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The Chemistry of Unsubstituted Mono- and Di-amidrazones

A.L.Rusanov

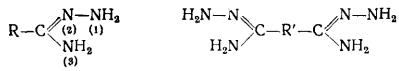
The literature data on the methods of preparation and the reactions of unsubstituted mono- and di-amidrazones are discussed. Particular attention has been devoted to the employment of di-amidrazones in the synthesis of heterochain polymers. The bibliography includes 111 references.

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I. INTRODUCTION

Unsubstituted mono- and di-amidrazones, which can be represented by the general formulae



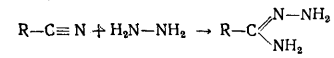
are finding increasing applications in the synthesis of monomeric and high-molecular-weight organic compounds. However, there are virtually no systematic literature data on the synthesis, properties, and applications of these compounds, since the reviews published previously were devoted mainly to the chemistry of substituted amidrazones[1,2] in which at least one of the hydrogen atoms at the nitrogen atoms was substituted by some group and also to the chemistry of compounds (for example, aminoguanidine) containing, together with amidrazone groups, other functional groups[3-5]. Moreover, the advances in the field of high-molecular compounds obtained on the basis of unsubstituted diamidrazones were not considered in any of the earlier reviews.

The present survey deals mainly with problems associated with the methods of synthesis, principal reactions, and applications of unsubstituted mono- and di-amidrazones, the employment of diamidrazones in the chemistry of high-molecular-weight compounds being analysed in greatest detail.

II. METHODS OF SYNTHESIS

1. Interaction of Nitriles with Hydrazine

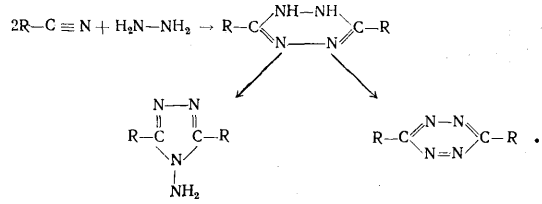
The simplest method for the preparation of amidrazones involves the interaction of nitriles with hydrazine or hydrazine hydrate[6]:



This reaction involves in its first stage nucleophilic attack by hydrazine on the carbon atoms of tne nitrile group and therefore its feasibility is to a large extent determined by the positive charge on the carbon atom of the nitrile group. The reaction of nitriles with hydrazine under mild conditions has been used successfully to synthesise unsubstituted amidrazones with one heterocyclic substituent: 2-thiazolylamidrazone, unsubstituted amidrazone[7], 4-alkyl- and phenyl-2-pyridylamidrazones[8,9], 2-quinolylamidrazone[8], 2-pyrimidinylamidrazone[8], 2-(1,10-phenanthrolinyl)-amidrazone[8], 3-isoquinolylamidrazone[10], and pteridinylamidrazones[11,12]. A number of perfluoroalkylamidrazones have been obtained in high yields by this method[13-15].

Certain unsubstituted diamidrazones have been synthesised by the reaction of hydrazine with dinitriles. Oxalodiamidrazone has been obtained from dicyanogen and hydrazine at room temperature[16-19]. Diamidrazones have been obtained under analogous conditions from the corresponding dinitriles of perfluoro-derivatives of dicarboxylic acids[13] and 2,6-dicyanopyridine[20].

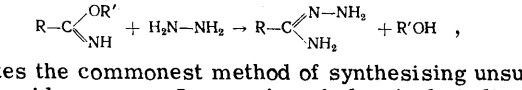
In some cases the reaction requires an increase of temperature, frequently to 100°C and above. Under these conditions, side products may be formed, including derivatives of 4-amino-1,2,4-triazole, dihydrotetrazine, and *s*-tetrazine[21]:



In order to synthesise amidrazones under the mildest possible conditions to avoid the occurrence of side reactions, one of the reaction components is frequently activated. Thus the "activated" state of nitriles is achieved by converting them into imidoesters, amidines, and thioamides.

2. Interaction of Imidoesters, Amidines, and Thioamides with Hydrazine

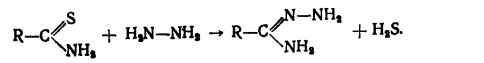
The reaction of imidoesters or their salts with hydrazine, which takes place according to the Scheme



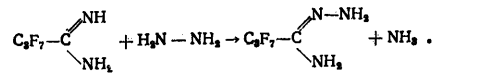
constitutes the commonest method of synthesising unsubstituted amidrazones. In a series of classical studies by

Pinner[22-27] amidrazones were synthesised from carbocyclic and heterocyclic aromatic acid imidoesters. In most cases amidrazones were not obtained in the form of free bases, but as their more stable salts. Subsequent investigations[28-31] demonstrated the applicability of this reaction to derivatives of a number of aromatic and aliphatic-aromatic acids, although the amidrazones were not isolated but were used *in situ* for further reactions. Subsequent studies of this reaction showed that it can be applied successfully to derivatives of aliphatic acids[32,33]. The extension of this method to the synthesis of unsubstituted diamidrazones made it possible to obtain the corresponding derivatives of isophthalic[34], terephthalic[35], pyridine-2,6-dicarboxylic[36], and oxalic[37] acids.

