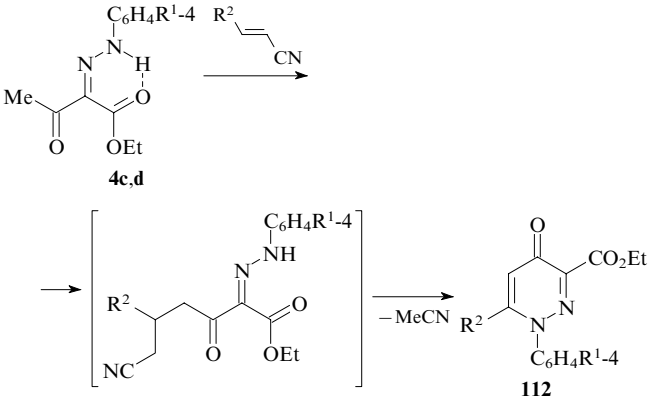
the intermediate undergoes double cyclization to give pyrazolopyrimidines **107**, **108**.

Ethyl 2-arylhydrazono-3-oxobutanoates **4c**,**d** react with arylidenemalononitrile yielding 2,4-dihydroxybenzonitriles **109**, while the reactions with ethyl 3-aryl-2-cyanoacrylate afford 4-oxo-1,4-dihydropyridazine-3-carboxylic acids **110**.[220] It is evident that the first step of these transformations is the Michael addition of the methyl group of the initial ester to the C=C bond of the arylidene fragment. The subsequent transformations of the intermediate depend on the structure of the added fragment. In the case of arylidenemalononitrile derivative **111** (Y = CN), cyclization occurs through condensation of the CH group attached to the electron-withdrawing cyano groups with the ethoxycarbonyl fragment with elimination of ethanol and hydrogen cyanide. In the case of 3-aryl-2-cyanoacrylate derivative **111** (Y = CO_2Et), heterocyclization is a result of addition of the CH group at the aryl substituent to the NH group of the arylhydrazone fragment and elimination of cyanoacrylate.



R = H (**c**), Me (**d**); Ar = Ph, 4-ClC_6H_4, 4-$MeOC_6H_4$.

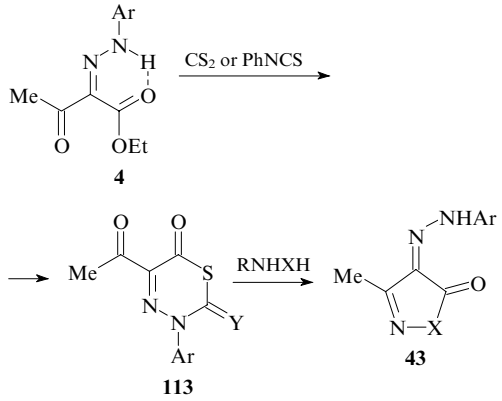
Similarly, cyclization of ethyl 2-arylhydrazono-3-oxobutanoates **4c**,**d** with acrylo- and crotononitriles gives pyridazinones **112**.[234]



R^1, R^2 = H, Me.

The reaction of ethyl 2-arylhydrazono-3-oxobutanoates **4** with carbon disulfide or phenyl isothiocyanate in the presence of a base gives 1,3,4-thiadiazine derivatives

113.[235, 236] The heterocyclization involves the NH group and the ethoxycarbonyl fragment of ester **4**. On treatment with α-dinucleophiles (hydrazines and hydroxylamine), thiadiazines **113** decompose giving substituted pyrazolinones and isoxazolinones **43**,[235, 236] similar to those synthesized by cyclocondensation of ester **4** with the corresponding α-dinucleophiles [see reaction (3)].



Ar = Ph, 4-$NO_2C_6H_4$, 4-$MeOC_6H_4$, 2,4,6-$Br_3C_6H_2$, 4-(2*H*-1,2,3-triazol-3-yl)phenyl; X = NH, O; Y = S, NHPh; R = H, Ph, 4-$NO_2C_6H_4$, C(=Z)NH_2 (Z = O, S).

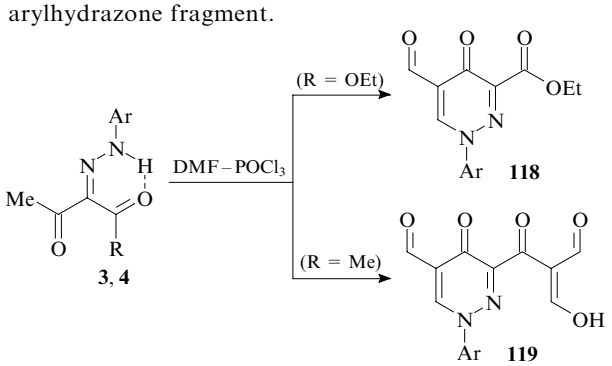
6. Miscellaneous cyclizations

Apart from the transformations considered above giving rise to heterocycles, 2-arylhydrazones of acetylacetone and acetoacetate can undergo cyclizations with participation of the methyl group.

An efficient method for the synthesis of 1-aryl-4-oxo-3-ethoxycarbonyl-1,4,5,6-tetrahydropyridazines has been proposed.[237] 6-Phenyltetrahydropyridazines **114** were obtained by treatment of ethyl 2-arylhydrazono-3-oxobutanoates **4** with benzaldehyde in the presence of a base (Scheme 2).

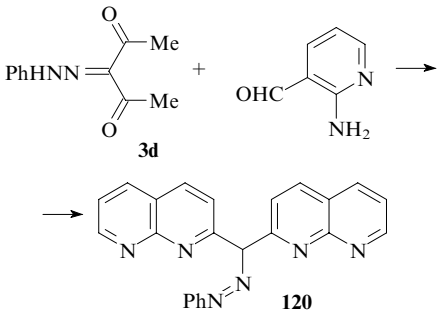
By changing the reaction conditions, it is possible to isolate an acyclic product of condensation of aldehyde with ester **4** at the methyl group (compound **115**), which undergoes intramolecular cyclization in a basic medium as a result of addition of a carbon atom of the C=C bond to the NH group of the arylhydrazone fragment. For preparing 6-iminotetrahydropyridazines **116**, Patel and Fernandes[237] propose using bromination of ethyl 2-arylhydrazono-3-oxobutanoates **4** and subsequent KCN-induced cyclization of intermediate **117** in DMF.

A method for preparation of substituted 1,4-dihydropyridazin-4-ones **118**, **119** by cyclization of 2-arylhydrazono-1,3-dicarbonyl compounds **3**, **4** under the action of the Vilsmeier–Haack reagent has been reported.[238, 239] The formylation of the methyl groups is followed by heterocyclization involving the NH group of the arylhydrazone fragment.



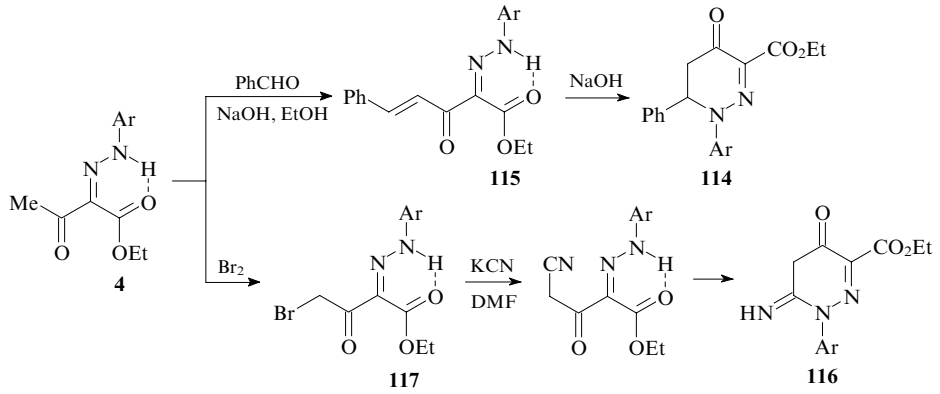
Ar = Ph, 4-$NO_2C_6H_4$, 2,4-$(NO_2)_2C_6H_3$, 4-BrC_6H_4, 2,4,6-$Br_3C_6H_2$, 4-(2*H*-1,2,3-triazol-2-yl)phenyl; R = Me, OEt.

For pentane-2,3,4-trione 2-phenylhydrazone (**3d**), a heterocyclization involving both acetyl groups with two equivalents of 2-aminonicotinaldehyde, resulting in 2,2′-[(phenylazo)methylene]bis(1,8-naphthyridine) **120** has been reported.[240]



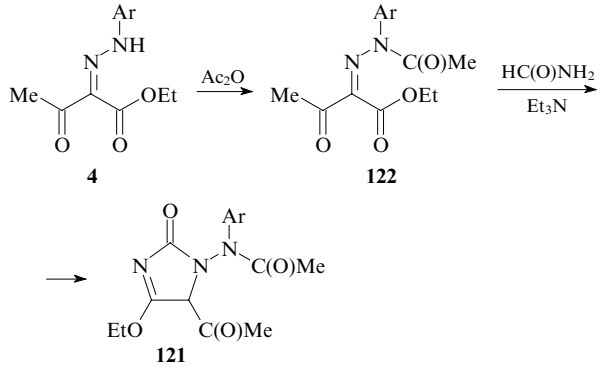
A method for the synthesis of imidazoles **121** from ethyl 2-arylhydrazono-3-oxobutanoates **4** has been proposed.[241] To this end, ester **4** is first acylated by acetic anhydride to protect the arylhydrazone NH group. Then acetyl derivative **122** is treated with formamide in the presence of triethylamine to give *N*-(5-acetyl-4-ethoxy-2-oxo-2,5-dihydroimidazol-1-yl)-*N*-arylacetamide **121**. The imidazole ring is formed with participation of the carbonyl carbon atom of the

Scheme 2



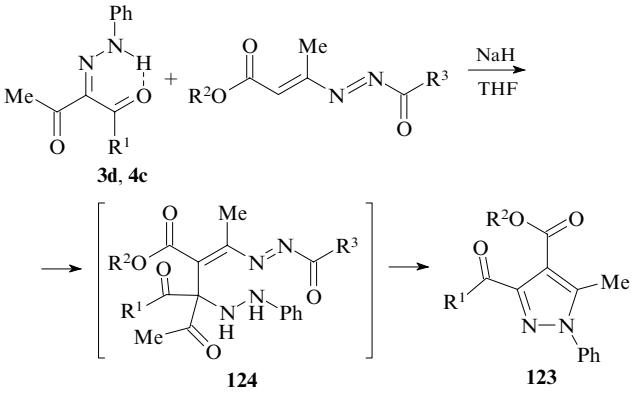
Ar = Ph, 4-$NO_2C_6H_4$, 4-BrC_6H_4, 2,4,6-$Br_3C_6H_2$.

ethoxycarbonyl fragment and nitrogen of the C=N bond of ester **4**.



4 **122** **121**

2-Arylhydrazono-1,3-dicarbonyl compounds **3d**, **4c** can react with 1,2-diazabuta-1,3-dienes in the presence of a base yielding 1-phenylpyrazole derivatives **123**.[242] In the researchers' opinion, this reaction proceeds *via* 1,4-addition of arylhydrazones **3**, **4** to 1,2-diazabutadiene with intermediate formation of **124**. The intramolecular nucleophilic attack of nitrogen of the Ph–NH fragment on carbon of the hydrazone residue accompanied by elimination of the hydrazine and acetyl groups results in the formation of the pyrazole ring **123**.

