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Advances in the Chemistry of Amidines

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The review surveys data published during the period 1971-1981 on the synthesis and physicochemical and chemical properties of various types of amidine systems. Particular attention has been devoted to the use of amidines in the synthesis of heterocycles.
The bibliography includes 259 references.

CONTENTS

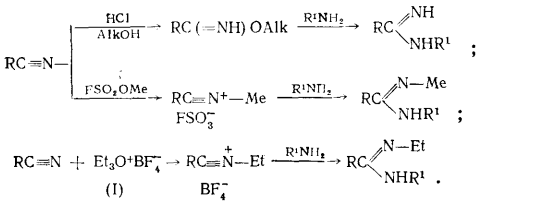
I. Introduction 377
II. Methods of synthesis 377
III. Structure and physicochemical properties 381
IV. Chemical properties 382

I. INTRODUCTION

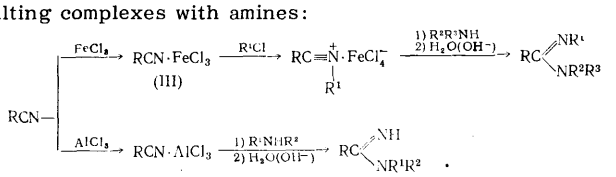
The chemistry of amidines has been recently attracting much attention by investigators in connection with their wide-scale employment in organic synthesis. The number of publications dealing with studies of the methods of synthesis and the properties of amidines has continuously increased and, despite the monograph published in 1975 [1] and a series of reviews dealing with various aspects of the chemistry of these compounds[2-7], most of the data published during the last decade have not been described in the review literature. The present review surveys new data on the synthesis, properties, and reactions of amidine systems of various types, particular attention being devoted to the application of amidines to the synthesis of heterocyclic compounds.

II. METHODS OF SYNTHESIS

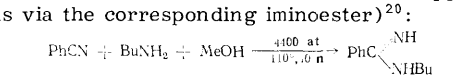
During the period considered, an extremely large number of studies dealing with the synthesis of various amidines were published. The traditional starting materials are nitriles, which are transformed into amidines via intermediate iminoesters. The latter are usually obtained by treatment with hydrogen chloride in alcohol and are then made to react with various amines[8-11]. Another method is based on the alkylation of nitriles with triethyloxonium tetrafluoroborate (I) followed by treatment of the nitrilium tetrafluoroborate salts (II) with amines[12,13]. A modification of this method involves the synthesis of nitrilium salts with the aid of methyl fluorosulphonate[14]:



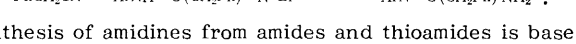
A general method of synthesis of various amidines is based on the reactions of nitriles with Lewis acids ($FeCl_3$ or $AlCl_3$ are usually employed)[15-19] followed by treatment of the resulting complexes with amines:



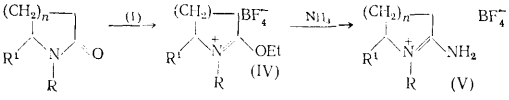
As can be seen from the scheme presented, the complexes of nitriles with iron(III) chloride can be alkylated by alkyl halides to form the corresponding *N*-substituted nitrilium salts, which can be transformed further into *N,N,N'*-trisubstituted amidines. An unusual method of synthesis of amidines at a high pressure is based on the reaction of nitriles with alcohols and amines (the reaction apparently proceeds via the corresponding iminoester)[20]:



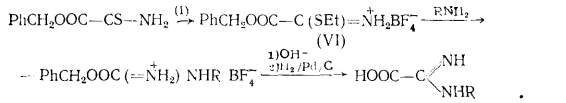
Nitriles can also interact with lithio-derivatives of arylamines[21]:



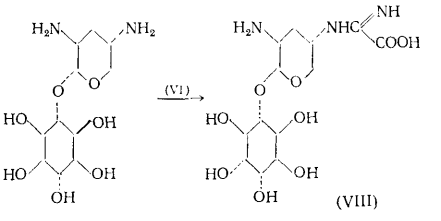
The synthesis of amidines from amides and thioamides is based on the preliminary activation of the amide functional group. Numerous reviews[22-27] dealing with such activation describe, in particular, also a considerable number of amidine syntheses. Such activation is usually achieved by alkylating amides with triethyloxonium tetrafluoroborate (or dimethyl sulphate)[12,28-30] or by acylation with reagents such as hexamethylphosphoramide (HMP),[31,32], phosphoryl chloride[33-35], phosphorus pentoxide[36], and acyl chlorides[37]. Thus the interaction of lactams with compound (I) [28] leads to the formation of the tetrafluoroborates (IV), which then readily react with ammonia to form amidinium salts (V). It is of interest to note that alkylation of 2-pyrrolidinone having a carbamoyl group in the 5-position [compound (IV, R = Me, $R^1 = CONH_2$, $n = 1$)] takes place selectively at the lactam carbonyl[28]:



The reaction involving compound (I) yielded the thioiminoester salt (VI)—the key compound in the method of synthesis of amidinoacids (VII):[29]

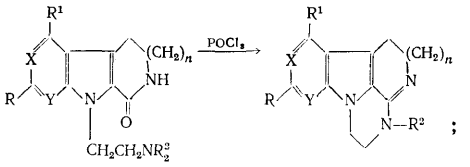


This method has been used in the synthesis of the antibiotic kasugamycin (VIII):[29]



It is of interest that only the equatorial amino-group reacts selectively with compound (VI).[29]

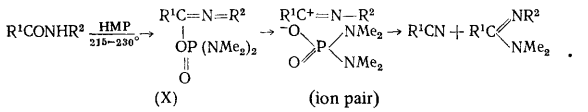
The activation of the amide functional group in tricyclic lactams of type (IX) made it possible to achieve their cyclisation to tetracyclic indole systems containing the amidine fragment[33,35]:



(IX)

X=Y=CH, R^1=R=H, X=Y=N, R^1=R=OH .