The method of synthesis of unsubstituted amidrazones based on the interaction of acid thioamides with hydrazine, has been widely used:



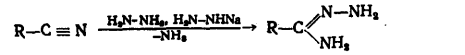
This reaction can be successfully employed to prepare various pyridylamidrazones[38,39] and benzamidrazone[38]. Oxalodiamidrazone has been synthesised in high yield by the reaction of dithioxamide with hydrazine[18,40]. The employment of the corresponding amidines as the "activated nitriles" for the synthesis of unsubstituted amidrazones is much less common. Nevertheless, Brown and coworkers[13] succeeded in synthesising perfluorobutyramidrazone by the reaction of perfluorobutyramidine with anhydrous hydrazine according to the following Scheme:



Together with the substitution of the cyano-group by more reactive functional groups, attempts were made to activate hydrazine. The employment of sodium hydrazide in place of hydrazine proved to be the most effective.

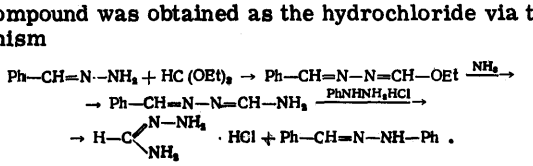
3. Interaction of Nitriles with Sodium Hydrazide

The synthesis of unsubstituted amidrazones from nitriles and sodium hydrazide via the mechanism



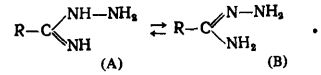
is a reaction common to many nitriles and takes place under mild conditions with high yields. It can be used successfully to synthesise unsubstituted monoamidrazones[41,42]—acetamidrazone, caprinamidrazone, myristamidrazone, heptadecanecarboxamidrazone, stearamidrazone, benzamidrazone, salicylamidrazone, α-naphthamidrazone and β-naphthamidrazone—and also for the synthesis of a number of unsubstituted diamidrazones of aliphatic dicarboxylic acids[43]—dodecanedicarboxylic, sebacic, suberic, pimelic, adipic, and glutaric.

A specific method of synthesis, differing from the processes described previously, has been proposed for the preparation of the first member of the homologous series of unsubstituted monoamidrazones—formamidrazone[44]. This compound was obtained as the hydrochloride via the mechanism



Other synthetic pathways, frequently used to prepare substituted amidrazones and discussed by Neilson et al.,[2] have not found extensive applications in the synthesis of unsubstituted amidrazones.

When the methods of their synthesis were considered, the structure proposed by Pinner[25] was attributed to all amidrazones. Nevertheless, many investigators[2,45] acknowledge the possibility of the tautomerism



There are at present no data confirming unambiguously the validity of any particular view, but study of the structures of certain substituted and unsubstituted amidrazones by infrared spectroscopy and NMR showed that structure (B) is preferable[46,47]. On the other hand, the infrared spectra of perfluoroalkylamidrazones contain three absorption bands in the range 3100–3500 cm^{-1} due to the stretching vibrations of the NH and NH_2 groups[13]; two other intense absorption maxima are associated with the vibrations of the C=N bond (1600–1700 cm^{-1}) and the deformation vibrations of the NH_2 groups (1655 cm^{-1}). Weak absorption maxima in the region of 1590 cm^{-1}, which are characteristic of NH deformation vibrations, have also been noted in the spectra of the products.

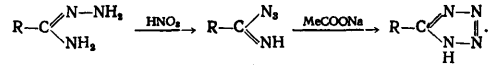
III. REACTIONS

1. Homocondensation of Amidrazones

Typical reactions of amidrazones, which greatly hinder their synthesis, are homocondensation processes, proceeding, according to Pinner's data[23,26] via the formation of dihydrotetrazines subsequently converted into compounds similar to those described above.

2. Interaction of Amidrazones with Nitrous Acid and Its Esters

When amidrazones are treated with nitrous acid or its esters, tetrazoles are formed[48,49]. This reaction proceeds via the formation of an azide imide, which subsequently rearranges to the tetrazole:

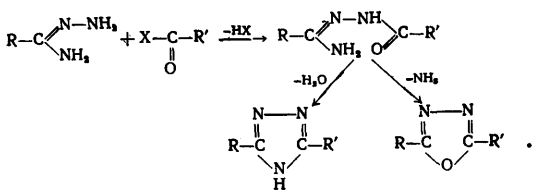


This reaction has been used successfully to synthesise tetrazoles containing alkyl[42], aryl[23,25,26], heterocyclic[24,38], and other substituents[50] in the 5-position and also to synthesise a number of bistetrazoles[43]. In all cases the tetrazoles were synthesised smoothly and the final products were obtained in nearly quantitative yields. An exception is acetamidrazone, which decomposes under the usual diazotisation conditions in an acid medium with formation of acetic acid, ammonium chloride, and hydrazoic acid; 5-methyltetrazole was synthesised successfully by the reaction of acetamidrazone with ethyl nitrite in ethanol[32,33].

3. Interaction of Amidrazones with Carboxylic Acids and Their Derivatives

The reaction of unsubstituted amidrazones with carboxylic acids and their derivatives (esters, anhydrides, and chlorides) leads to the formation of acylamidrazones,

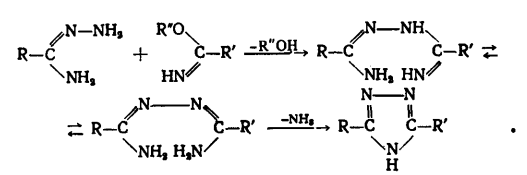
which are then converted into either 1,2,4-triazoles or 1,3,4-oxadiazoles, depending on the conditions in their subsequent treatment:



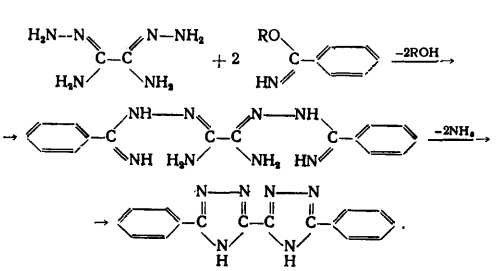
1,2,4-Triazoles are synthesised[51,52] by the above method via the thermal cyclodehydration of acylamidrazones in the absence of solvent or in *m*-cresol, *N*-methyl-2-pyrrolidinone, and hexamethylphosphoramide[53]. This reaction has been used successfully to synthesise 1,2,4-triazoles from aromatic acid amidrazones[26,53-55]. Mono- and arylbis-[3-(*o*-nitrophenyl)-1,2,4-triazoles], which are intermediates in the synthesis of triazoloquinazoline systems, have been obtained under analogous conditions[56-62].