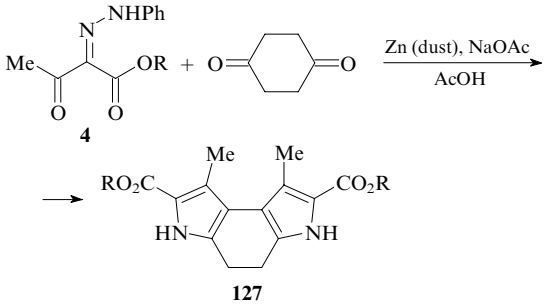


3d, **4c** **124** **123**

R^1 = Me, OEt; R^2 = Me, Et, Pr^i, $(CH_2)_2OMe$; R^3 = OBu^t, NH_2.

The reaction of 2-arylhydrazono-3-oxobutanoates **4** with chlorosulfonyl isocyanate at 0–5 °C followed by hydrolysis of the intermediate formed in the presence of benzenethiol gives 7-aryl-3-methyl[1,2,5]thiadiazolo[3,2-*f*][1,2,4]triazine-4,6-dione 1,1-dioxides **125**.[243] The temperature was found to have a crucial influence on the transformation route. When the reaction is carried out at 105–110 °C, 8-aryl-4-methyl[1,2,3,6]thiatriazino[3,4-*d*][1,2,3,4]-oxathiadiazin-5-one 2,2,7,7-tetroxides **126** are formed (Scheme 3).

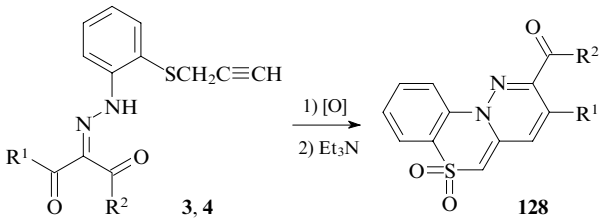
A convenient one-step method for preparing 1,8-dimethyl-3,4,5,6-tetrahydropyrrolo[3,2-*e*]indoles **127** based on the reaction of alkyl 2-phenylhydrazono-3-oxobutanoates **4** with cyclohexane-1,4-dione in the presence of a reducing agent was proposed.[244]



4 **127**

R = Me, Et, Bn.

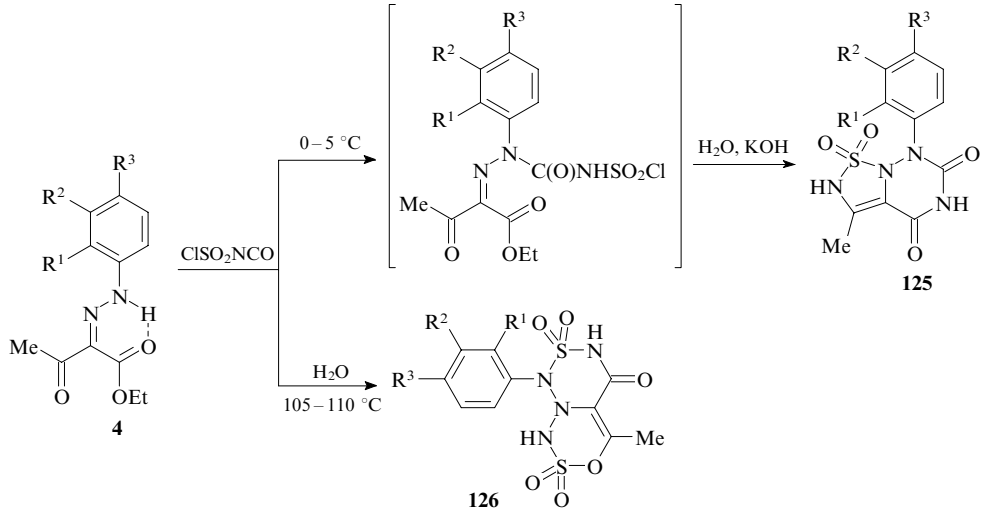
2-[2-(Propargylthio)phenylhydrazono]-1,3-dicarbonyl compounds are oxidized with peroxy acids to sulfones, which then cyclize in triethylamine to give pyridazino[3,2-*c*]-[1,4]benzothiazine *S*,*S*-dioxides **128**.[51]



3, **4** **128**

R^1 = Me, Ph; R^2 = Me, Ph, OEt.

Scheme 3

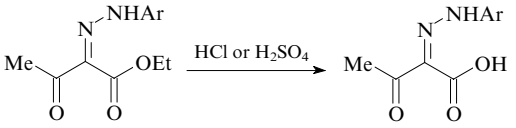


4 **125** **126**

R^1 = R^2 = H: R^3 = Cl, Me, OMe; R^1 = R^3 = H: R^2 = Br, Cl; R^2 = R^3 = H: R^1 = NO_2, Cl, OMe.

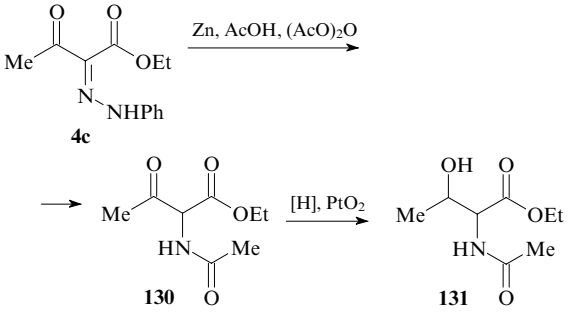
7. Miscellaneous reactions

Under the action of strong acids, the ester group in 2-arylhydrazono-3-oxobutanoates **4** may be hydrolyzed giving rise to acids **129**.[245]

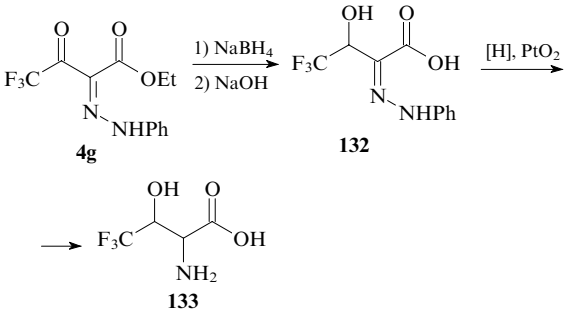


4 **129**

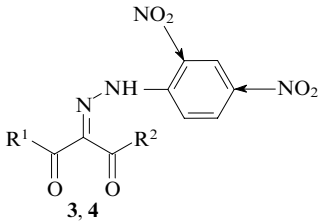
Data on the possibility of reduction of 2-arylhydrazono-3-oxoesters have been reported. Depending on the reducing agent used, primary selective reduction of either the C=N bond[246,247] or the C=O bond is possible.[248] It was reported[247] that the arylhydrazone fragment of 2-arylhydrazono-3-oxobutanoates **4** was converted to acetamide residue on treatment with zinc dust in an acetic acid – acetic anhydride mixture as a result of reductive acylation. Hydrogenation of the resulting 2-acetamide-substituted acetoacetate (**130**) led to reduction of the carbonyl group and provides D,L-threonine and D,L-allothreonine derivatives (**131**), whose ratio depends on the nature of the catalyst used and the reaction conditions.[247,248]



Transformations under the action of sodium borohydride were described for ethyl 2-phenylhydrazono-4,4,4-trifluoro-3-oxobutanoate **4g**; this gave 3-hydroxy acid **132**. However, the product yield was relatively low (~40%). Further catalytic hydrogenation (with hydrogen in the presence of platinum oxide) of the C=N bond of acid **132** to 2-amino acid **133** also has low efficiency (yield ~30%).[248]

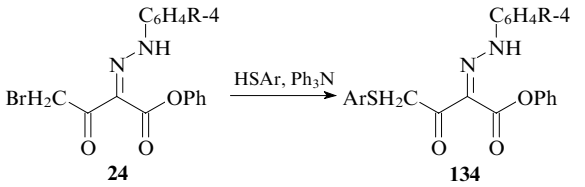


The aromatic nitration of 2-phenylhydrazono-1,3-dicarbonyl compounds **3** under the action of nitric acid, resulting in 4-nitro (yield 55% – 66%) and 2-nitro derivatives (yield 12% – 17%) has been described.[249]



R^1 = Me, Ph; R^2 = Me, OEt, OMe.

For 2-arylhydrazono-4-bromo-3-oxobutanoates **24**, replacement of the halogen atom in the alkyl group by an arylthio group is known.[177]



R = H, OMe, NO_2; Ar = Ph,  (X = NH, S).

V. Practical applications of 2-(het)arylhydrazono-1,3-dicarbonyl compounds and their derivatives

2-Arylhydrazono-1,3-dicarbonyl compounds and their derivatives are valuable compounds from the practical standpoint, first of all, due to their biological activities. Some of 2-arylhydrazono-1,3-dicarbonyl compounds were found to exhibit considerable pesticide activity.[17,24] 2-(1,2,4-Triazol-3-yl)phenylhydrazono-3-oxobutanoates are effective against the bacteria *Staphylococcus aureus* and *Mycobacterium fortuitum*.[250] 3-(1,3-Benzothiazol-2-yl)hydrazones of pentane-2,3,4-trione are active against *Staphylococcus aureus*[27] and against some kinds of tumours.[28] Ethyl 2-(3,5-dimethyl-1*H*-pyrazol-4-yl)hydrazono-3-oxobutanoate inhibits the growth of *Mycobacterium tuberculosis*.[251] 2-(1,3-Thiazol-2-yl)hydrazone and 2-(1,3,5-triazol-2-yl)hydrazone of pentane-2,3,4-trione (**60**) show high fungicidal activities.[194] Representatives of 2-arylhydrazono-1,3-dicarbonyl compounds were patented as cardiotonics, hypotensive and vasodilatory agents.[252,253]

2-(Het)arylhydrazono-1,3-dicarbonyl compounds find extensive use as intermediates in the synthesis of biologically active compounds. Thus ethyl 2-arylhydrazono-3-oxobutanoate is used to obtain threonine.[246] 2-Arylhydrazono-3-oxoesters are used to synthesize morphine derivatives, δ-opioid receptor agonists and antagonists.[254,255]

Substances with diverse biological activities have been found in the series of heterocyclic derivatives of 2-(het)arylhydrazono-1,3-dicarbonyl compounds **42**, **43**. 4-(Het)arylhydrazones 3-methylpyrazole-4,5-diones has high antiinflammatory[15,43,49] and diuretic activities and acted on the central nervous system.[256] 4-Arylhydrazone 3-methyl-1-nicotinoyl-1*H*-pyrazoline-4,5-dione exhibited antitumour action,[141] 3-(2-arylazo-3,5-dimethyl-1*H*-pyrazol-1-yl)-3-oxo-*N*-arylpropionamide had antibacterial and anti-HIV activities,[139] 4-(3,5-dimethyl-4-[(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)azo]-1*H*-pyrazol-1-yl)phenylsulfonylamide showed antiinflammatory and antibacterial activities.[257] An antibacterial and antifungal action was

noted for 2-(3,5-dimethyl-4-phenylazo-1*H*-pyrazol-1-yl)-3-phenyl-1,8-naphthyridine.[143]