When amides are heated with HMP, nitriles and amidines are formed via the phosphorodiamidate derivative (X):[31]



(X) (ion pair)

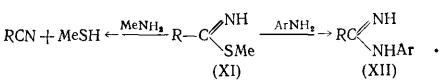
The reaction of an aromatic amine, formic acid, and HMP gives rise to amidines[32]:

$$ArNH_2 + HCOOH \xrightarrow{HMP} ArN{=}CH{-}NMe_2 .$$

The interaction of acetanilides with dimethylformamide (DMF) in the presence of $POCl_3$, $SOCl_2$, PCl_3,[34] P_2O_5,[26] or *N,N*-diethylthiocarbamoyl chloride[37] leads to the corresponding amidines:

$$ArNHCOCH_3 + Me_2NCHO \xrightarrow{POCl_3\ (or\ PCl_3, SOCl_2, P_2O_5, Et_2NCSCl)} ArN{=}CH{-}NMe_2 .$$

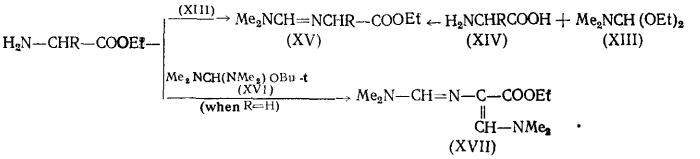
When thioiminoesters (XI) were used in the amidine synthesis, it was established that the esters react with aromatic amines to form the amidines (XII), while the reaction with highly basic amines proceeds with formation of nitriles[38]:



(XI) (XII)

Schnur[38] was able to find a method of synthesis of amidines from compounds (XI) even with the aid of aliphatic amines, which makes it necessary to carry out the reaction in an acetate buffer solution.

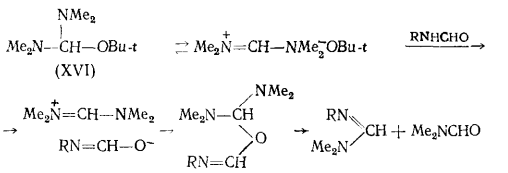
Other types of activated amides—amide acetals, lactams, and related compounds, dichloromethyleneimmonium salts, and diethoxymethylammonium salts—are also widely used for the synthesis of amidines. The majority of studies of the amidine synthesis based on these compounds have been described in detail in reviews[25-27,39,40] and here we shall consider only those studies which were not included in the above reviews. A number of investigations were devoted to the synthesis of *N*-heteroarylamidines by the reaction of the acetals of DMF (XIII) and dimethylacetamide with heteroaromatice amines. Derivatives of *N*-pyrazinyl-2-formamidines[41], *N*-pyrimidinyl-2-formamidines[42], *N*-pyridyl-2-formamidines[42], *N*-purinyl-6-formamidines[43], *N*-pyrazolyl-3-formamidines[44], and *N*-pyrazolyl-3-acetamidines[44] were obtained via this procedure. The reaction of compound (XII) with aminoacids (XIV) is accompanied by alkylation and results in the formation of the amidinoesters (XV).[45] Compounds of the same type have also been obtained by the reaction of compound (XIII) with aminoacid esters[46]. When the more reactive aminal-ester (XVI) is used in this reaction, the enaminoamidines (XVII) are formed[46]:



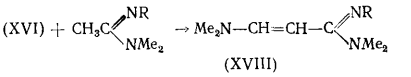
(XV) (XIV) (XIII)

(XVII)

The reaction of the aminal-ester (XVI) with secondary amides is of interest: *N,N*-disubstituted amides and amidines are formed in this instance. The authors suggested the following reaction mechanism[46]:

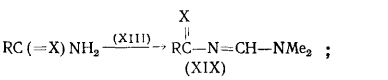


In the same study it was shown that the interaction of the aminal-ester (XVI) with acetamidine derivatives leads to the enaminoamidines (XVIII):[46]



(XVIII)

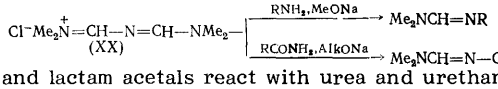
A series of studies have been published recently, according to which the acetal (XIII) readily reacts with primary amides and thioamides, which leads to the formation of acyl- or thioacyl-amidines (XIX)—interesting intermediates in various types of syntheses[47-49]:



(XIX)

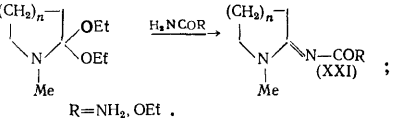
X = O, S .

It has been shown[50] that the immonium salt (XX), obtained previously[51] by the reaction of DMF and cyanuric acid chloride, can be used successfully in the synthesis of amidines and acylamidines instead of the DMF acetal (XIII):



(XX)

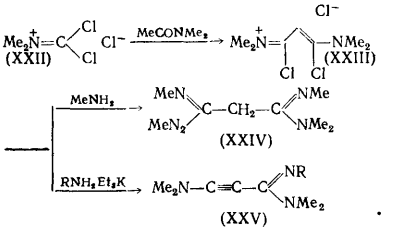
Amide and lactam acetals react with urea and urethane to form the corresponding *N*-carbamoyl- and *N*-ethoxycarbonylamidines (XXI).[52] We may note that the former form complexes with one or several urea molecules:



(XXI)

R=NH_2, OEt .

The interaction of dichloromethyleneimmonium chloride (XXII) with *N,N*-dimethylacetamide leads to the salt (XXIII) which can be converted into the diamidines (XXIV) or the ynaminoamidines (XXV), depending on the reaction conditions[53]:

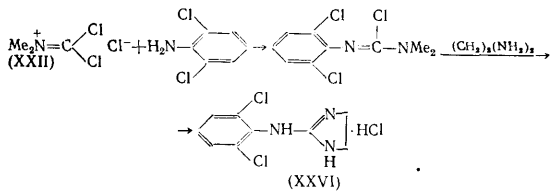


(XXII) (XXIII)

(XXIV)

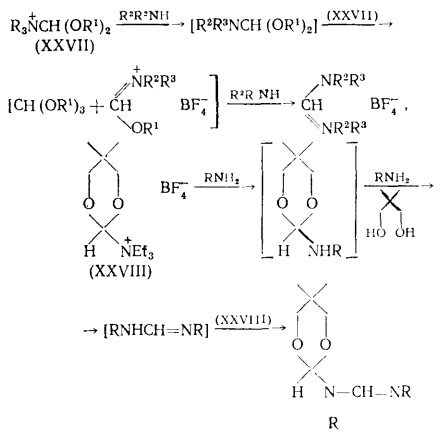
(XXV)

A new synthesis of the valuable medicinal preparation clofelin (XXVI), based on the reaction of the immonium chloride (XXII) with 2,6-dichloroaniline involving the intermediate formation of chloroformamidine, was published recently[54]:

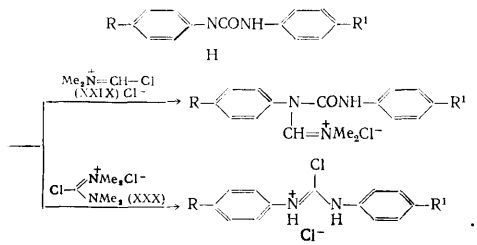


(XXVI)