1,2,4-Triazoles have been synthesised under the same conditions from the amidrazones of aliphatic monocarboxylic acids[42] and oxalodiamidrazone[63,64]. However, the cyclisation of acylamidrazones in the presence of strong acids (dichloroacetic[53,63-65], trifluoroacetic, phosphoric, and sulphuric[53]) is accompanied by the liberation of ammonia and the conversion of the acylamidrazone moieties into 1,3,4-oxadiazole moieties.

The possibility of the alternative formation of 1,2,4-triazole and 1,3,4-oxadiazole rings disappears when imidoesters are used as the carboxylic acid derivatives, since the "dihydrazidines" formed in the first stage of the reaction are converted only into the corresponding 3,5-disubstituted 1,2,4-triazoles[22-27]:



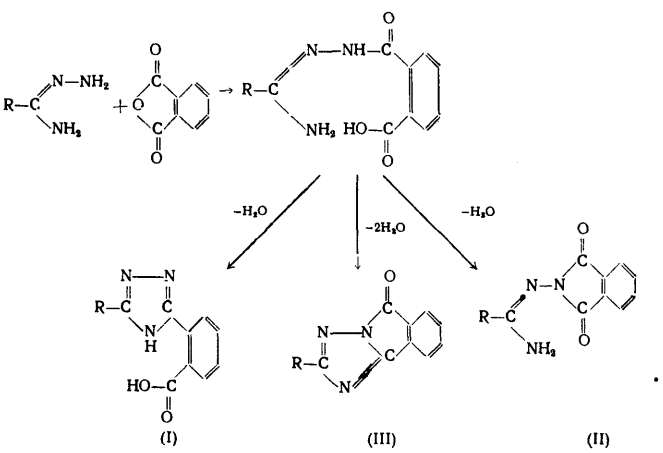
The above reaction, like the homocondensation of amidrazones discussed previously, greatly hinders their synthesis from imidoesters. This synthetic method has been used to prepare bi-5-phenyl-1,2,4-triazol-3-yl by the reaction of oxalodiamidrazone with ethyl benzimidate or its hydrochloride[66,67]:



4. Interaction of Amidrazones with Cyclic Anhydrides of Aromatic Di- and Tetra-carboxylic Acids

In contrast to the reactions of amidrazones with carboxylic acid derivatives, their interaction with aromatic *ortho*- and peri-dicarboxylic acids and their derivatives (particularly anhydrides) was investigated comparatively recently in connection with research in the field of thermostable heterocyclic polymers[34,67-78].

According to the results of the majority of investigators[34,67-73], the first stage of the reaction of unsubstituted amidrazones with phthalic anhydride involves the formation of *o*-carboxybenzamidrazones, the subsequent cyclodehydration of which gives rise to compounds having the structures, according to the data of various workers, of *o*-carboxyphenyl-1,2,4-triazoles (I)[67], *N*-phthalimidoamidines (II)[72], and isoindolo[1,2-]-*s*-triazol-5-ones (III)[34,68-71]:

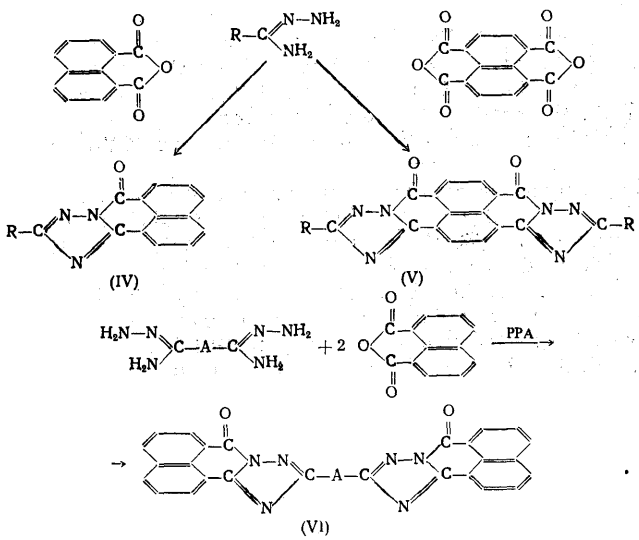


(I) (III) (II)

Subsequent studies on these reactions[73-75] established unambiguously that the final products have isoindolo[1,2]-*s*-triazol-5-one structures of type (III), while *o*-carboxyphenyl-1,2,4-triazoles and *N*-phthalimidoamidines are intermediates. The process takes place via the interaction of the initial amidrazones with phthalic anhydride in polar aprotic solvents and subsequent heating of the resulting *o*-carboxybenzamidrazones. It could not be carried out in polyphosphoric acid (PPA)[79], probably because of the possible interaction of the final heterocycle with the amidrazone (which has not yet reacted) via the O=C–N< linkage[71,75].