4-Arylhydrazono-3-methylisoxazolin-5-ones were demonstrated[258] to have fungicidal activity. Bactericide action was found for 2-[4-(5-hydroxy-3-methylisoxazol-4-yl)phenylazo]-4*H*-chromen-4-one [24] and 4-(1,2-dihydroacenaphthylen-5-ylazo)-3,5-dimethyl-1*H*-pyrazole.[26]

Among 4-arylhydrazono-3-methylpyrazolin-5-ones and 4-arylhydrazono-3-methylisoxazolin-5-ones **43**, compounds were found with antibacterial and antifungal action, in particular, action against *Mycobacterium tuberculosis* (H37Rv),[259] *Staphylococcus aureus*, *Escherichia coli* and *Candida albicans*.[260]

A hypoglycemic action was noted for 4-[(1,1-dioxo-2*H*-1,2,6-thiadiazin-4-yl)azo]phenylsulfonylamides **48**.[20]

Substituted thiadiazines **113** proved to be active against *Staphylococcus aureus*, *Salmonella typhi*, *Escherichia coli*, *Bacillus subtilis*.[235] 1,5-Benzodiazepine derivatives **49**, **50** suppress the activity of the central nervous system.[186] 4,8-Diarylpyrazolo[5,1-*c*][1,2,4]triazines **8** were also active for the central nervous system.[86]

1-(4-Propylazolo[5,1-*c*][1,2,4]triazin-3-yl)butan-1-ones and 6-butyryl-7-propyl[1,2,3]triazolo[5,1-*c*][1,2,4]triazine-3-carboxamide (**13**) showed inhibitory action with respect to *Pseudomonas aeruginosa*, *Candida albicans and Staphylococcus aureus*.[39]

The ruthenium(2,2′-bipyridine)$_2$[3-(2-naphthyl)hydrazonopentane-2,4-dione] complex showed considerable antiinflammatory activity.[261]

1,2,3-Trione 2-(antipyrin-4-yl)hydrazones and *N*-(2-hydroxyethyl)-substituted pyrazole (**42**) show analgesic activities.[262] Note that fluoroalkyl-containing compounds are less toxic than non-fluorinated analogues and than analgin used as the reference.[262]

Heterocycles **42** and **43** containing (het)arylhydrazone substituent are applied as azo dyes [144, 263–268] for polyamide textiles. The copper complexes of formazans were patented as dyes for cellulose,[269] and Fe(II) complexes as dyes for polyamide textiles.[270] Some of such pyrazolines are used as light-sensitive materials in photographic developers.[271]

2-(Het)arylhydrazono-1,3-dicarbonyl compounds and their derivatives are widely used for determining the contents of metal ions in solutions. Thus 3-(2-carboxyphenyl)-hydrazone of pentane-2,3,4-trione is employed for quantification of Cu(II) and Co(II) ions,[272] and 3-(1,3-thiazol-2-yl)hydrazone of pentane-2,3,4-trione is used to determine traces of Cu(II), Co(II), Zn(II) and Ni(II) ions.[273] 3-(2-Hydroxy)naphthylhydrazone of pentane-2,3,4-trione is effective for determination of lanthanide ions [Gd(III), Eu(III) and Yb(III)] in aqueous solutions.[110]

1-(4-Antipyrinylazo)propan-2-one can be used as a metallochromic indicator for bismuth titration with ethylenediaminetetraacetate and for determining Cu(II) ions in highly acidic solutions (0.5 M HCl, pH ~ 1).[29]

Copper(II) complexes with a tetraaza chelate unit based on *N*,*N*′-polymethylenebis(arylazoaminovinyl ketones) **68** are efficient in the liquid-phase oxidation of cyclohexene with molecular oxygen.[203–205]

VI. Conclusion

Analysis of the published data shows that 2-(het)arylhydrazono-1,3-dicarbonyl compounds represent an extensive class of organic substances combining a 1,3-dicarbonyl fragment and a (het)arylhydrazone substituent in their structure. The diversity of 2-(het)arylhydrazono-1,3-dicarbonyl compounds is provided by facile and convenient methods for their preparation. The key method is azo coupling of 1,3-dicarbonyl compounds with (het)aryldiazonium salts in which substituents in any molecular fragment can be varied. Structural features account for the abundant synthetic potential of these derivatives. Unlike 1,3-dicarbonyl compounds, they can react not only at the 1,3-dicarbonyl fragment, but also at the active NH group of the hydrazone residue thus generating heterocyclic systems of various classes. Of primary interest are the transformations of 2-(het)arylhydrazono-1,3-dicarbonyl compounds with dinucleophiles, as these reactions serve as the base for the synthesis of diverse heterocyclic molecules. In most cases, cyclization processes are regioselective, which allows using 2-(het)arylhydrazono-1,3-dicarbonyl compounds for targeted synthesis of particular heterocycles.

2-(Het)arylhydrazono-1,3-dicarbonyl compounds, their open-chain and heterocyclic derivatives are of interest as polydentate ligands for complexation, and this line of research is fairly promising for further development.

The practical applications of 2-(het)arylhydrazono-1,3-dicarbonyl compounds and products of their transformation are diverse; of these, especially valuable are heterocyclic derivatives having a broad spectrum of physiological action.

Nevertheless, the chemistry of 2-(het)arylhydrazono-1,3-dicarbonyl compounds is far from being exhausted. The subsequent studies of their properties and the scope of application in organic synthesis appear quite topical. For example, one trend is the study of fluorine-containing 2-(het)arylhydrazono-1,3-dicarbonyl compounds whose chemical behaviour considerably differs from the chemistry of non-fluorinated derivatives. This review can stimulate the development of investigations into the biological activities of 2-(het)arylhydrazono-1,3-dicarbonyl compounds and their heterocyclic derivatives.

Thus, 2-(het)arylhydrazono-1,3-dicarbonyl compounds are readily accessible and convenient 'building blocks' for the design of various open-chain and heterocyclic structures and, hence, they can be considered as promising subjects of research in the coordination, heterocyclic and medicinal chemistry.

This review was prepared with the financial support of the Russian Foundation for Basic Research (Project No. 09-03-00274a), the Federal Agency on Science and Innovations (State Contract No. 02.740.11.0260), and by the Project of the Programme 'Fundamental Science for Medicine' of Presidium of the RAS.

VII. Appendix

Table 1. Products of reactions (1) – (3).

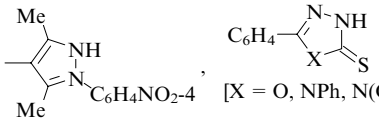
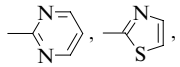
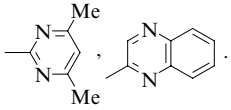
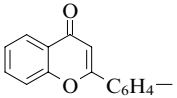
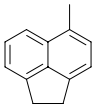
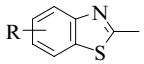
R^1	R^2	Ar (Het)	M	X	Ref.
Me	Me	 [X = O, NPh, $N(CH_2)_2Ph$, NC_6H_{13}-n]	–	–	14
Me	OEt	$C_6H_{4-n}R_n$ [R_n = SMe-2, SMe-3, CF_3-3, $(CF_3)_2$-3,5, F_2-2,4]	–	NR [R = H, Ph, SO_2Ph, CH_2OMe, $CH_2N(CH_2CH_2)_2O$]	15
Me	Me, OEt	$C_6H_4(SC_6H_4NO_2$-4)-4	–	NH, NPh, O	16
CH_2Br	OEt	C_6H_4R (R = Cl-2, Br-4, OMe-4, Ac-4)	–	–	17
CH_2SCN	OEt	C_6H_4R (R = Cl-2, Cl-3, Cl-4, OMe-2, OMe-4)	–	–	18
Me, Ph	Me, Ph, OEt	$C_6H_4SO_2NHR$-4 [R = H, Ac, C(=NH)NH_2],	–	–	19, 20, 38
		$C(O)C_6H_4OPr^i$-4, 4-Py, 	–	–	
		 .			
Me	OEt	C_6H_4OH-2	–	NH, NPh, O	21
Me	Me, OEt	$C_6H_4CO_2H$-2, $C_6H_3CO_2H$-2-NO_2-3	–	–	22
Me	Me, OEt	$C_6H_4N_3$-2	–	–	23
Me	Me, OEt		–	NH, NPh, O	24
Me	OEt	$C_6H_4C(Me)$=NAd-1	–	NH, O	25
Me	Me		–	NH, NPh, NAc	26
Me	Me, OMe, OEt, NHPh	 (R = H, Me-4, Me-5, Me-6, Cl-4, Cl-5, Cl-6, OMe-4, OMe-5, OMe-6, OEt-4, OEt-6, Cl-4, Cl-5, Cl-6, Cl_2-4,7, Me_2-4,5, CN-5, NO_2-6, Br-6)	–	–	27, 28, 42

Table 1 (continued).

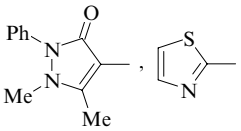
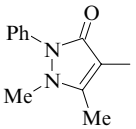
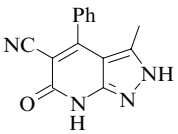
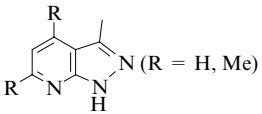
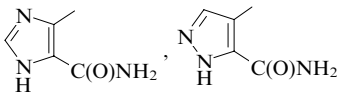
R^1	R^2	Ar (Het)	M	X	Ref.
Me	Me		Ni^{2+}, Cu^{2+}, Co^{2+}	–	29
Me, Ph	Me, OEt, NHPh, NHC_6H_4Cl-4		–	–	30, 64
Me	Me, OEt		–	–	32
Me, Et, Pi^n, Pr^i, Bu^t, CF_3, C_6H_4R-4 (R = H, Me, OMe), 2-Fu, 2-Th, 2-Py, 1-Naph	Me, Et, Pr^i, Bu^t, CF_3, C_6H_4R-4 (R = H, Me, OMe, NO_2, CO_2Et), 2-Fu, 2-Th, 2-Py, OMe, OEt	$C_6H_{4-n}R_n$ (R_n = NO_2-4, Me-4, OMe-4, CO_2Et-4, Br-4, Cl-4, Cl_3-2,4,6)	–	–	33
Me	Me, OEt	Ph	–	–	34
Me, Ph	Me, OEt		–	–	35, 56
Me, Ph	Me, Ph, OEt	 (R = H, Me)	–	NH, NPh	31, 36
Me, Ph	Me, Ph	C_6H_4R (R = NO_2-2, NO_2-3, NO_2-4, OMe-2, OMe-3, OMe-4)	–	–	37
Me, Et, Pr^n	Me, Et, Pr^n, OEt	 (X = N, CH; Y = N, CR^1 (R^1 = H, NHMe, SBn, SO_2Bn, C_6H_4OMe-4); Z = N, CR^2 [R^2 = H, Br, CO_2Et, $C(O)NH_2$, C_6H_4Cl-4)]	–	–	39
Me, Ph, Bn, CH_2CO_2Et	Me, OMe, OEt		–	–	40, 41

Table 1 (continued).