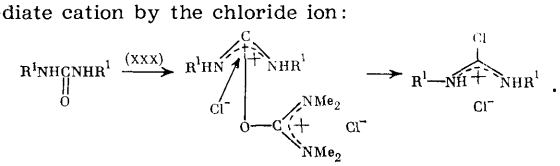
Certain chloroformamidines have been synthesised analogously from compound (XXIII) and different amines including heterocyclic amines[55,56]. A series of substituted formamidines have been synthesised by the reaction of the dialkoxymethylammonium salts (XXVII) and (XXVIII) with aliphatic amines[57,58]:



Processes involving the synthesis of formamidine derivatives by the reaction of diarylureas with chloromethylenedimethylammonium chloride (XXIX) and chlorodimethylaminomethylenedimethylammonium chloride (XXX) are closely related to the reactions described above[59]:

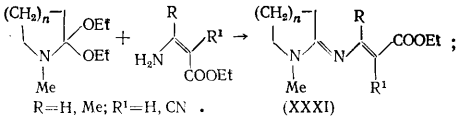


Tritschler and Kausz[57] believe that direct *N*-dimethylaminomethylenation takes place in the former case, while in the latter case it is impossible due to steric hindrance and the reaction involves oxygen with subsequent attack on the intermediate cation by the chloride ion:

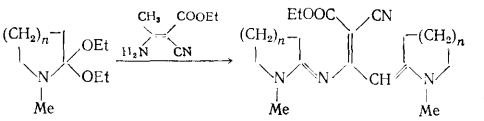


A number of pieces of experimental evidence supporting the above theoretical considerations have been published[59].

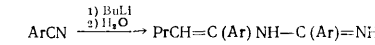
Amide and lactam acetals have also been used in the synthesis of an interesting class of organic compounds—enamidines, which have been used in a number of instances for the synthesis of condensed heterocycles (see below). The enamidines (XXXI) are formed readily and in high yields by the reaction of amide and lactam acetals with primary enamines[60,61], even weakly basic enamines such as aminomethylenecyanoacetic ester:



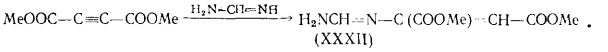
It is of interest to note that the reaction of amide and lactam acetals with β-amino-α-cyanocrotonic ester involves not only the amino-group but also the β-methyl group[61]:



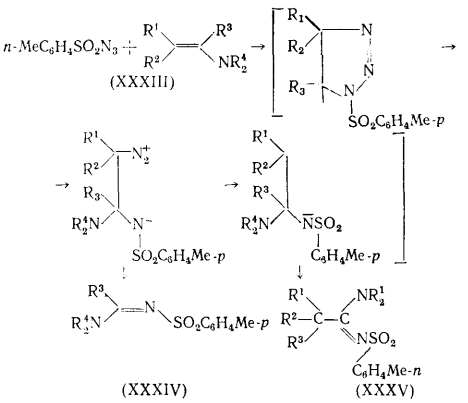
Enamidines have also been synthesised[60,61] by the reaction of aryl cyanides with butyl-lithium or organomagnesium compounds[62,63]:



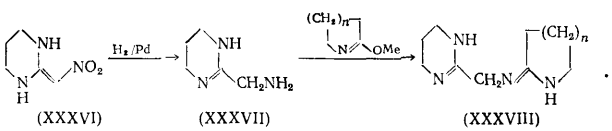
Substituted *sym*-triazines are formed as side products in this reaction[63]. Yet another mention of the synthesis of the enamidine (XXXII) has been made in a study[64] where it was obtained by the reaction of dimethyl acetylenedicarboxylate with formamidine at −10 °C:



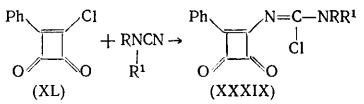
The reaction of the enamines (XXXIII) with toluene-*p*-sulphonyl azide proceeds in a very interesting manner—a mixture of the amidines (XXXIV) and (XXXV) is then formed[65]. It has been noted that, when R^1 and R^2 are alkyls (and not hydrogen atoms), the number of rearranged amidines (XXXV) increases, probably as a consequence of the ability of the alkyl group to stabilise the carbocationic centre:



Amidines (including cyclic amidines) can be obtained by the hydrogenation of nitroalkylenediamines (XXXVI). The bisamidines (XXVIII) have been synthesised from the aminomethylamidines (XXXVII) formed[66]:

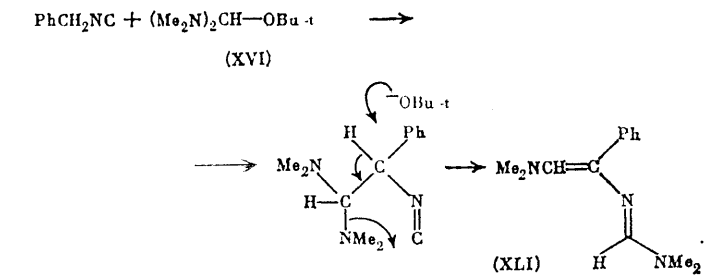


The reduction of carbodiimides with sodium tetrahydroborate[67] or of urea derivatives with lithium tetrahydroaluminate[68] leads to formamidine derivatives. Various formamidines can be synthesised from urea and thiourea derivatives. Thus chloroformamidines are formed when *N*,*N'*-dialkyl-*N*-heteroarylureas react with Ph_3P and CCl_4 [69] or on chlorination of *N*,*N'*-bis(arenesulphonyl)-*S*-methylisothioureas[70]. The chloroformamidine (XXXIX) is also formed on reaction of halogenocyclobutenedione (XL) with cyanamides[71]:



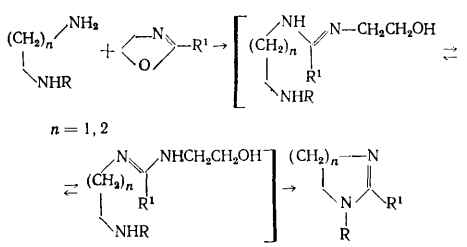
(XL) (XXXIX)

N-Hydroxyamidines have been obtained by the reaction of chloroimides with hydroxylamine[72,73] or by the reaction of substituted hydroximoyl chlorides with amines[74]. The reactions of isonitriles with sulphonamides[75], amines[76–78], and an aminal-ester[46] are used very frequently for the synthesis of amidines. One should note that it has been shown[76,77] that the reactions involving the addition of secondary amines to isonitriles take place stereospecifically with formation of *Z*-formamidines, which then rearrange to the thermodynamically more stable *E*-isomers. The interaction of the aminal-ester (XVI) with benzyl isocyanide involves the methylene unit with subsequent rearrangement[46] involving the formation of the amidine (XLI):