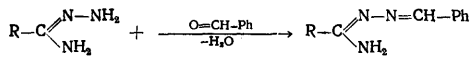
In contrast to the reaction of amidrazones with phthalic anhydride, their reaction with naphthalic anhydride takes place most successfully in PPA[71,74-78]. Condensation of monoamidrazones with the anhydrides of naphthalic and naphthalene-1,4,5,8-tetracarboxylic acids and also of diamidrazones with naphthalic acid anhydride in PPA gave nearly quantitative yields of substituted benzo-*s*-triazoloisoquinolinones (IV), bis(benzo-*s*-triazoloquinazolinones)

(V), and also benzobis-1,2,4-triazolophenanthrolinediones (VI):

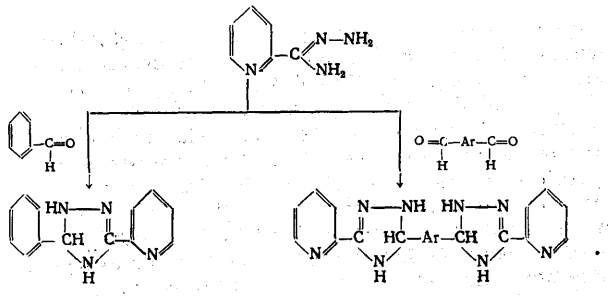


5. Interaction of Amidrazones with Aldehydes and Ketones

This reaction was first investigated by Pinner[23,24], who showed that, when unsubstituted amidrazones interact with benzaldehyde in an acid medium, Schiff bases are formed:



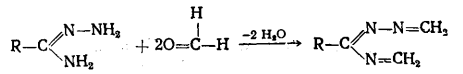
By extending this reaction to fluorinated monoamidrazones[15], it was possible to obtain *N*-benzylideneheptafluorobutyramidrazone whose subsequent treatment with I_2 and then $NaHSO_3$ led to the formation of 2-(heptafluoropropyl)-5-phenyl-1,2,4-triazole. According to Hergenrother and Carlson[80], who investigated the reaction of 2-pyridylamidrazone with aromatic mono- and di-aldehydes, the cyclic products of this reaction are disubstituted mono- and bis-triazolines:



These are not converted into the corresponding 1,2,4-triazoles on treatment with sulphur, chloranil, dimethyl sulphoxide (DMSO), and $FeCl_3$ under different conditions.

These workers carried out the reaction of 2-pyridylamidrazone with a number of mono- and di-ketones: acetophenone, *pp'*-diacetylbiphenyl, *p*-diacetylbenzene and 2,6-diacetylpyridine; the corresponding 3-methyl-substituted mono- and bis-triazolines were obtained[80].

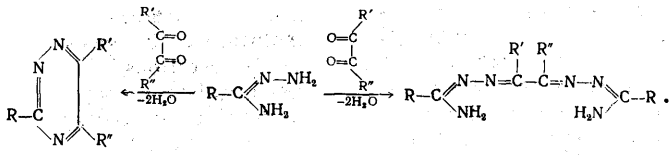
The condensation of amidrazones with an excess of highly reactive carbonyl compounds, for example with formaldehyde, involves both $N_{(1)}$ and $N_{(3)}$ atoms of the amidrazone group[27]:



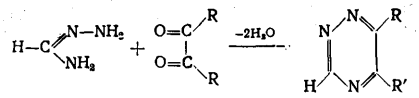
The possibility, in principle, of the interaction of both reaction centres with the carbonyl compounds led to a successful reaction between unsubstituted amidrazones and α-dicarbonyl compounds.

6. Interaction of Unsubstituted Amidrazones with α-Dicarbonyl and Polycarbonyl Compounds

This reaction results in the formation of 1,2,4-triazines[26] or acyclic products[81]:

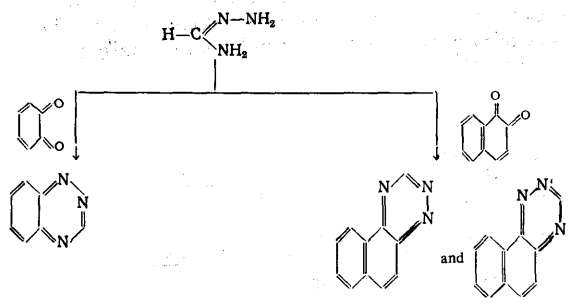


It has been widely used to synthesise a number of 1,2,4-triazines by the interaction of monoamidrazones with α-dicarbonyl and bis-α-dicarbonyl compounds and also of diamidrazones with α-dicarbonyl compounds. Thus the reaction of formamidrazone with various α-dicarbonyl compounds yielded mono- and di-substituted 1,2,4-triazines[82]:



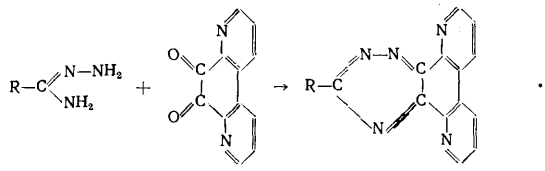
A series of 1,2,4-triazines with aromatic carbocyclic and heterocyclic substituents were synthesised from unsubstituted mono- and di-amidrazones by Case[8,9], Culbertson[83,84], and Hergenrother[85-87].