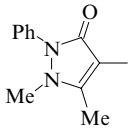
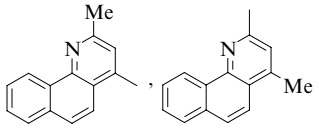
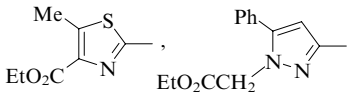
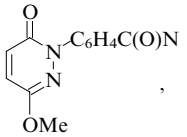
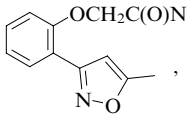
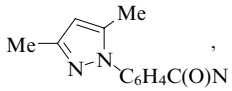
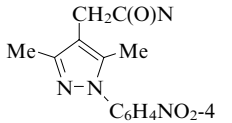
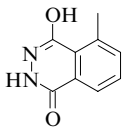
R^1	R^2	Ar (Het)	M	X	Ref.
Me, Ph	Me, OEt, NHPh, NHC_6H_4Cl-4		–	NH, $NC_6H_3(NO_2)_2$-2,4, $C_6H_4R^1$ (R^1 = H, Me-2, Me-4, Cl-4, Br-4, SO_2NHR^2-4 (R^2 = H, Ac, 2-Py, pyrimidin-2-yl, 4,6-dimethylpyrimidin-2-yl)	43
Me	Me, Ph, C_6H_4OH-4	C_6H_3Me-2-Br-4, C_6H_3Me-3-Br-4, C_6H_3Br-2-Me-4	–	NPh, O	44
Me, Ph	Me, Ph		–	–	45
Me	Me, OEt		–	–	46
Me	Me	Ph, C_6H_4OH-2, 1-Naph	–	–	47
Me	Me	$C_6H_4SO_2NHR$-4 (R = Ph, $C_6H_4NO_2$-4, CH_2CO_2H); $C_6H_4SO_3H$-4, 1-NaphSO_3H-4	–	 ,  ,  , 	48
Me	Me, OEt	$C_6H_4NO_2$-2, C_6H_4OR-4 (R = Me, Et)	–	NR (R = H, Ac, CH_2OH, CH_2NEt_2, Ph, SO_2Ph)	49, 61
Me, Ph	Me, Ph		–	–	50

Table 1 (continued).

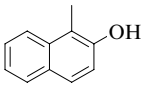
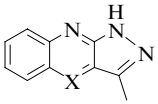
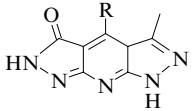
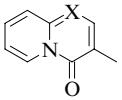
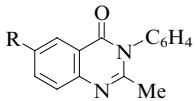
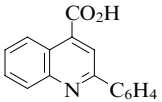
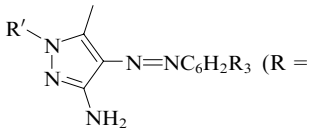
R^1	R^2	Ar (Het)	M	X	Ref.
Me, Ph	Me, Ph, OEt	$C_6H_4(SCH_2C{\equiv}CH)$-2	–	–	51
Me, Ph	OEt	$C_6H_4CO_2H$-2, $C_6H_4SO_3Na$-4	–	–	52
Me	OEt	$C_6H_4SO_2R$-4 [R = OH, NH_2, NHPh, NHPy-2, $N(CH_2)_5$]	–	–	53
Me, Ph	Me, Ph		–	–	54
Me	OEt	 (X = CH, N)	–	NPh	55, 58
Me, Ph	Me, OEt	 (R = Ph, C_6H_4Cl-4, 2-Fu)	–	–	57
Me, CH_2Cl, Ph	OMe, OEt, Me, Ph, CO_2Et	 (X = N, CCN, CCO_2Et)	–	–	59
Me	Me, OEt	 (R = H, Br)	–	NH, NPh	60
Me	Me, OEt, NHPh		–	–	62
Me	$OCH{=}CH_2$	C_6H_4R-4 (R = OMe, Me, H, Cl, NO_2)	UO^{2+}	–	63
Me, CF_3	Me, OEt	 (R = H, OMe; R′ = H, Ph)	–	NH, NPh	65, 74
Me, Ph, CF_3	Me, Ph	C_6H_4Ac-4	Gd^{3+} – Lu^{3+}	–	66

Table 1 (continued).

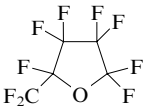
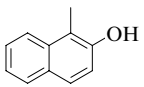
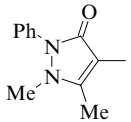
R^1	R^2	Ar (Het)	M	X	Ref.
Me, Ph, 2-Th, Bu^t, $CHEt_2$	CF_3, CF_2OCF_3, C_3F_7, 	C_6H_4R-4 (R = H, Me, SO_2CHF_2, NO_2, Cl)	–	NH, NPh, O	67
C_6F_5	OEt	Ph	–	–	68
CF_3	2-Th	Ph	Ni^{2+}, Cu^{2+}, Pd^{2+}, VO^{2+}	–	69
Me, 2-Th	Me, CF_3, Ph, OMe, NHPh		Ni^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}	–	70
CF_3, $(CF_2)_2H$, C_3F_7, C_4F_9, C_6F_5	Me, Ph, OMe, OEt, CO_2Me, CO_2Et	C_6H_4R-4 (R = H, Me, OMe)	–	NH, NPh, O	71 – 73
Me	Me	$C_6H_4Bu^n$-4	Ni^{2+}	–	98
Me	Me	C_6H_4R-4 (R = Bu^n , n-C_8H_{17})	Cu^{2+}	–	99
Me, Ph	Me, Ph, CF_3	C_6H_4Ac-2	Ni^{2+}, Cu^{2+}, Co^{2+}, Fe^{3+}, Mn^{2+}, Zn^{2+}, VO^{2+}, UO^{2+}	–	100
Me	Me, Ph	C_6H_4OH-2	Ni^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}	–	101
Me	Me	C_6H_4R-4 (R = Me, OMe, Br)	Th^{2+}, Ni^{2+}, Cu^{2+}, UO^{2+}	–	102, 103
Me	Me	C_6H_4OH-2	Cu^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}	–	104
Me, Ph	Me, Ph	Ph	Ni^{2+}, Cu^{2+}, Pd^{2+}	–	105
Me	Me	C_6H_4R-4 (R = Me, OMe, Br)	Cu^{2+}	–	106
Me	Me	C_6H_4R (R = H, CO_2H-2, CO_2H-4)	Hg^{2+}, Pd^{2+}	–	107
Me	Me	C_6H_4R (R = H, OMe-2, Cl-2, Br-2, F-4)	Cu^{2+}	–	108
Me, Ph	Me, Ph	C_6H_4R-2 (R = OH, CO_2H)	Ni^{2+}, Cu^{2+}, Co^{2+}, Fe^{3+}, Mn^{2+}, Zn^{2+}	–	109
Me, Ph	Me, Ph		Gd^{3+}, Eu^{3+}, Yb^{3+}	–	110
Me	Me		Ni^{2+}, Co^{2+}, Pd^{3+}, Mn^{2+}	–	111

Table 1 (continued).

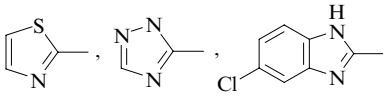
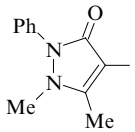
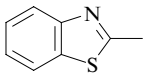
R^1	R^2	Ar (Het)	M	X	Ref.
Me	Me		Ni^{2+}, Cu^{2+}	–	112
Me, Ph	Me, Ph	Ph	Co^{2+}	–	113
Me	$OCH{=}CH_2$	C_6H_4R-4 (R = Me, OMe, Br)	Ru^{3+}	–	114
Me	Me		Ni^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}	–	115
Me	Me	C_6H_4R-4 (R = H, Ac, I, Br, Cl, NO_2)	Ni^{2+}, Cu^{2+}, UO^{2+}, Co^{2+}, Fe^{3+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Mg^{2+}, Ca^{2+}	–	116, 117, 119, 122
Me	Me	$C_6H_{4-n}R_n$ (R_n = Me-4, NO_2-2, OH-4, Me_2-2,6, Me_2-3,5, Me-2-NO_2-6)	Ni^{2+}, Cu^{2+}	–	118
Me	Me	C_6H_4OH-2	Cu^{2+}	–	120
Me	Me	C_6H_2OH-2-SO_3H-3-NO_2-5	Cu^{2+}	–	121
Me	OEt	Ph	Ni^{2+}, Cu^{2+}, Co^{2+}, Fe^{3+},	–	123
Me, Ph	Me, Ph, OEt		Mn^{2+}, VO^{2+}, UO_2^{2+} Ni^{2+}, Cu^{2+}, UO_2^{2+}, Co^{2+}, Fe^{3+}, Ru^{3+}	– – –	124, 125
Me	OMe	C_6H_4R-4 (R = H, Me, OMe)	Ni^{2+}, Cu^{2+}, Be^{2+}, Co^{2+}	–	126
Me	OEt	C_6H_4R (R = H, Me-4, Me-2, NO_2-2, NO_2-3, NO_2-4, Br-4)	Ni^{2+}, Cu^{2+}, Zn^{2+}	–	127
Me	OEt	Ph	Ni^{2+}, Cu^{2+}, Co^{2+}	–	128
Me	OEt	Ph	Fe^{2+}, Pd^{2+}, VO^{2+}, UO_2^{2+}	–	129
Me	OEt	C_6H_4OH-2	Ni^{2+}, Cu^{2+}, Co^{2+}	–	130
Me	OEt	$C_6H_4CO_2H$-2	Ni^{2+}, Cu^{2+}, Co^{2+}, Cd^{2+}, Hg^{2+}	–	131
Me	Me, OEt		–	NH	137
Me	Me, OEt	$C_6H_4SO_2NHR$-4 [R = H, $C(=NH)NH_2$, pyrazin-2-yl, 5,6-dimethoxypyrimidin-2-yl, 4,6-dimethylpyrimidin-2-yl, 5-methylisoxazol-3-yl]	–	$NC(=S)NH_2$	138

Table 1 (continued).

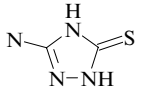
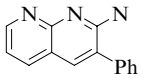
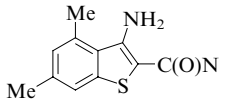
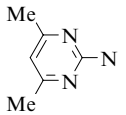
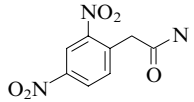
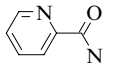
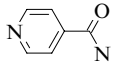
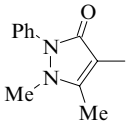
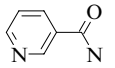
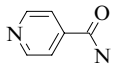
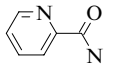
R^1	R^2	Ar (Het)	M	X	Ref.
Me	Me	C_6H_4R-2 (R = H, Cl, Br)	–	$NC(O)CH_2C(O)NHAr$	139
Me	Me	$C_6H_4R^1$-4 (R^1 = H, CO_2H, CO_2Et), SO_2NHR^2 (R^2 = H, 4-methylpyrimidin-2-yl, 4,6-dimethylpyrimidin-2-yl)	–		142
Me	Me	Ph, substituted Ph	–		143
Me	Me	C_6H_4R (R = H, Cl-4, Me-2, Me-2, OMe-4, CN-2, N_2-2, NHAc-4)	–		144
Me, Ph	Me, Ph, OEt	$C_6H_{4-n}R_n$ (n = H, Cl-3, Cl-4, Me-2, Me-3, Me-4, Me-2, OMe-4, OEt-2, OEt-4, Br-3, Br-4, F-4, N_2-2, N_2-3, N_2-4, Me_2-2,3, Me_2-2,5, Cl_2-2,6, Cl_2-2,5)	–		147
Me	OEt	C_6H_4R (R = H, OEt-4, N_2-2, N_2-3, N_2-4)	–		148
Me, Ph	Me, Ph	substituted Ph	–	C(=S)SMe	150
Me	OEt	$C_6H_{4-n}R^1_n$ (R^1_n = Me_2-2,4, Me-4-NO_2-3, Cl-2-NO_2-4, Br_3-2,4,6, H, Cl-3, Cl-4, Br-4, Me-5, OMe-2, OMe-3, OMe-4, OH-4, CO_2H-2, NH_2-4, NHAc-4,	–		149, 151
		SO_2NHR^2-4 [R^2 = H, Ac, C(=NH)NH_2, 2-Py, thiazol-2-yl, pyrimidin-2-yl, 4,6-dimethylpyrimidin-2-yl,	–		146, 156
		quinoxalin-2-yl], 1-Naph, 2-Naph, 	–		141, 161, 165
Me	Me	$C_6H_4R^1$ (R^1 = H, Cl-3, Cl-4, Br-4, Me-2, Me-4, Me-2, OMe-3, OMe-4, OH-2, N_2-4, NH_2-4, NHAc-4,	–		140, 145, 152
		SO_2NHR^2-4 [R^2 = H, Ac, C(=NH)NH_2, 2-Py, thiazol-2-yl, pyrimidin-2-yl, 4,6-dimethylpyrimidin-2-yl, quinoxalin-2-yl]	–		149
Me	OEt	$C_6H_4SO_2NHR$-4 [R = H, Ac, C(=NH)NH_2, 2-Py, thiazol-2-yl, pyrimidin-2-yl, 4,6-dimethylpyrimidin-2-yl, 4,5-dimethyloxazol-2-yl]	–	NPh	153

Table 1 (continued).