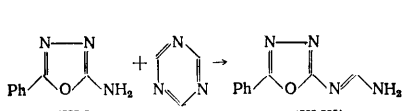


(XVI) (XLI)

A number of studies have been devoted to the synthesis of amidines using certain heterocyclic agents in the corresponding reactions. Thus the reaction of derivatives of ethylene- and propylene-diamines with Δ^2-1,3-oxazoline leads to cyclic amidines[79]:

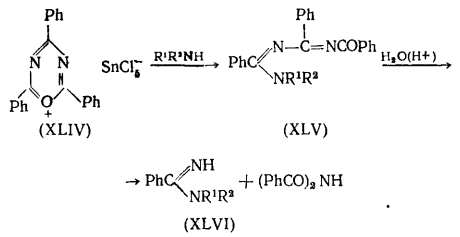


The reaction of 2-amino-5-phenyl-1,3,4-oxadiazole (XLII) with *sym*-triazine leads to the formamidine derivative (XLIII):[80]



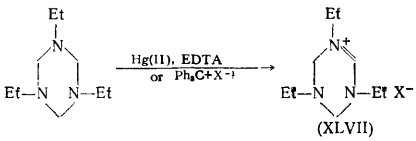
(XLII) (XLIII)

When 1,3,5-oxadiazinium salts (XLIV) react with amines, the products are *N*-(*N*-benzoylimino)benzylamidines (XLV), which hydrolyse in an acid medium to benzamidines (XLVI) and dibenzoylamine[81]:



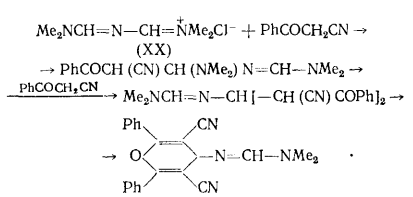
(XLIV) (XLV) (XLVI)

Cyclic amidinium salts (XLVII) can be obtained by oxidising *N*,*N'*,*N''*-triethylhexahydrotriazine or by treating it with $Ph_3C^+X^-$:[82]

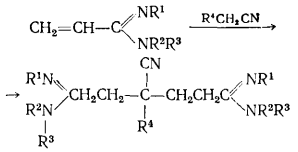


(XLVII)

It has been shown recently[83] that the immonium salt (XX) can be used to introduce the formamidine fragment into compounds with an active methylene unit:



It has been established in recent years that the amidinium group can be introduced into various organic compounds (amines, alcohols, compounds with an active methylene unit, and mercaptans) by the amidinoethylation reaction which is of the same type as the Michael reaction[84–87], for example:

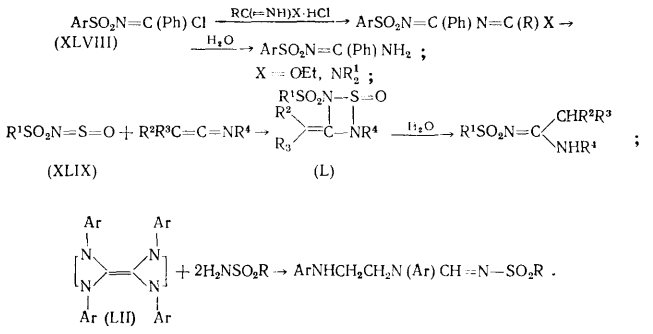


Derivatives of formamidine and homologous amidines are formed when alkali metal amides react with aldehydes in liquid ammonia[88] and *N*,*N'*-dimethylformamidine has been obtained by the thermal decomposition of potassium methylamide[89].

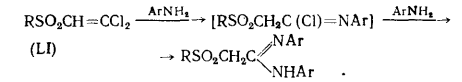
A series of studies have been devoted to the synthesis of amidines with sulphur-, phosphorus-, and silicon-containing substituents at the nitrogen atoms†. Thus sulphonylamidines have been synthesised by the reaction of arenesulphonylchloroimides (XLVIII) with iminoester (or amidine) hydrochlorides followed by the hydrolysis of the intermediate or imidoylamidines[90], by the reaction of *N*-sulphinylsulphonamides (XLIX) with keten imines via [2 + 2] cycloadditions

†See also the study[65] described earlier in this review, which was transferred to the section dealing with the synthesis of amidines from enamine compounds.

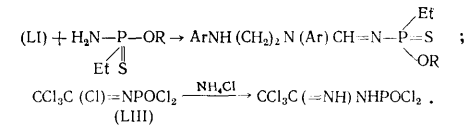
(L),[91] and by the reactions of sulphonamides with the ethylenetetramine (LI):[92]



The reaction of dichlorovinyl sulphones (LII) with aromatic amines takes place via the intermediate formation of chloroimides[93]:

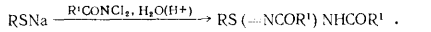


Phosphorus-containing amidines have been synthesised by the phosphorylation of the ethylenetetramine (LI) [92] and also by the reaction of the chloroimide (LIII) or related compounds with ammonium salts[94]:

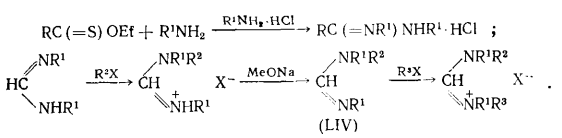


In addition, compounds of this type can be synthesised by the reaction of *N*-unsubstituted amidines with phosphorus halides[95,96]. *N*-Trimethylsilylamidines have been obtained analogously by the reaction of amidines with chlorotrimethylsilane; they are also formed in the reaction of trimethylsilylamine with butyl-lithium, followed by the treatment of the lithio-derivative with chloroimides[97].