The syntheses of condensed systems incorporating 1,2,4-triazine rings, based on the interaction of unsubstituted amidrazones with *o*-quinones and related systems, are widely used[8,9,82]. Thus the reaction of formamidrazone with *o*-benzoquinone and 1,2-naphthoquinone gave rise to 1,2,4-benzotriazine and two isomeric naphthotriazines[82]:

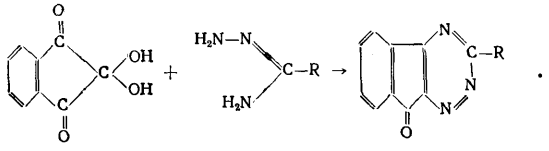


Even more condensed systems—substituted 1,2,4-triazino[5,6-*f*]-4,7-phenanthrolines—were obtained by Case

by the reaction of a number of amidrazones with 4,7-phenanthroline-5,6-dione[8,9]:



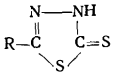
Together with α-dicarbonyl compounds, polycarbonyl compounds can also be made to react with amidrazones; thus triketones or their hydrates condense with amidrazones to form condensed heterocycles, incorporating 1,2,4-triazine moieties[35]:



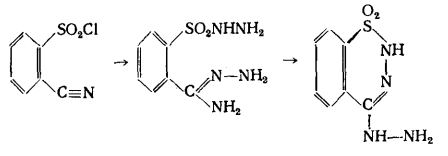
Ketoacids and ketoesters having the general formula RO–CO–CO–CO–CO–OR can also be employed as polycarbonyl compounds in condensation reactions with amidrazones[88,89]. The products of their condensation with amidrazones are 1,2,4-triazinepolycarboxylic acids or their esters.

7. Other Reactions of Amidrazones

Together with the syntheses of heterocyclic compounds from amidrazones which were discussed above, other reactions of these compounds were investigated. Thus, when amidrazones derived from aromatic carbocyclic and heterocyclic acids were treated with CS_2, 1,3,4-thiadiazole-5-thiones were obtained in high yields (73–95%):

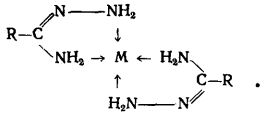


(R = phenyl, naphthyl, 2-, 3-, and 4-pyridyl, 2-quinolyl, etc.). Aromatic acid amidrazones containing a sulphonyl hydrazide group in the *o*-position, undergo intramolecular cyclisation; thus benzamidrazone-*o*-sulphonyl hydrazide—the product of the interaction of *o*-cyanobenzenesulphonyl chloride with hydrazine—readily cyclises to 4-hydrazino-1,2,3-thiadiazine 1,1-dioxide[91]:



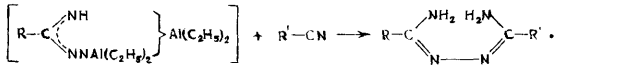
8. The Formation of Metal Complexes

Amidrazones form complexes with transition metal ions which are highly coloured with distinct melting points.



Complex formation proceeds so readily that it can serve as a basis of analytical methods for the determination of microamounts of both amidrazones and transition metal ions. In particular, it has been observed that oxalodiamidrazone can be used to detect microamounts of nickel[18].

The reaction of two equivalents of triethylaluminium with amidrazones in benzene results in the formation of tetrameric bis(diethylalumino)amidrazones[92]:



These compounds are soluble in benzene and on reaction with nitriles are converted into 1,4-disubstituted diazabuta-1,3-diene-1,4-diamines.

IV. UNSUBSTITUTED DIAMIDRAZONES IN THE SYNTHESIS OF HETEROCHAIN POLYMERS

Whereas unsubstituted monoamidrazones have found only limited applications (among derivatives of the pyridine series, several substances with pharmacological and antimicrobial activities were found[31,39,93–95]), unsubstituted diamidrazones of dicarboxylic acids have been assuming increasing importance as monomers for the synthesis of a number of heterochain and in particular heterocyclic polymers.

Examination of the reactions involving the formation of heterocycles from amidrazones which were discussed above shows that, like *o*-phenylenediamine, unsubstituted amidrazones readily react with (1) carboxylic acids and their derivatives forming on subsequent cyclisation 1,3,4-oxadiazole or 1,2,4-triazole rings (2-substituted benzimidazoles are formed from *o*-phenylenediamine), (2) with the cyclic anhydrides of aromatic *ortho*- or peri-dicarboxylic acids and subsequent formation of heterocycles which can be combined under the common name aroylene-*s*-triazoles (under analogous conditions, *o*-phenylenediamine gives rise to aroylenebenzimidazoles), and (3) with α-dicarbonyl compounds to form 1,2,4-triazines (under analogous conditions, *o*-phenylenediamine leads to the quinoxaline ring). Since bis-(*o*-phenylenediamines) have been widely used in recent years in the synthesis of thermostable heterocyclic polymers[96], their "analogues" (diamidrazones) have naturally also attracted attention as potential polyfunctional monomers.

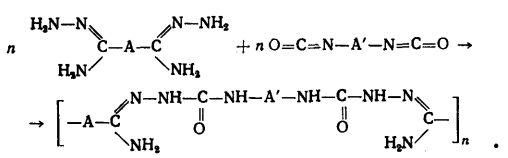
Since the nucleophilic reactivity of the hydrazine moieties of amidrazones is comparable to that of the imido-groups in *o*-phenylenediamine or is actually superior[80], polymers based on diamidrazones can be synthesised under the same conditions as the polymers based on bis-(*o*-phenylenediamines).