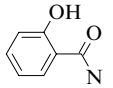
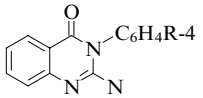
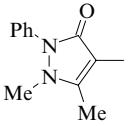
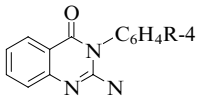
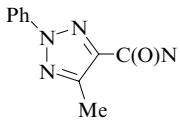
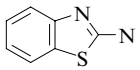
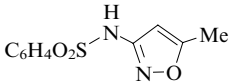
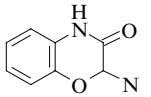
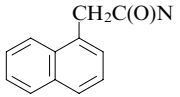
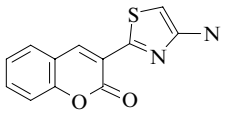
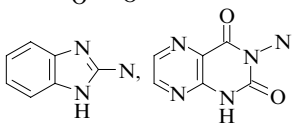
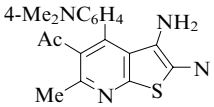
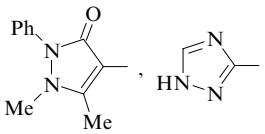
R^1	R^2	Ar (Het)	M	X	Ref.
Me	Me, OEt	C_6H_4R (R = H, Cl-2, Cl-4, Br-4, Br-2, F-3, CO_2H-4, Me-4, Me-2, OH-4, SO_2NH_2-4), 2-Naph, C_6H_3Cl-2, NO_2-4	–		154, 155, 159, 162
Me	OEt	SO_2NHR^2 [R^2 = H, Ac, C(=NH)NH_2, 2-Py, thiazol-2-yl, pyrimidin-2-yl, 4,6-dimethylpyrimidin-2-yl, quinoxalin-2-yl]	–		156
Me	Me		–		157
Me, Ph	Me, Ph	$C_6H_{4-n}R_n$ (R_n = Me-2, Me-4, Me-2, OMe-4, Cl_2-2,5)	–	$NC(O)CH_2C(O)NHC_6H_4R$ (R = H, Cl-2, Cl-3, Cl-4, Me-2, Me-3, Me-4, Me-2, OMe-3, OMe-4)	158
Me	OEt	$C_6H_4SO_2NHR$-4 [R = H, C(=NH)NH_2, pyrimidin-2-yl, 4,6-dimethylpyrimidin-2-yl]	–	$NC_6H_4NO_2$-4	160
Me	OEt	C_6H_4R (R = Cl-4, Me-4, OMe-4, NO_2-2, NO_2-3, NO_2-4)	–	NPh	163
Me	Me, OEt	Ph, substituted Ph	–		164
Me	OEt	Ph	–		166
Me, Ph	Me, OEt		–	NPh, NC(=S)NH_2, NC(=S)SMe, NC(=S)SBn	167
Me	OEt	Ph, 4-substituted Ph, thiazol-2-yl	–	NC(=S)NH_2	168
Me	OEt	Ph, substituted Ph	–	$NC_6H_3(NO_2)_2$-2,4	169
Me	OEt	Ph	–		170
Me	OEt	Ph, substituted Ph	–		171

Table 1 (continued).

R^1	R^2	Ar (Het)	M	X	Ref.
Me	OEt	Ph, substituted Ph	–		172
Me	OEt	$C_6H_{4-n}R_n$ (R_n = F-2, F-3, F-4, F_2-2,4)	–		173
Me	OEt	$C_6H_{4-n}R_n$ (R_n = F-2, F-3, F-4, F_2-2,4)	–	NH, NPh, O	174
Me	OEt	$C_6H_3(NO_2)_2$-2,4	–	NPh, NC_6H_4Cl-4	175
Me	OEt	Ph	–		176
$ArSCH_2$	OPh	C_6H_4R-4 (R = H, OMe, NO_2)	–	NH, NMe, NPh	177
CF_3, $(CF_2)_2H$	Me, Ph, Bu^t	C_6H_4R-4 (R = H, Me), 	–	NH, NPh, $N(CH_2)_2OH$	83, 178
Me	OEt	C_6H_4R (R = H, Me-4, Cl-3, Cl-4, OMe-4, NO_2-4)	–	O	180
Me, Ph	Me, Ph	$C_6H_4SO_2NHR$-4 [R = H, Ac, C(=NH)NH_2, 2-Py, pyrimidin-2-yl, 4,6-dimethylpyrimidin-2-yl, thiazol-2-yl, 1-phenylpyrazol-2-yl, 6-methoxypiperidazin-3-yl]	–		181

Note. Ad is adamantyl, Th is thienyl.