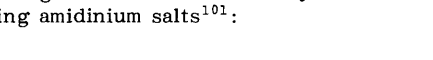
Sulphinamidines, which are an interesting class of compounds, have been synthesised by the reactions of *N*,*N*-dichlorourea[98], *N*,*N*-dichloroamines[99], or *N*,*N*-dichloroamides of diphenoxyphosphoric acid[100] with sodium thiolates:



In conclusion of this section, we may point out two new syntheses of amidines, the first of which is based on the reaction of *O*-ethyl thioesters with amines in the presence of their hydrochlorides[101] and the second is based on the alkylation of di- and tri-substituted amidines[102]:



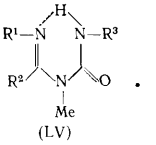
It is of interest that, when the trisubstituted amidines (LIV) are alkylated by the relatively unreactive alkyl halides, the alkylation may be accompanied by the abstraction of the elements of hydrogen halides from the alkyl halides to form the corresponding amidinium salts[101]:



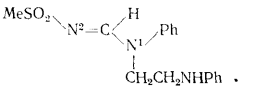
III. STRUCTURE AND PHYSICOCHEMICAL PROPERTIES

When the structure of amidines is considered, one must take into account the possibility of the prototropic "amidine" tautomerism due to proton transfer from one nitrogen atom to another. However, in many instances, it is possible to detect by physicochemical methods only one of the tautomeric forms. Thus it has been established by infrared spectroscopy for a series of cyclic amidines derived from 2-amino-Δ^1-piperideines that these compounds exist in the amino-form[103]. When there is an electron-accepting substituent at one of the nitrogen atoms, the tautomer in which the C=N bond is conjugated with this substituent usually predominates[75,95].

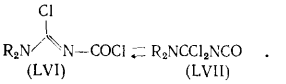
The study of the structure of *N*-carbamoylamidines (LV) by infrared spectroscopy made it possible to detect a strong intramolecular hydrogen bond in these compounds[104]:



The infrared spectra proved to be extremely useful also for the study of the hydrogen bonds between amidines and the solvent. Thus it has been established that formamidine derivatives form complexes of two types with chloroform: with participation of both the imino- and amino-nitrogen atoms[105], while in cyclic amidines[103] the hydrogen bond with $CHCl_3$ is formed only with participation of the ring nitrogen. Infrared spectra have also been used to elucidate the character of the coordination in boramidines[106]. The problem of the relative position of the substituents with respect to the C=N bond in amidines has attracted much attention. The *syn-anti* isomerisation in amidines of various types has been studied[107,108] by ^{1}H NMR. In the investigation of the addition of secondary amines to isonitriles[76,77] the authors concluded that *Z*-formamidines are formed initially and, being thermodynamically unstable, then rearrange to the *E*-isomers#. On the other hand, it has been stated[92] that stable *Z*- and *E*-isomeric *N*-sulphonylamidines have been isolated. However, subsequently, in a detailed study of their structures by infrared spectroscopic, ^{1}H NMR, and ^{13}C NMR methods, it was established that the substances isolated are rotational isomers relative to the C–N^1 bond[110]:



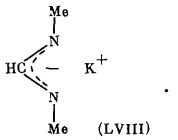
Interesting data have been obtained in a study[111] of the structure of *N*-chlorocarbonylchloroformamidines (LVI)—it was established that they are in equilibrium with the corresponding *N*,*N*-dialkylamino-1,1-dichloromethyl isocyanates (LVII):



A series of studies have been devoted to the hindered rotation relative to the C=N bond in amidines by ^{1}H NMR [108, 112–117]. The free energies of activation for the process ($\Delta G^{\neq}$) are usually not unduly high and, depending on the amidine structure, vary in the range 11–21 kcal mol^{-1}, the

#The assignment of amidines to the *Z*- or *E*-series can also be achieved by ^{13}C NMR.[109]

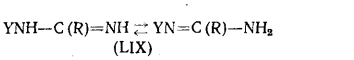
values for amidinium salts being appreciably higher[108]. It is of interest that the phenomenon of hindered rotation relative to the C=N bond could not be observed for the potassium salt of the amidine (LVIII):[112]



(LVIII)

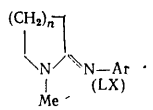
We may note that the "amidine" tautomerism was investigated in the same study by ^{1}H NMR and the thermodynamic parameters of the tautomeric equilibrium were obtained[112].

The position of the tautomeric equilibrium was estimated quantitatively by ultraviolet spectroscopy and by comparing the ionisation constants of certain amidines and model compounds[118,119]. It was shown that the equilibrium



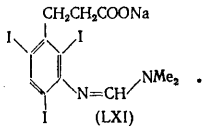
(LIX)

involving the amidines (LIX), where Y is an electron-accepting substituent, is significantly displaced to the right and that $K_T \cong 30$ for Y = acyl and $K_T \cong 10^7$ for Y = SO_2R.[118] If Y is a substituted phenyl group, the equilibrium is not displaced quite so much and $K_T = 2.4$.[119] The ionisation constants of a series of cyclic amidines have been measured[120–122] and it has been shown that the pK_a depend significantly on the ring size§ and that the basicity decreases in the sequence $C_6 > C_7 > C_8 \cong C_5$.[122] The authors explain this phenomenon by conformational factors—for the six-membered ring there is a possibility of a planar configuration of the amidine fragment, which is energetically unfavourable for the five-, seven-, and eight-membered compounds due to the non-bonding interactions of the protons in the ring methylene groups[122]. The study of the ionisation constants of a series of amidines and of the correlation between the pK_a and the σ constants[124,125] led the authors to the conclusion that the values of ρ and in general the basicity of the amidines depend to a greater extent on the substituents at the imino-nitrogen atom than on the substituents at the amino-atom. The study of the protonation of 2-arylimino-1-aza-cycloalkanes (LX) showed[126] that it involves the exocyclic, imino-nitrogen atom:



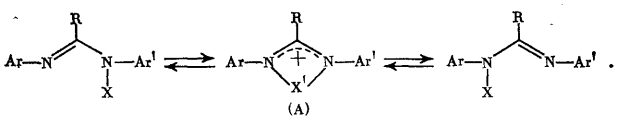
(LX)

The amidines (LX) are extremely strong bases (pK_a = 6.5–9.6), whose basicity also depends on the ring size[123,126]. On the basis of correlation analysis involving a comparison of the pK_a with the σ and σ^- constants, it was established in the above studies that the arene ring has been rotated relative to the C=N bond by approximately 50–60 °C. A similar rotation of the heteroaryl residue apparently occurs also in derivatives of *N*-(3-pyrazolyl)-amidines[44]. The high basicity of amidines is used in analytical chemistry for their quantitative analysis—one of the methods of analysis¶ of the radiocontrast agent bilimin (LXI) is its titration with $HClO_4$ in acetic acid[127]:



(LXI)

As already stated, the "amidine" tautomerism is due to proton transfer from one nitrogen atom of the triad to another. The 1,3-transfer of various groups within the amidine system, which has been studied by dynamic ^{1}H NMR [134–138] and by quantum-chemical calculations[139], is closely related to tautomerism of this type:



(A)

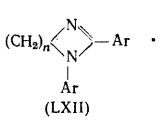
This reversible process has been studied for various substituents (X = acyl[134,138], 2,4-dinitrophenyl and picryl[135,138], or suphenyl[136,137]). Special experiments[134] estalbished that the 1,3-transfer process is intramolecular.