However, one should note that diamidrazones have one significant advantage over bis-(*o*-phenylenediamines). Thermostable heterocyclic polymers are usually synthesised[97] by a two-stage process involving polyfunctional monomers; linear prepolymers are synthesised in the first stage under mild conditions, which means that each monomer used in the process must have two functional groups. The linear polymers formed in the first stage have free functional groups distributed in such a way that in the second stage heterocycles can be formed under the influence of heat or chemical agents. The synthesis of linear polymers in the first stage entails the necessity for a selective polycondensation process, usually selective polyamidation. When the polyamidation is carried out by

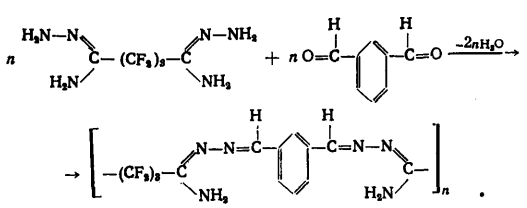
the interaction of polyfunctional nucleophilic compounds with polycarboxylic acid derivatives, process selectivity is achieved more readily the greater the difference between the nucleophilic reactivities of the reaction centres in the *o*- or α-positions relative to one another[98,99]. An alternative condition for selective polyamidation is rapid deactivation of the reaction centre after the group in the *o*- or α-position relative to it has entered into the amidation reaction. Since the amino-groups of bis-(*o*-phenylenediamines) exhibit comparatively similar nucleophilic reactivities, their reactions with highly reactive carboxylic acid derivatives frequently involve the breakdown of the selectivity of the processes, leading to gel formation and the prepolymers cannot therefore be converted into the desired products. In contrast to bis-(*o*-phenylenediamines), in diamidrazones the nucleophilic reactivities of the hydrazine and amidine centres differ sharply, which makes it possible to carry out polycondensation processes involving them with a high degree of selectivity. In combination with the relative availability of many diamidrazones and their resistance to oxidation, this factor makes these compounds extremely promising monomers.

All that has been said above applies not only to the reactions of diamidrazones with polycarboxylic acid derivatives but also to their reactions with dicarbonyl compounds and di-isocyanates.

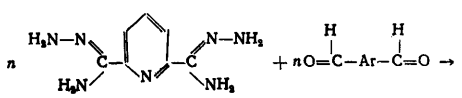
High-molecular-weight film- and fibre-forming poly-(carbamoylamidrazones) were obtained by the reaction of diamidrazones with di-isocyanates in aprotic dipolar solvents containing lithium chloride at 20–50°C:[100]

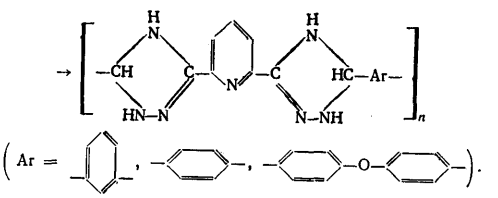


Polymers incorporating fragments of the Schiff base type (polyarylidene-amidrazones) have been obtained by the reaction of hexafluoroglutarodiamidrazone with isophthalaldehyde[101]:



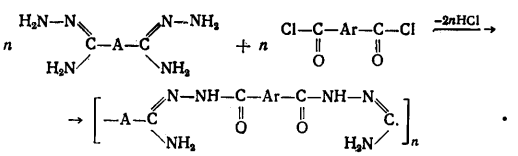
In both instances[100,101] there is a possibility of the conversion of the resulting polymers into heterocyclic systems, but there are no unambiguous data showing that this possibility is in fact realised. In contrast to these studies, Hergenrother and Carlson[80] showed unambiguously that the reaction of the diamidrazone of pyridine-2,6-dicarboxylic acid with aromatic dialdehydes leads to the formation of polytriazolines:





Polytriazolines are soluble to a limited extent in *m*-cresol, dimethylacetamide, dimethyl sulphoxide, and formic and trifluoroacetic acids. The intrinsic viscosities of solutions of these polymers are 0.51–0.61 dl g^{-1}, which makes it possible to obtain strong elastic films from their solutions in acids. According to the results of thermogravimetric analysis, the degradation of these polymers begins in the temperature range 280–400°C; attempts to convert them into the corresponding poly-1,2,4-triazoles were unsuccessful.

A number of studies were made on the interaction of diamidrazones with dicarboxylic acid dichlorides with consequent conversion of the resulting poly(acylamidrazones)[53-54,63,64,101-108]. Poly(acylamidrazones) were synthesised by the reaction of oxalic[63,64,103-108], isophthalic[102], terephthalic[102], and pyridine-2,6-dicarboxylic acid[53,54] diamidrazones with aromatic dicarboxylic acid dichlorides under the conditions of interfacial polycondensation[53,54,63,64,103-108] and low-temperature polycondensation in aprotic amide solvents[53,54,63,64,102,104]:

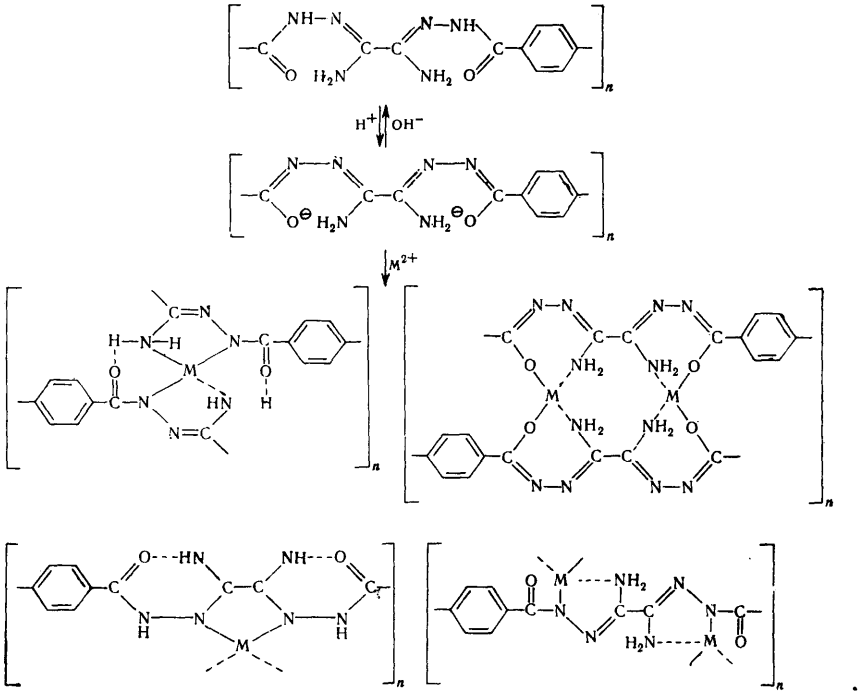


The poly(acylamidrazones) with the highest molecular weights among those obtained exhibit film- and fibre-forming properties[53,54,103,105,107-110].

The poly(acylamidrazones) were converted into the corresponding poly-1,2,4-triazoles by heating in high-boiling solvents, for example *m*-cresol[53,54], or by heat treatment in the solid phase at a temperature exceeding 250°C.[53,54,63,64,102,105,108] The polymers obtained by the solid-phase heat treatment of poly(acylamidrazones) contain 1.4–4% of oxadiazole rings according to the analysis of the products formed[53,54]. The cyclisation of poly(acylamidrazones) in strong acids (dichloroacetic[63,64], trifluoroacetic[53,54], PPA[53,54], and sulphuric[53,54]) was accompanied by the formation of poly-1,3,4-oxadiazoles.

The poly-1,2,4-triazoles and poly-1,3,4-oxadiazoles obtained in this way are soluble in concentrated sulphuric acid and, according to the results of dynamic thermogravimetric analysis, begin to undergo degradation in air at about 420°C.

Chelate polymers, produced by the interaction of poly-(acylamidrazones) with various metal cations (Ca^{2+}, Ba^{2+}, Sn^{2+}, Zr^{2+}, Zn^{2+}, Cd^{2+}, Bi^{2+}, Pb^{2+}, Cu^{2+}, Fe^{2+}, Au^{+}, etc.), are of exceptional interest in connection with the urgent problem of the synthesis of fire-resistant polymers[103,109]. Chelate polymers have been most widely synthesised from poly(acylamidrazones) based on oxalodiamidrazones and terephthaloyl chloride and the following structure has been proposed for them[103]:



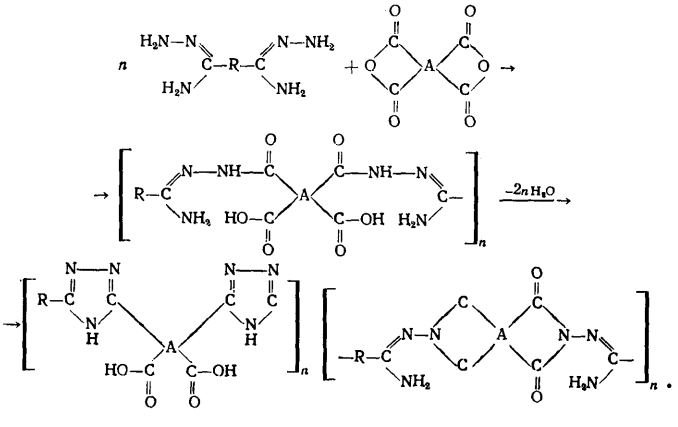
These polymers are highly fire-resistant and are used as the fire-resistant fibre Enkatherm[103]. The Table presents the comparative oxygen indices of various fibres, demonstrating the appreciable advantage of Enkatherm over other fibres.

Characteristics of the fire resistance of a number of fibres.

Polymer fibre	Temp. of spontaneous inflammation, °C	Oxygen index	Polymer fibre	Temp. of spontaneous inflammation, °C	Oxygen index
Cotton	400	0.18	Polyacrylonitrile	560	0.18
Polypropylene	440	0.18	Wool	590	0.25
Acetate	480	0.18	Nomex	—	0.28
Polyester	510	0.20	Polybenzimidazole	—	0.41
Nylon	530	0.22	Enkatherm	—	0.52

Among the series of other attempts at the synthesis of polymers based on diamidrazones and dicarboxylic acid derivatives, special mention should be made of the work of Ried and Giesse[67], who achieved the reaction of oxalo- and terephthalo-diamidrazones with the ethyl bisimidoesters of the same acids in lower alcohols with subsequent heat treatment. According to the authors[67], the reaction products are low-molecular-weight poly-1,2,4-triazoles.

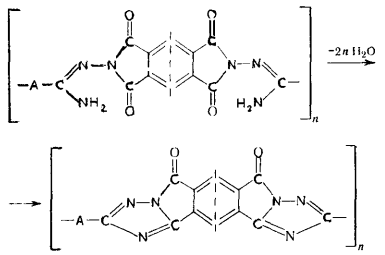
The synthesis of partly "ladder-types" polymers based on the diamidrazones of dicarboxylic acids has been attracting increasing attention recently. The interaction of diamidrazones with dianhydrides was achieved for the first time by Ried and Giesse[67] in the specific instance of the reaction of oxalodiamidrazones and pyromellitic and cyclopentanetetracarboxylic acid dianhydrides in pyridine. The structure of polytriazoles containing carboxylic acid side chains was attributed to the products. Another structure (polyamidinoimide) was proposed for the products of the reaction of diamidrazones with pyromellitic acid dianhydride[72]:



The first stage of the process—the synthesis of poly-(*o*-carboxy)acylamidrazones—was carried out in dimethyl sulphoxide. The resulting high-molecular-weight polymers were converted into films and subjected to polycyclodehydration.