References

1. K I Pashkevich, V I Saloutin *Usp. Khim.* **54** 1997 (1985) [*Russ. Chem. Rev.* **54** 1185 (1985)]
2. K I Pashkevich, V I Saloutin, I Ya Postovskii *Usp. Khim.* **50** 325 (1981) [*Russ. Chem. Rev.* **50** 180 (1981)]
3. G G Furin *Zh. Org. Khim.* **30** 1704 (1994) [a]
4. G A Gevorgyan, A G Agababyan, O L Mndzhoyan *Usp. Khim.* **53** 971 (1984) [*Russ. Chem. Rev.* **53** 561 (1984)]
5. M D Mashkovskii *Lekarstvennye Sredstva* (Drugs) (Moscow: Novaya Volna, 2002) Vol. 12
6. A D Garnovskii, I S Vasil'chenko *Usp. Khim.* **71** 1064 (2002) [*Russ. Chem. Rev.* **71** 943 (2002)]
7. A D Garnovskii, I S Vasil'chenko *Usp. Khim.* **74** 211 (2005) [*Russ. Chem. Rev.* **74** 193 (2005)]
8. V V Skopenko, V M Amirkhanov, T Yu Sliva, I S Vasil'chenko, E L Anpilova, A D Garnovskii *Usp. Khim.* **73** 797 (2004) [*Russ. Chem. Rev.* **73** 737 (2004)]
9. G Aromi, P Gamez, J Reedijk *Coord. Chem. Rev.* **252** 964 (2008)
10. E I Tsyganova, L M Dyagileva *Usp. Khim.* **65** 334 (1996) [*Russ. Chem. Rev.* **65** 315 (1996)]
11. G V Bazuev, L D Kurbatova *Usp. Khim.* **62** 1037 (1993) [*Russ. Chem. Rev.* **62** 981 (1993)]
12. M A Katkova, A G Vitukhnovskii, M N Bochkarev *Usp. Khim.* **74** 1193 (2005) [*Russ. Chem. Rev.* **74** 1089 (2005)]
13. G Tennant *Comprehensive Organic Chemistry* (Eds D H R Barton, W D Ollis) (Oxford: Pergamon Press, 1979)
14. M V Pabuccuoglu, S Rollas *Marmara Univ. Eczacilik Derg.* **7** 39 (1991); *Chem. Abstr.* **117** 90214j (1992)
15. A Tantawy, H Eisa, A Ismail, M El-Kerdawy *Alexandria J. Pharm. Sci.* **2** 113 (1988); *Chem. Abstr.* **111** 57616v (1989)
16. S M Radwan, M S Abbady, R A Ahmed *Phosphorus, Sulfur Silicon Relat. Elem.* **63** 363 (1991)
17. V N Bodnar, M O Lozinskii, P S Pel'kis *Ukr. Khim. Zh.* **47** 424 (1981)
18. M O Lozinskii, V N Bodnar, Yu A Sokolova, O A D'yachenko, L Yu Atovmyan *Izv. Akad. Nauk SSSR, Ser. Khim.* 1612 (1988 [b]
19. G Saduikis, D Kazlauskas *Chemija* 68 (1993); *Chem. Abstr.* **121** 179193g (1994)
20. R N Goyal, S Bhargava *Curr. Sci.* **58** 287 (1989); *Chem. Abstr.* **112** 35818f (1990)
21. F M Atta, M A Abd Alla, M E Abd Elmonem, S A M Metwally *Bull. Fac. Sci., Assiut. Univ.* **18** 41 (1989); *Chem. Abstr.* **114** 61997z (1991)
22. J M A Al-Rawi, M A R Khayat *Magn. Reson. Chem.* **27** 112 (1989)
23. A W Stocker, R R Smalley, M Tequiche *J. Chem. Res., (S)* 192 (1992); *Chem. Abstr.* **117** 26446j (1992)
24. D L M Coutinho, P S Fernandes *Indian J. Heterocycl. Chem.* **1** 109 (1991); *Chem. Abstr.* **116** 151370k (1992)
25. A Tantawy, F Goda *Zhonghua Yaoxue Zazhi* **44** 295 (1992); *Chem. Abstr.* **118** 6888x (1993)
26. F H Havaldar, P S Fernandes *J. Indian Chem. Soc.* **65** 691 (1988)
27. B Liu, H Gao, X Zhou *J. Chin. Pharm. Sci.* **2** 151 (1993); *Chem. Abstr.* **121** 9212v (1994)
28. R Jain, A Dixit *J. Indian Chem. Soc.* **67** 179 (1990)
29. T Ishizuki, H Wada, G Nakagawa *Anal. Chim. Acta* **212** 253 (1988)
30. M H Elnagdi, A H H Elghandour, K V Sadek, M M M Ramiz *Z. Naturforsch., B* **44** 951 (1989)
31. A M K El-Dean, A A Geies, T A Mohamed, A A Atalla *Bull. Fac. Sci., Assiut. Univ.* **20** 15 (1991); *Chem. Abstr.* **116** 106161g (1992)
32. M El-Mobayed, A N Essawy, A El-Bahnasawa, A M Amer *Gazz. Chim. Ital.* **121** 209 (1991)
33. A Mitchell, D C Nonhebel *Tetrahedron* **35** 2013 (1979)
34. A Lyčka, D Šnobl *Collect. Czech. Chem. Commun.* **46** 892 (1981)
35. B G Tennant, J S Vevers *J. Chem. Soc., Perkin Trans. 1* 421 (1976)
36. M Kočevar, B Stanovnik, M Tišler *J. Heterocycl. Chem.* **15** 1175 (1978)
37. M S Masoud, A M Kaddah, A M Khalil, N I Tawfik *Indian J. Chem., Sect. A* **17** 502 (1979)
38. C P Singh, A C Ojha *Acta Chim. Acad. Sci. Hung.* **104** 113 (1980)
39. T Novinson, T Okabe, R K Robins, T R Matthews *J. Med. Chem.* **19** 517 (1976)
40. M Kočevar, D Kolman, H Krajnc, S Polanc, B Porovne, B Stanovnik, M Tišler *Tetrahedron* **32** 725 (1976)
41. G U Baig, M F G Stevens *J. Chem. Soc., Perkin Trans. 1* 1424 (1981)
42. R N Goyal, R Jain, S Tyagi *J. Indian Chem. Soc.* **58** 504 (1981)
43. A M Farghaly, S M El-Khwass, M A Khalil, F M Sharabi, T T Daabees *Pharmazie* **36** 93 (1981)
44. A K Mittal, O P Singhal. *J. Indian Chem. Soc.* **58** 1089 (1981)
45. N P Singh, O P Verma, R P Tyagi *Indian J. Chem., Sect. B* **21** 457 (1982)
46. E A A Hafez, N M Abed, I A Elsakka, M H Elnagdi *J. Heterocycl. Chem.* **20** 285 (1983)
47. A T Pilipenko, L I Savranskii, V L Sheptun *Dokl. Akad. Nauk SSSR* **269** 1390 (1983) [c]
48. P S Fernandes, D Desai, N Gawri, S Pandey, H Patel *J. Indian Chem. Soc.* **61** 818 (1984)
49. A M Ismaiel, M Y Yousif, M A Metwally, M El-Kerdawy *Indian J. Chem., Sect. B* **25** 1238 (1986)
50. N Thankarajan, K Krishnankutty, T K K Srinivasan *Indian J. Chem. Soc.* **63** 977 (1986)
51. L Bruche, G Zecchi *J. Chem. Res.* (*S*) 346 (1987); *Chem. Abstr.* **108** 186675a (1988)
52. N A Ibrahim *Alexandria J. Pharm. Sci.* **4** 4 (1990); *Chem. Abstr.* **114** 5655z (1991)
53. M S Abbady, S M Radwan, E A Bakhite *Indian J. Chem., Sect. B* **32** 1281 (1993)
54. A A Mahmoud, G M El-Sayed, N S Morsy *Al-Azhar J. Pharm. Sci.* **14** 1 (1994); *Chem. Abstr.* **124** 271776j (1996)
55. A M K El-Dean, A A Geies, O S Moustafa *Afinidad* **55** 295 (1998); *Chem. Abstr.* **130** 81492q (1999)
56. M A El-Taher, M T El-Haty, A A Montaser *Mikrochim. Acta* **129** 133 (1998)
57. F A Attaby, S M Eldin, M A A El-Neairy *J. Chem. Res. (S)* 632 (1998)
58. E A Bakhite *J. Chin. Chem. Soc.* **48** 1175 (2001)
59. S Rešnik, J Svete, B Stanovnik *Heterocycles* **57** 2091 (2002)
60. M A Saleh, M F Abdel-Megeed, M A A Shokr, A-B M Shokr *Molecules* **8** 363 (2003)
61. E V Sadchikova, V S Mokrushin *Vestn. UGTU-UPI, Ser. Khim.* 85 (2003)
62. N N Kondrashova, M-G A Shvekhgeimer *Dokl. Akad. Nauk* **398** 349 (2004) [c]
63. A Z El-Sonbati, A A El-Bindary, R M Issa, H M Kera *Des. Monomers Polym.* **7** 445 (2004)
64. S Cunha, S M Oliveira, M T Rodrigues, R M Bastos, J Ferrari, C M A De Oliveira, L Kato, H B Napolitano, I Vencato, C Lariucci *J. Mol. Struct.* **752** 32 (2005)
65. M K A Ibrahim *Pak. J. Sci. Ind. Res.* **80** 799 (1987); *Chem. Abstr.* **109** 149477n (1988)
66. B A El-Shetary, S L Stefan, M S Abbel-Moez, M Mashaly *Can. J. Chem.* **66** 2362 (1988)
67. A F Shivanyuk, L S Kudryavtseva, M O Lozinskii, V M Neplyuev, Yu A Fialkov, A G Bratolyubova *Ukr. Khim. Zh.* **47** 1078 (1981)
68. A T Prudchenko, G S Shchegoleva, V A Barkhash, N N Vorozhtsov *Zh. Obshch. Khim.* **37** 2487 (1967) [d]
69. K Krishnankutty, J Michael *J. Indian Chem. Soc.* **70** 238 (1993)
70. K Krishnankutty, D K Babu *J. Indian Chem. Soc.* **73** 379 (1996)
71. O G Kuzueva, Ya V Burgart, V I Saloutin *Izv. Akad. Nauk, Ser. Khim.* 695 (1998) [b]
72. Ya V Burgart, A S Fokin, O G Kuzueva, O N Chupakhin, V I Saloutin *J. Fluorine Chem.* **92** 101 (1998)
73. I L Knunyants, M D Bargamova, S I Pletnev *Izv. Akad. Nauk SSSR, Ser. Khim.* 1861 (1980) [b]

74. M K A Ibrahim, A A El-Bahnasawy, A A Amer, M Abdallah, G A Farahat *Indian J. Heterocycl. Chem.* **14** 123 (2004); *Chem. Abstr.* **143** 405838 (2005)
75. M U Anwar, S Tragl, T Ziegler, L R Subramanian *Synlett* 627 (2006)
76. H Mackie, G Tennant *Tetrahedron Lett.* **13** 4719 (1972)
77. M H Elnagdi, M R H El-Moghayar, D H Fleita, E A A Hafez, S M Fahmy *J. Org. Chem.* **41** 3781 (1976)
78. M H Elnagdi, E M Zayed, M A El-Sayed Khalifa, S A Ghozlan *Monatsh. Chem.* **112** 245 (1981)
79. M H Elnagdi, N H Taha, F A M Abd El All, R M Abdel-Motaleb, F F Mahmoud *Collect. Czech. Chem. Commun.* **54** 1082 (1989)
80. K U Sadek, M A Selim, M H Elnagdi, H H Otto *Bull. Chem. Soc. Jpn.* **66** 2927 (1993)
81. R Allmann, T Debaerdemaeker, W Grahn, C Reichardt *Chem. Ber.* **107** 1555 (1974)
82. J M C Golec, R M Scrowston, M Dunleavy *J. Chem. Soc., Perkin Trans. 1* 239 (1992)
83. O G Khudina, E V Shchegol'kov, Ya V Burgart, M I Kodess, O N Kazheva, A N Chekhlov, G V Shilov, O A Dyachenko, V I Saloutin, O N Chupakhin *J. Fluorine Chem.* **126** 1230 (2005)
84. E V Shchegol'kov, E V Sadchikova, Ya V Burgart, V I Saloutin *Izv. Akad. Nauk, Ser. Khim.* 599 (2008) [b]
85. E V Shchegol'kov, E V Sadchikova, Ya V Burgart, V I Saloutin *Zh. Org. Khim.* **45** 586 (2009) [a]
86. K C Joshi, V Pathak, U J Garg *J. Indian Chem. Soc.* **60** 1074 (1983)
87. M R Shaaban. *J. Fluorine Chem.* **129** 1156 (2008)
88. V Bertolasi, V Ferretti, P Gilli, G Gilli, Y M Issa, O E Sherif *J. Chem. Soc., Perkin Trans. 2* 2223 (1993)
89. V Bertolasi, P Gilli, V Ferretti, G Gilli, K Vaughan *New J. Chem.* **23** 1261 (1999)
90. O G Khudina, Ya V Burgart, E V Shchegol'kov, M I Kodess, V I Saloutin, O N Kazheva, G V Shilov, O A D'yachenko, M A Grishina, V A Potemkin, O N Chupakhin *Zh. Org. Khim.* **43** 381 (2007) [a]
91. O G Khudina, Ya V Burgart, E V Shchegol'kov, V I Saloutin, O N Kazheva, A N Chekhlov, O A D'yachenko, O N Chupakhin *Zh. Org. Khim.* **45** 819 (2009) [a]
92. G U Baig, M F G Stevens *J. Chem. Soc., Perkin Trans. 1* 665 (1987)
93. A O Abdelhamid, M A M Afifi *Sulf. Lett.* **6** 125 (1987)
94. M S K Youssef, A M K El-Dean, M S Abbady, K M Hassan *Collect. Czech. Chem. Commun.* **56** 1768 (1991)
95. B Narayana, K K V Raj, B V Ashalatha, N S Kumari *Indian J. Chem., Sect. B* **45** 1704 (2006)
96. H V Patel, K A Vyas, S P Pandey, F Tavares, P S Fernandes *Synth. Commun.* **21** 1583 (1991)
97. V O Bondar, V M Britsun, A M Esipenko, M O Lozinskii *Ukr. Khim. Zh.* **71** 110 (2005)
98. R I Kuliev, N A Andronova, T M Ivanova, V V Titov, A V Ivashchenko *Koord. Khim.* **13** 1487 (1987) [c]
99. A V Ivashchenko, R I Kuliev, A Ts Sarkisyan, E M Syskova, T M Ivanova, E I Polyakova, V N Shamraev, V V Titov *Koord. Khim.* **14** 606 (1988) [c]
100. M S Abdel-Moez, S L Stefan, M M El-Bahairy, M M Mashely, B A El-Shetary *Can. J. Chem.* **68** 774 (1990)
101. B B Mahapatra, S K Kar. *J. Indian Chem. Soc.* **68** 542 (1991)
102. M T El-Haty, E Aboul-Kasim, A A Moneam, M M A Hassan *Bull. Fac. Sci., Assiut. Univ., B* **24** 175 (1995); *Chem. Abstr.* **124** 213150q (1996)
103. M T El-Haty, K E Aboul, A A Monaem, M M A Hassan *Bull. Fac. Sci., Assiut. Univ., B* **24** 83 (1995); *Chem. Abstr.* **124** 248720c (1996)
104. R Jain, D D Agarwal, A K Jain *Chim. Acad. Sci. Hung.* **111** 27 (1982)
105. N Thankarajan, K K Kutty *Indian J. Chem., Sect. A* **23** 401 (1984)
106. O Hugo, C D Carrilo *Reu. Latinoam. Qium.* **12** 127 (1981); *Chem. Abstr.* **96** 207919j (1982)
107. E A El-Sawi, S M Shendy *Bull. Soc. Chim. Belg.* **94** 171 (1985)
108. B A El-Shetary, M S Abdel-Moez, K A Rizk *J. Chem. Soc. Pak.* **9** 221 (1987); *Chem. Abstr.* **107** 167665k (1987)
109. H A Dessouki, R M Issa, M M Moustafa *Acta Chim. Hung.* **126** 653 (1989)
110. G M El-Sayed *Al-Azhar J. Pharm. Sci.* **13** 155 (1994); *Chem. Abstr.* **124** 277088h (1996)
111. F A El-Sayed, M M Aly, A M Anwar *Transition Met. Chem.* **18** 588 (1993)
112. L Mishra, A Jha *Synth. React. Inorg. Met.-Org. Chem.* **25** 601 (1995)
113. S Sharma *Himalayan Chem. Pharm. Bull.* **14** 1 (1997); *Chem. Abstr.* **127** 325601f (1997)
114. A T Mubarak, S A El-Assiery *Appl. Organomet. Chem.* **18** 343 (2004)
115. N A El-Wakiel, S Sirry *Egypt. J. Chem.* **45** 869 (2002); *Chem. Abstr.* **141** 324490w (2004)
116. S R Gadzhieva, K T Makhmudov *Zh. Neorg. Khim.* **49** 1397 (2004) [f]
117. S R Gadzhieva, F G Pashaev, F M Chyragov, A G Gasanov, K T Makhmudov *Zh. Neorg. Khim.* **52** 701 (2007) [f]
118. J Marten, W Seichter, E Weber *Z. Anorg. Allg. Chem.* **631** 869 (2005)
119. S R Gadzhieva, T M Mursalov, K T Makhmudov, F M Chyragov *Koord. Khim.* **32** 316 (2006) [e]
120. S R Gadzhieva, T M Mursalov, K T Makhmudov, F G Pashaev, F M Chyragov *Zh. Anal. Khim.* **61** 598 (2006) [g]
121. S R Gadzhieva, K T Makhmudov, F M Chyragov *Zh. Anal. Khim.* **61** 690 (2006) [g]
122. S R Gadzhieva, K T Makhmudov, F G Pashaev, A G Gasanov, F M Chyragov *Koord. Khim.* **34** 543 (2008) [e]
123. A Y Desal, A D Sawant *Asian J. Chem.* **5** 920 (1993)
124. F A El-Saied, I A El-Sakka, A Mashaly *Pol. J. Chem.* **67** 1201 (1993)
125. F A El-Saied, R M El-Bahnasawy, M Abdel Azzem, A K El-Sawaf *Polyhedron* **13** 1781 (1994))
126. K Krishnankutty, P Ummer *J. Indian Chem. Soc.* **66** 194 (1989)
127. N Prasad, A Sahay, A K Srivastava *Proc. Natl. Acad. Sci., Sect. A* (*India*) **60** 147 (1990); *Chem. Abstr.* **114** 198459v (1991)
128. A Y Desai, S B Khatavkar, A D Sawant *Asian J. Chem.* **5** 881 (1993); *Chem. Abstr.* **121** 98313u (1994)
129. A Y Desai, A D Sawant *Chem. Environ. Res.* **4** 177 (1995); *Chem. Abstr.* **128** 123100b (1998)
130. B B Mahapatra, B K Patel, S C Choudhury *J. Inst. Chem.* (*India*) **60** 131 (1988); *Chem. Abstr.* **110** 164992r (1989)
131. B B Mahapatra, B K Patel, K C Satpathy *Acta Chim. Hung.* **126** 207 (1989
132. E B Fomicheva, V K Bel'skii, G V Panova *Koord. Khim.* **15** 937 (1989) [e]
133. K Balakrishnan, V Krishnan *Transition Met. Chem.* **3** 337 (1978)
134. A C Banciu *Rev. Roum. Chim.* **33** 225 (1988)
135. E V Shchegol'kov, Ya V Burgart, P A Slepukhin, O N Kazheva, G V Shilov, O A D'yachenko, V I Saloutin *Zh. Org. Khim.* **43** 1786 (2007) [a]
136. E V Shchegol'kov, Ya V Burgart, V I Saloutin *J. Fluorine Chem.* **128** 779 (2007)
137. B Liu, H Gao, J Liu, X Zhou *Hangzhou Daxue Xuebao, Ziran Kexueban* **21** 63 (1994); *Chem. Abstr.* **121** 83163w (1994)
138. R Jain, H K Pardasani *J. Indian Chem. Soc.* **68** 415 (1991)
139. V S Jolly, G D Arora, P Talwar *J. Indian Chem. Soc.* **67** 1001 (1990)
140. R Jain, P Pandey, N Jain *J. Indian Chem. Soc.* **65** 298 (1988)
141. C P Singh, A Singh *Asian J. Chem.* **1** 294 (1989); *Chem. Abstr.* **112** 158129q (1990)
142. S Rollas, N Dogan, M Vegen, Y Ozger *Marmara Univ. Eczacilik Derg.* **6** 41 (1990); *Chem. Abstr.* **114** 247213w (1991)
143. H S Rani, K Mogilaiah, B Sreenivasulu *Indian J. Heterocycl. Chem.* **5** 45 (1995); *Chem. Abstr.* **124** 202094y (1996)
144. J W Ho, I J Wang *Dyes Pigm.* **29** 295 (1995)
145. A C Ojha, C P Singh *J. Indian Chem. Soc.* **56** 1233 (1979)
146. C P Singh, A C Ojha *J. Indian Chem. Soc.* **57** 1172 (1980)