The energetic characteristics of the process depend on the structure of X and also on the structure of the substituents R, Ar, and Ar'. It is significant that the activation entropy $\Delta S^{\neq}$ for X = acyl is small and positive and that in such cases (A) is not a transition state but an intermediate. On the other hand, when X = SR^1, we have $\Delta S^{\neq} = -14$– -24 e.u., so that the transition state is more ordered than the ground state, which agrees with a structure of type (A). In the ^{1}H NMR studies of acyl- and sulphenyl-amidines at low temperatures, hindered rotation relative to the N–CO and N–S bonds respectively was observed.

IV. CHEMICAL PROPERTIES

1. Reactions With Nucleophiles and Electrophiles

The simplest reaction of amidines or their salts with nucleophiles is their hydrolysis. The mechanism of the hydrolysis of amidines was studied in detail in a monograph[1] and new investigations[121,122,140] did not introduce significant changes into the existing ideas. Examination of the question of the influence of ring size on the rate of alkaline hydrolysis of the cyclic amidines (LXII) [122,123] enabled the authors to establish the following sequence of decreasing rate constants: $C_5 > C_6 > C_7 > C_8$:[122]



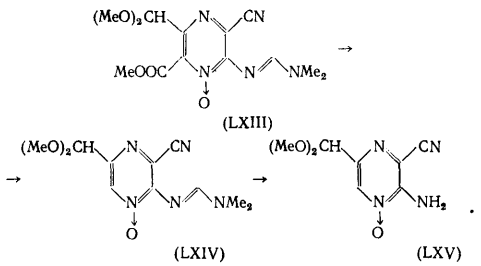
(LXII)

The authors attributed the highest rate of cleavage of compound (LXII, *n* = 2) to the strain in the five-membered ring, while the low rate of hydrolysis of seven- and eight-membered amidines is caused in their view by steric hindrance to the

§ For a review of the dependence of the properties of organic compounds on ring size, see Granik[123].

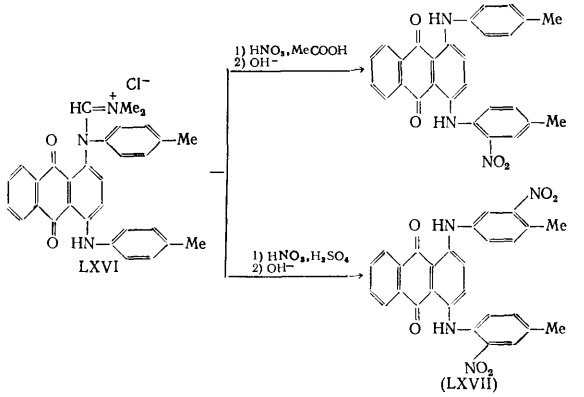
¶ In general amidines can be analysed quantitatively most effectively by titrating them as monoacidic bases. A study has been published recently[128], according to which certain amidines can also be analysed by gas–liquid chromatography (GLC).

attack by the hydroxide ion on these rings[122]. Comparison of the rates of the acid and alkaline hydrolysis of *N,N'*-dimethylformamidine showed that in an alkaline medium the process is significantly faster. An interesting study[41] of the conditions governing the retention and cleavage of the amidine group on hydrolysis as a function of the synthetic aim has been published recently. Thus it has been possible to hydrolyse selectively (and then decarboxylate) the methoxycarbonyl group of the substituted pyrazine (LXIII) without affecting the amidine group, by refluxing a solution of this compound in moist pyridine in the presence of lithium iodide. On the other hand, in the next stage it was necessary to remove selectively the formamidine group without involving the acetal group. The usual method, involving treatment with aqueous ammonia, proved to be unsuitable, since closure of the pyrimidine ring was observed under these conditions; acid hydrolysis in aqueous solution was also impossible owing to the dissociation of the acetal protecting group:



(LXIII) (LXIV) (LXV)

Taylor and Dumas[41] found an unexpected solution and obtained the amino-derivative (LXV) by keeping the formamidine (LXIV) in the 1 : 1 MeOH–$CH(OMe)_3$ mixture in the presence of $TsOH.H_2O$. In the case considered above, in order to protect the amino-group the latter was transformed into the formamidine group. This type of protection made it possible to solve the problem of the synthesis of mononitro- (or monobromo- and mono-*N*-acyl) derivatives of anthraquinone (LXVI):[141–143]



LXVI (LXVII)

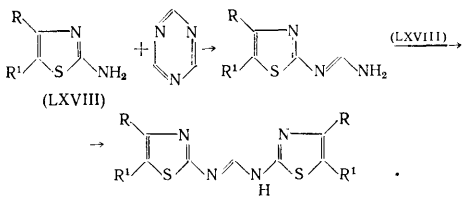
The use of an amidinium protecting group with its subsequent hydrolysis permitted the synthesis of derivatives of type (LXVII), which are extremely difficult to obtain by other methods and which have *o*- and *m*-substituents in the symmetrical aryl substituents in the 1,4-positions in the anthraquinone ring[141]. The hydrolysis of the amidine fragment was the concluding stage in a new synthesis of imides[49]:

$$RCON{=}C(R^1)NMe_2 \xrightarrow{H_2O(MeCOOH)} RCONHCOR^1 .$$

The discussion of investigations of this kind must be completed by stating that the hydrolysis of cyclic amidines is a model reaction for the investigation of the enzymic transfer of single-carbon components[144,145]. This problem has been reviewed[146]. One of the extremely important reactions of amidines or their salts with nucleophiles, which is used as one of the stages in heterocyclic synthesis (see below), is the transamination reaction. The synthesis of *N,N'*-disubstituted amidines by means of this reaction has been described recently[147]:

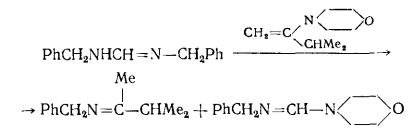
$$RC(=\overset{+}{N}H_2)NH_2Cl^- \xrightarrow{R^1NH_2} RC(=\overset{+}{N}HR^1)NH_2Cl^- \xrightarrow{R^1NH_2} RC(=\overset{+}{N}HR^1)NHR^1Cl^- .$$

The interaction of heterocyclic amines [for example, compound (LXVIII)] with *sym*-triazine is also accompanied by transamination[148]:

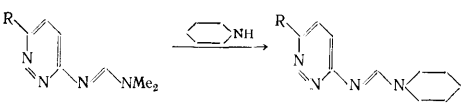


(LXVIII)