In the course of subsequent investigations[34,68-71] it was shown that poly(amidinoimides) are merely intermediates formed under comparatively mild cyclisation conditions;

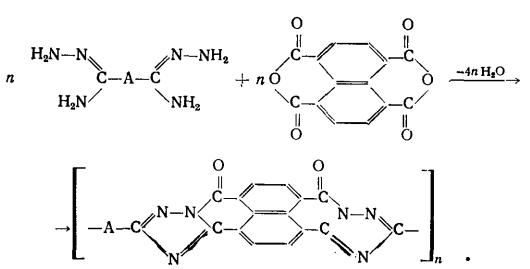
at higher temperatures they are converted into polytriazoloisoindolones:



In the spectroscopic study of the structures of the polymers obtained the authors[67,72] probably failed to take into account the fact that polytriazoloisoindolones, like many other heterocyclic polymers, are incompletely cyclised polymeric structures and contain a considerable number of defective units, which are responsible for the appearance of additional absorption bands in the infrared spectra of the polymers.

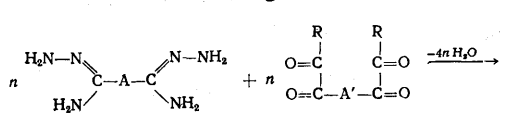
The presence of defective units in the polymeric structures under consideration and also the tendency of the isoindolotriazolone rings themselves to undergo degradation at the $\rangle C-CO-$ and $-OC-N\langle$ bonds and to hydrolyse are responsible for the comparatively poor thermal characteristic of these polymers—the majority of polytriazoloisoindolones begin to undergo degradation at temperatures not exceeding 400°C.[69-71]

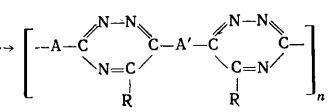
Polybenzobistriazolophenanthrolines (polynaphthoylenetriazoles), produced by the reaction of dicarboxylic acid diamidrazones with naphthalene-1,4,5,8-tetracarboxylic acid or its dianhydride, have a much higher thermal stability[71,73,76-78]. They are synthesised by single-stage polycyclocondensation in PPA or by two-stage polycyclocondensation with the first stage carried out in hexamethylphosphoramide in accordance with the following scheme:



The single-stage process in PPA, whereby film-forming polymers with a logarithmic viscosity of the solutions of about 2.5 dl g^{-1} may be obtained, is more effective in relation to the above polymers. Polybenzobistriazolophenanthrolines, which are soluble in sulphuric and methanesulphonic acids, begin to lose weight appreciably in air at 500°C under the conditions of dynamic thermogravimetric analysis and at a temperature in excess of 400°C under the conditions of isothermal thermogravimetric analysis.

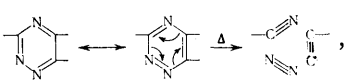
A number of high-molecular-weight poly-1,2,4-triazines have been obtained by the reaction of dicarboxylic acid diamidrazones with bis-(α-dicarbonyl) compounds[85-87,111] in accordance with the following scheme:





The reaction of dicarboxylic acid diamidrazones with diglyoxals was achieved by Hergenrother[85,87] and Culbertson[111] in polar organic solvents (*m*-cresol[85,87], hexamethylphosphoramide[111], etc.) between 0°C and the boiling point of the solvent with subsequent heat treatment of the polymers or without it. The initial diamidrazones were derived from pyridine-2,6-dicarboxylic[85,111], oxalic[87,111], and also malonic, succinic, glutaric, adipic, sebacic, isophthalic and terephthalic acids[111]. The diglyoxals employed were *pp'*-oxybis(phenyleneglyoxal) hydrate[85,87,-111], 1,4-diglyoxaloylbenzene, *pp'*-thiobis(phenyleneglyoxal)[87,111], 1,2-diglyoxaloylnaphthalene, 2-chloro-1,3-dioxalylbenzene, etc.[111]

The fully aromatic poly-1,2,4-triazines exhibit limited or partial solubility in polar solvents of the type of *m*-cresol, dimethyl sulphoxide, dimethyl acetamide, and hexamethylphosphoramide. According to the results of dynamic thermogravimetric and differential thermal analyses, they begin to undergo intense degradation at about 400°C in air and at 450°C in an inert medium. The comparatively low thermo-oxidative and thermal stability of these polymers can be accounted for by the ease of liberation of nitrogen,



and the oxidation of the $\rangle C-H$ fragment of the triazine ring[85].

Poly-1,2,4-triazines, which are much more soluble in polar solvents and have a much higher thermo-oxidative stability compared with the polymers discussed above, were obtained by the reaction of dicarboxylic acid diamidrazones with dibenzils. The dicarboxylic acid diamidrazones employed were derived from pyridine-2,6-dicarboxylic[85,86] and oxalic[87] acids and the dibenzils were *pp'*-oxydibenzil[85-87] 1,3- and 1,4-bis(phenylglyoxaloyl)benzenes, *pp'*-thiodibenzil[86,87], as well as *pp'*-methylenedibenzil, and *pp'*-carbonyldibenzil[86]. The resulting polymers soften at 270–330°C, in contrast to unsubstituted poly-1,2,4-triazines, and exhibit a high resistance to isothermal heat-induced ageing in air at 260°C in the course of 1000 h[87]; at 290°C these polymers lose 20–25% of the initial weight in the course of 45 h. The polymers can be used as thermostable adhesive films and binders for fibreglass[86].

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