147. V K Mahesh, R N Goyal, R Gupta, R Sharma *J. Indian Chem. Soc*. **57** 1037 (1980)
148. V S Misra, C Chaudhary, R Agarwal *Indian J. Chem., Sect. B* **21** 466 (1982)
149. D R Gupta, R K Arora *Acta Chim. Hung*. **118** 79 (1985)
150. M Mohan, C P Arora, H K Gupta *Acta Pharm. Jugosl*. **34** 207 (1984); *Chem. Abstr*. **103** 71241k (1985)
151. C P Singh *J. Indian Chem. Soc*. **62** 222 (1985)
152. C P Singh *Natl. Acad. Sci. Lett*. (*India*) **9** 381 (1986); *Chem. Abstr*. **108** 150365k (1988)
153. R Jain, D D Agarwal, M Damodharan *Indian J. Heterocycl. Chem*. **2** 265 (1993); *Chem. Abstr*. **120** 217413t (1994)
154. C P Singh, A Singh, K P Singh *Himalayan Chem. Pharm. Bull*. **6** 37 (1989); *Chem. Abstr*. **112** 178781z (1990)
155. S M Sharma, A C Ojha, R Manohar *Int. J. BioChemiPhysics* **21** 63 (1993); *Chem. Abstr*. **122** 290767g (1995)
156. R Jain, A Shukla *J. Indian Chem. Soc*. **67** 575 (1990)
157. A M Farghaly, I Chaaban, M A Khalil, A A Bekhit *Arch. Pharm*. **323** 833 (1990)
158. V Dhingra, R Bhatawdekar, L Agarwal, V S Jolly *J. Indian Chem. Soc*. **68** 672 (1991)
159. A C Ojha, S M Sharma, R Manohar *Rev. Roum. Chim*. **38** 881 (1993)
160. R Jain, S Gupta *J. Indian Chem. Soc*. **75** 325 (1998)
161. S S Nayal, C P Singh *Asian J. Chem*. **11** 207 (1999); *Chem. Abstr*. **130** 153602a (1999)
162. P V Ramana, L K Ravindranath *J. Indian Chem. Soc*. **76** 112 (1999)
163. E Omparakash, J T Rao *J. Inst. Chem. (India)* **71** 97 (1999); *Chem. Abstr*. **132** 308285s (2000)
164. F Liu, W Lu, Z Zhang, Y Liu *Huaxue Shiji* **22** 75 (2000); *Chem. Abstr*. **133** 164022z (2000)
165. B Kalluraya, R M Chimbalkar *Indian J. Heterocycl. Chem*. **11** 171 (2001); *Chem. Abstr*. **137** 337819c (2002)
166. S P Patel, A M Joshi, K V Hirapara, H H Parekh *Orient. J. Chem*. **19** 435 (2003)
167. S M Hassan, H A Emam, M A Habib *J. Chem. Res. (S)* 64 (2002)
168. B S Rawat, S C Mehra *Asian J. Chem*. **15** 1545 (2003); *Chem. Abstr*. **140** 163761x (2004)
169. E O Prakash, E S Devi, J T Rao *Asian J. Chem*. **15** 1607 (2003); *Chem. Abstr*. **140** 181365a (2004)
170. V V Dabholkar, R P Gavande. *J. Serb. Chem. Soc*. **68** 723 (2003)
171. A M Joshi, S P Patel, K V Hirpara, A R Parikh *J. Inst. Chem. (India)* **75** 146 (2003); *Chem. Abstr*. **141** 207113q (2004)
172. B Kalluraya, A M Isloor, P V Frank, R L Jagadeesha *Indian J. Heterocycl. Chem*. **13** 245 (2004); *Chem. Abstr*. **141** 314226a (2004)
173. K Sharma, V Sareen, V Khatri *Indian J. Heterocycl. Chem*. **14** 161 (2004); *Chem. Abstr*. **142** 355239w (2005)
174. U Gupta, V Sareen, V Khatri, S Chugh *Indian J. Heterocycl. Chem*. **13** 351 (2004); *Chem. Abstr*. **141** 395469g (2004)
175. S A El-Assiery, G H Sayed, A Fouda *Acta Pharm*. **54** 143 (2004)
176. M Elneairy, M Gad-Elkareem, A Abdel-Fattah *Phosphorus, Sulfur, Silicon Relat. Elem*. **181** 1451 (2006)
177. V N Bodnar, V N Britsun, M O Lozinskii *Khim. Geterotsikl. Soedin*. 1169 (2003) [h]
178. E V Shchegol'kov, Ya V Burgart, O G Khudina, V I Saloutin, O N Chupakhin *Izv. Akad. Nauk, Ser. Khim*. 2478 (2004) [b]
179. O G Khudina, E V Shchegol'kov, Ya V Burgart, M I Kodess, V I Saloutin, O N Chupakhin *Heterocycles* **68** 2515 (2006)
180. N T Abdel Ghani, I M Abbas, A L El-Ansary *Egypt. J. Chem*. **32** 301 (1989) (Publ. 1991); *Chem. Abstr*. **117** 191733h (1992)
181. R N Goyal, A Minocha, S Sharma *Curr. Sci*. **56** 1093 (1987)
182. R G Pearson *J. Chem. Educ*. **45** 581 (1968)
183. P Shinge, P Latthe, B Badami *Synth. Commun*. **35** 2169 (2005)
184. R Jain, S Tomar, J Bhadauria *J. Indian Chem. Soc*. **74** 643 (1997)
185. M A Metwally, M Y Yousif, A-K M Ismaiel, H A Etman *Heterocycles* **23** 2251 (1985)
186. A S Tantawy, M B El-Ashmawy, M M El-Kerdawy *Mansoura J. Pharm. Sci*. **5** 118 (1989); *Chem. Abstr*. **112** 158210j (1990)
187. P Sharma, N Kapoor, P Indapurkar *Bull. Electrochem*. **13** 263 (1997); *Chem. Abstr*. **127** 293198m (1997)
188. F M Abd Latif, E A El-Rady, M A Khalil, M A El-Maghraby *J. Heterocycl. Chem*. **39** 299 (2002)
189. O G Khudina, E V Shchegol'kov, Ya V Burgart, V I Saloutin, O N Chupakhin *J. Fluorine Chem*. **125** 1363 (2005)
190. O G Khudina, E V Shchegol'kov, Ya V Burgart, V I Saloutin *Zh. Org. Khim*. **40** 854 (2004) [a]
191. V N Pathak, R Joshi, N Gupta, V M Rao *Indian J. Heterocycl. Chem*. **12** 331 (2003); *Chem. Abstr*. **139** 381462w (2003)
192. O G Khudina, Ya V Burgart, N V Murashova, V I Saloutin *Mendeleev Commun*. 228 (2003)
193. O G Khudina, E V Shchegol'kov, Ya V Burgart, V I Saloutin, D V Bukhvalov, D V Starichenko, Yu N Shvachko, A V Korolev, V V Ustinov, O N Kazheva, G V Shilov, O A D'yachenko, G G Aleksandrov, I L Eremenko, O N Chupakhin *Izv. Akad. Nauk, Ser. Khim*. 103 (2007) [b]
194. L Mishra, A Jha, A K Yadaw *Transition Met. Chem*. **22** 406 (1997)
195. O G Khudina, Ya V Burgart, N V Murashova, V I Saloutin *Zh. Org. Khim*. **39** 1493 (2003) [a]
196. O G Khudina, Ya V Burgart, V I Saloutin, O N Chupakhin *J. Fluorine Chem*. **125** 401 (2004)
197. E B Fomicheva, V K Bel'skii, G V Panova *Zh. Obshch. Khim*. **56** 607 (1986) [d]
198. G V Panova, V M Potapov, O V Ovchinnikova, A N Kosina *Zh. Obshch. Khim*. **57** 2346 (1987) [d]
199. E B Fomicheva, V K Bel'skii, G V Panova *Koord. Khim*. **15** 209 (1989) [e]
200. E B Fomicheva, V K Bel'skii, G V Panova *Koord. Khim*. **15** 403 (1989) [e]
201. A D Garnovskii *Koord. Khim*. **19** 394 (1993) [e]
202. V T Rema, K Krishnankutty, J Michael *J. Indian Chem. Soc*. **74** 391 (1997)
203. A N Zakharov, G V Panova *Koord. Khim*. **16** 485 (1990) [e]
204. A N Zakharov, G V Panova, A B Mazaletskii, V G Vinogradova, O V Ovchinnikova *Zh. Obshch. Khim*. **61** 237 (1991) [d]
205. A N Zakharov, G V Panova, N S Zefirov *Kinet. Katal*. **35** 654 (1994) [i]
206. L Mishra, A Jha *Indian J. Chem., Sect. A* **33** 638 (1994)
207. L Mishra, A Jha *Transition Met. Chem*. **18** 559 (1993)
208. K P Balakrishnan *J. Chem. Eng. Data* **25** 186 (1980)
209. G V Panova, A N Zakharov, N S Zefirov *Zh. Obshch. Khim*. **64** 18 (1994) [d]
210. A N Zakharov, G V Panova, N S Zefirov *Zh. Obshch. Khim*. **65** 110 (1995) [d]
211. M A Metwally, A K M Ismaiel, M Y Yousif, F Eid *J. Indian Chem. Soc*. **66** 179 (1989)
212. F Karci, A Demircali *Dyes Pigm*. 74 288 (2007)
213. H F Zohdi *J. Chem. Res*. (*S*) 392 (1997)
214. H Y Afeefy *Boll. Chim. Farm*. **137** 480 (1998); *Chem. Abstr*. **131** 73623p (1999)
215. E S Semichenko, E V Root, L M Pokrovskii, G A Suboch *Zh. Org. Khim*. **43** 407 (2007) [a]
216. P Sharma, A Kumar, P Pandey, N Rane *Indian J. Chem., Sect. B* **43** 1320 (2004)
217. I D Komaritsa, I G Chaban, V M German *Farm. Zh*. (*Kiev*) 39 (1992); *Chem. Abstr*. **118** 80851w (1993)
218. M H Elnagdi, M E Hassan, M A Elmaghraby, A M Abdul *Aswan Sci. Technol. Bull*. **13** 45 (1992); *Chem. Abstr*. **119** 95452m (1993)
219. S M El-Kousy, R M Mohareb, M Riad, M H Elnagdi *Pak. J. Sci. Ind. Res*. **41** 81 (1998); *Chem. Abstr*. **130** 168313f (1999)
220. M H Elnagdi, M Barsy, F M Abdel-Latif, K U Sadek *J. Chem. Res., (S)* 26 (1998)
221. I A El-Sakka *J. Chem. Res., (S)* 434 (1996); *Chem. Abstr*. **125** 300927n (1996)
222. A A El-Bannany, A A El-Assar, M N El-Nagdy *J. Prakt. Chem*. **331** 726 (1989)

223. S Al-Mousawi, A-Z Elassar, M A El-Apasery *Phosphorus, Sulfur, Silicon Relat. Elem.* **181** 1755 (2006)
224. E Sotelo, R Mocelo, M Suarez, A Loupy *Synth. Commun.* **27** 2419 (1997)
225. H V Patel, K A Vyas, S P Pandey, F Tavares, P S Fernandes. *Synth. Commun.* **21** 1021 (1991)
226. H V Patel, K A Vyas, S P Pandey, F Tavares, P S Fernandes *Synth. Commun.* **21** 1935 (1991)
227. A A Nada, A W Erian, N R Mohamed, A M Mahran *J. Chem. Res.* (*S*) 236 (1997)
228. K Gewald, M Rehwald, H Mmller, P Belmann, H Schifer *Monatsh. Chem.* **126** 341 (1995)
229. M A Barsy *J. Chin. Chem. Soc.* **47** 951 (2000)
230. E A El Rady, M A Barsy *J. Heterocycl. Chem.* **43** 243 (2006)
231. M H Helal *Pigm. Resin Technol.* **33** 165 (2004)
232. E A El Rady, M A Barsy *J. Heterocycl. Chem.* **45** 1233 (2008)
233. M A Barsy, M A Elmaghraby, S M Ahmed *J. Chin. Chem. Soc.* **45** 655 (1998)
234. M A Barsy, F A El Latif, E A El Rady, M E Hassan, M A El Maghraby *Synth. Commun.* **31** 2569 (2001)
235. H V Patel, P S Fernandes, K A Vyas *Indian J. Chem., Sect. B* **29** 1044 (1990)
236. B K N Singh, P S Fernandes *Indian J. Heterocycl. Chem.* **16** 33 (2006); *Chem. Abstr.* **147** 301132 (2007)
237. H V Patel, P S Fernandes. *Indian J. Chem., Sect. B* **28** 733 (1989)
238. H V Patel, P S Fernandes *Indian J. Chem., Sect. B* **27** 1154 (1988)
239. K Sharma, B K Singh, P S Fernandes *Indian J. Heterocycl. Chem.* **15** 249 (2006); *Chem. Abstr.* **145** 377284 (2006)
240. H S Rani, K Mogilaiah, B Sreenivasulu *Indian J. Heterocycl. Chem.* **5** 33 (1995); *Chem. Abstr.* **124** 202062m (1996)
241. P Sharma, S Sharma, N Rane *Bioorg. Med. Chem.* **12** 3135 (2004)
242. O A Attanasi, P Filippone, C Fiorucci, F Mantellini *Tetrahedron Lett.* **40** 3891 (1999)
243. J Daniel, D N Dhar *Heterocycles* **32** 1517 (1991)
244. T D Lash, J R Bellettini, S J Voiles *J. Heterocycl. Chem.* **30** 525 (1993)
245. N Prasad, R M Prasad, A Sahay, A K Srivastava, J Prasad *Asian J. Chem.* **6** 901 (1994); *Chem. Abstr.* **122** 213346s (1995)
246. A A Vedepyanin, I P Murina, T N Kuznetsova, E I Klabunovskii *Izv. Akad. Nauk SSSR, Ser. Khim.* 2584 (1986) [b]
247. K Pfister, C A Robinson, A C Shabica, M Tishler *J. Am. Chem. Soc.* **71** 1101 (1949)
248. H M Walborsky, M E Baum *J. Am. Chem. Soc.* **80** 187 (1958)
249. H V Patel, K A Vyas, S P Pandey, P S Fernandes *Org. Prep. Proceed. Int.* **26** 118 (1994); *Chem. Abstr.* **120** 322869u (1995)
250. S G Kucukguzel, S Rollas, H Erdinez, M Kiraz *Eur. J. Med. Chem.* **34** 153 (1999)
251. B K Kocyigit, S Rollas *Farmaco* **57** 595 (2002)
252. Eur. P. 383449; *Chem. Abstr.* **114** 81895t (1991)
253. Br. P. 2228004; *Chem. Abstr.* **114** 228967d (1991)
254. WO 0230395; *Chem. Abstr.* **136** 310065w (2002)
255. WO 0230396; *Chem. Abstr.* **136** 325721f (2002)
256. H G Garg *J. Med. Chem.* **15** 446 (1972)
257. A A Bekhit, H M A Ashour, A A Guemei *Arch. Pharm.* **338** 167 (2005)
258. K Tanaka, K Matsuo, A Nakanishi, M Jo, H Shiota, M Yamaguchi, S Yoshino, K Kawaguchi *Chem. Pharm. Bull.* **32** 3291 (1984)
259. S G Kucukguzel, S Rollas, H Erdinez, M Kiraz, A C Ekinci, A Vidin *Eur. J. Med. Chem.* **35** 761 (2000)
260. F E Goda, A R Maarouf, E R El-Bendary *Saudi Pharm. J.* **11** 111 (2003); *Chem. Abstr.* **140** 357248f (2004)
261. L Mishra, A K Yadaw, S Bhattacharya, S K Dubey *J. Inorg. Biochem.* **99** 1113 (2005)
262. E V Shchegol'kov, O G Khudina, L V Anikina, Ya V Burgart, V I Saloutin *Khim.-Farm. Zh.* **40** 27 (2006) [j]
263. H Mustroph *J. Prakt. Chem.* **330** 97 (1988)
264. Eur. P. 524147; *Chem. Abstr.* **119** 29970c (1993)
265. Eur. P. 524148; *Chem. Abstr.* **120** 56678r (1994)
266. Br. P. 2024265; *Chem. Abstr.* **93** 9492q (1980)
267. US P. 4568738; *Chem. Abstr.* **105** 116538x (1986)
268. US P. 4579938; *Chem. Abstr.* **105** 99139y (1986)
269. BRD P. 3843135; *Chem. Abstr.* **113** 233335e (1990)
270. Pol. P. 185677; *Chem. Abstr.* **142** 281525n (2005)
271. GDR P. 207270; *Chem. Abstr.* **101** 120546h (1984)
272. S M Sirry, G M Taha *J. Chin. Chem. Soc.* **49** 39 (2002)
273. R M Awadallah, M A El Taher, A H Amrallah, A A Gaber, S M Sirry *Aswan Sci. Technol. Bull.* **18** 41 (1997); *Chem. Abstr.* **133** 144226r (2000)

[a] — *Russ. J. Org. Chem. (Engl. Transl.)*
[b] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[c] — *Dokl. Chem. (Engl. Transl.)*
[d] — *Russ. J. Gen. Chem. (Engl. Transl.)*
[e] — *Russ. J. Coord. Chem. (Engl. Transl.)*
[f] — *Russ. J. Inorg. Chem. (Engl. Transl.)*
[g] — *J. Anal. Chem. (Engl. Transl.)*
[h] —*Chem. Heterocycl. Compd. (Engl. Transl.)*
[i] — *Kinet. Catal. (Engl. Transl.)*
[j] — *Pharm. Chem. J. (Engl. Transl.)*