The reaction of amidines with tertiary enamines is extremely interesting—here too the final result is transamination[149]:



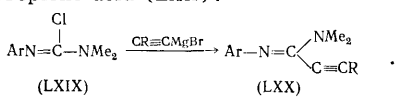
On heating, secondary amines are also capable of undergoing reactions of this type[150]:



The study of the properties of *N*-anthraquinonylformamidines showed that they react with nucleophiles only in the protonated form[151]. Studies of the transamination of enamidines established that, instead of involving the amidine meso-carbon atom, the reaction takes place at the enamine α-position with formation of enamines (and not pyrimidines as might have been expected)[152]:

$$Me_2N{-}CH{=}N{-}CH{=}C(CN)COOEt \xrightarrow{RR^1NH} RR^1N{-}CH{=}C(CN)COOEt$$

Substituted chloroformamidines readily react with nucleophiles, forming guanidines of various types[55,56,71], urea derivatives[70], and *O*-alkylisoureas[154]. The interaction of the amidines (LXIX) with ethylmagnesium bromide leads to amidines of propiolic acid (LXX):[155]

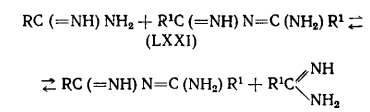


(LXIX) (LXX)

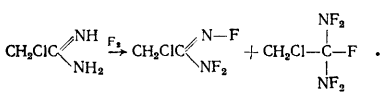
On treatment with sodium alkoxide at low temperatures, *N,N,N'*-trifluoroamidines yield a mixture of *N*-fluoroiminoesters and esters[156]:

$$RC(=NF)NF_2 \xrightarrow{EtONa,EtOH} RC(=NF)OEt + RCOOEt .$$

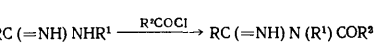
When amidines react with fairly strong C-acids, salts are formed[157]. The reaction is of first order with respect to both components. However, when the deutero-analogue of the C-acid instead of the C-acid itself is introduced into the reaction, complex kinetics, induced by numerous isotope exchange processes, are observed[157]. The exchange reactions involving imidoylamidines (LXXI) have been investigated by ^{19}F NMR,[158,159] for example:



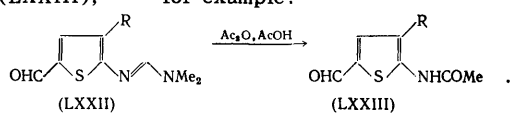
Among the reactions of amidines with electrophiles investigated in recent years, we may mention in the first place fluorination, which occurs mainly with formation of *N,N,N'*-trifluoro-derivatives[160], although in some cases products of the addition of fluorine to the C=N bond have also been isolated[160]:



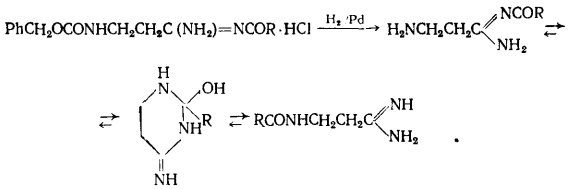
A series of investigations of the acylation of amidines have been made. *N*-Monosubstituted amidines are acylated by acyl chlorides at the substituted nitrogen atom[161]:



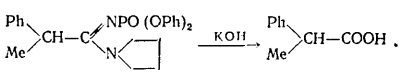
The acylation of *N*-heteroaryl-*N,N'*-dimethylformamidines (LXII) results in the formation of the corresonding acylamides (LXXIII), [42,162] for example:



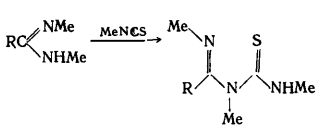
The acylation of compounds containing simultaneously the amino- and amidino-groups has been studied and an analytical method has been developed whereby it is possible to determine the position of the acyl group[163]. The observation[163] that the acyl group is transferred in acylaminoamidines is extremely interesting:



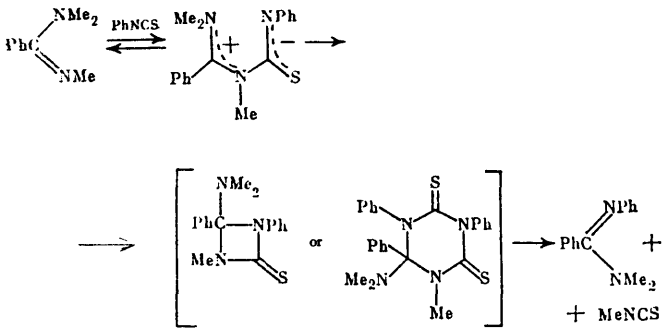
The acylation of *N*-dichlorophosphonylamidines by acyl chlorides takes place at the unsubstituted nitrogen atom[94]. Compounds substituted at a nitrogen atom by the $PO(OEt)_2$, PCl_3, and PCl_4 groups have also been synthesised by the reaction of amidines with triethyl phosphite[164] and phosphorus pentachloride[165,166]. Amidines substituted at a nitrogen atom by the phosphoric acid residue have served as starting materials in a new synthesis of substituted acetic acids[167]:



The interaction of amidines with alkyl isothiocyanates results in the formation of *N*-thiocarbamoylamidines[168,169]:



On the other hand, the exchange reaction



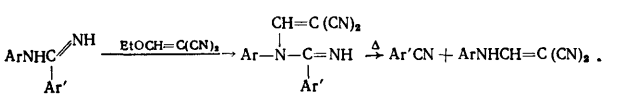
takes place when *N, N, N'*-trisubstituted amidines interact with aryl isothiocyanates[170]. The hypothesis of stringent steric requirements which must be met by the transition state is confirmed by the high negative entropy of activation (−36.1 e.u.).[170]

The study of the synthesis of fluorinated imidoylamidines by the reaction of amidines with nitriles is closely related to the above investigations[171]:

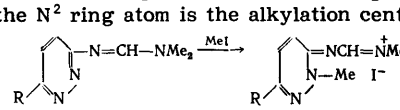


where R_F and R_F^1 are fluorinated groups. It is noteworthy that this reaction is extremely sensitive to the steric factor and that its rate decreases sharply with increase in the bulk of R_F^1.[171]

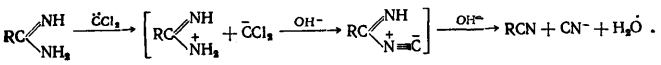
In a few studies of the alkylation of amidines having the NH group it has been shown that the reaction usually proceeds fairly smoothly. This is observed in the interaction of amidines with propiolic acid ester[172], alkyl halides[173] (in the latter case lithium salts of amidines have also been used), and ethoxymethylenemalononitrile[172,174]. We may note that the enamidines thus formed are cleaved to enamines and nitriles on heating[174]:



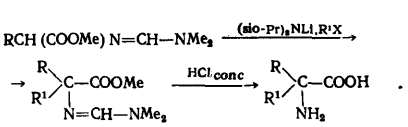
The alkylation of *N,N*-dimethyl-*N'*-(3-pyridazinyl)formamidine by methyl iodide takes place in an interesting manner—in this case the N^2 ring atom is the alkylation centre[150]:



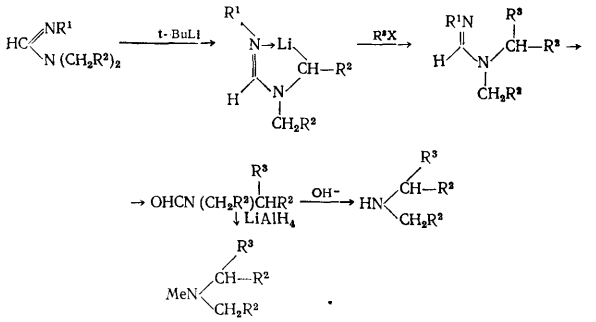
Dichlorocarbene also attacks amidines at the unsubstituted nitrogen atom—the final result of the reaction (appearing under the conditions of phase-transfer catalysis) is a nitrile and a cyanide ion[175]:



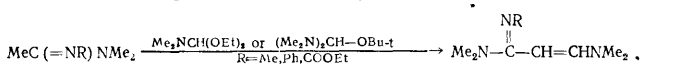
A new method of synthesis of α-substituted aminoacids based on the alkylation of *N,N,N'*-trisubstituted amidines has been published recently[45]:



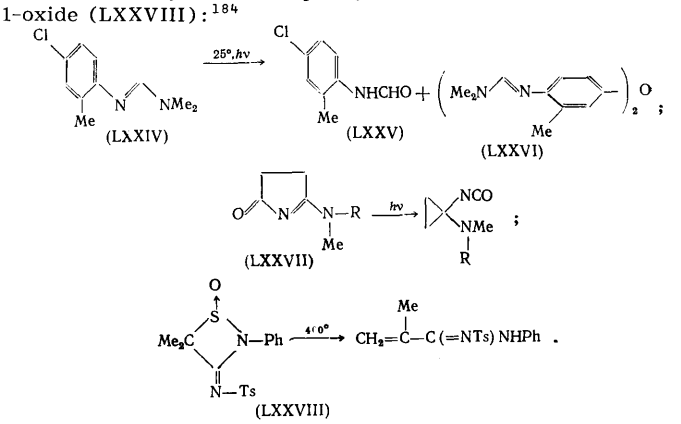
A new method of synthesis of α-substituted amines is also based on an analogous principle[176]:



In the studies of the reactions of amidines with electrophiles discussed above, the process involved either a nitrogen atom or a carbon atom of an alkyl group attached to a nitrogen atom. The possibility of the substitution of the protons of the methyl (methylene) group attached to the amidine meso-carbon atom† follows from a comparison of the electron-accepting influences of the iminoester and amidine functional groups[177]. The ability of amidines of type (LX) (see Section III above) to react with electrophiles at the α-$CH_3(CH_2)$ groups was first demonstrated in relation to the deuterium exchange reaction[177]. It was established that compounds (LX) exchange the ring α-protons for deuterons under mild conditions (CD_3OD, 20 °C) and that the exchange is accelerated in the presence of acid and basic catalysts[177]. The ring α-protons of enamidines (XXXI) (see Section II above) are also exchanged for deuterium albeit under more severe conditions[60]. A series of studies demonstrating that amide acetals and aminal-esters are capable of condensing via the methyl (methylene) group attached to the amidine meso-carbon atom have been published recently[46,52]:



In conclusion of this section, we may point to studies of the photolysis of *N*-(*p*-chloro-*o*-methylphenyl)-*N'*,*N'*-dimethylformamidine (LXXIV), which is converted into the corresponding formyl derivative (LXXV) and the bisamidinoester (LXXVI) on ultraviolet irradiation in water[182], the photochemical rearrangement of the cyclic amidine (LXXVII),[183] and the thermolysis of 3-sulphonylimino-1,2-thiazetidine 1-oxide (LXXVIII):[184]

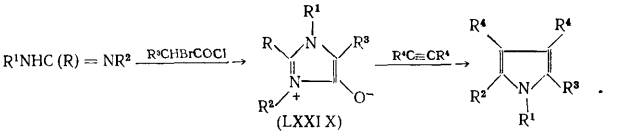


†This principle of the introduction of substituents into the α-$CH_3(CH_2)$ group, called the "principle of potential enaminisation", was also used in the study of the reactions of amide and lactam acetals and also various types of enamines with electrophiles and proved to be the most effective when applied in heterocyclic synthesis (see, for example, Refs.178–181).

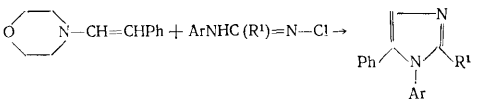
2. Heterocyclisation Reactions

The synthesis of heterocycles using amidines is also based on their reactions with electrophiles or nucleophiles. However, bearing in mind the importance of this field of study, we thought it useful to consider the heterocyclisation reactions separately in their own section of the review.

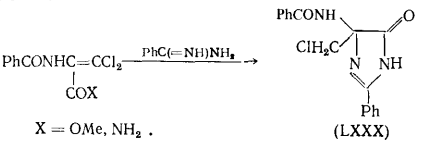
Amidines have been the starting materials for the synthesis of a large group of five-membered heterocycles. Thus 2-dialkylamidino-2,4,5-triphenyl-2,3-dihydro-3-pyrrolones have been synthesised by the reaction of *N*,*N*-dialkylbenzamidines with diphenylcyclopropenone[185]. A number of studies have been made on the synthesis of the mesoionic compounds (LXXIX), which are converted into pyrroles on treatment with acetylenic derivatives[186–188]:



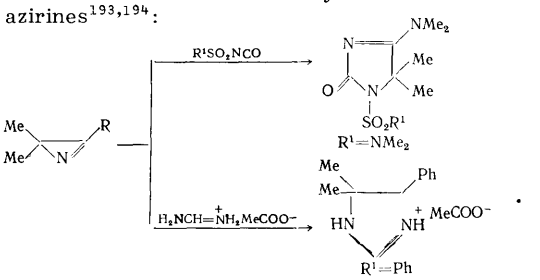
When tertiary enamines react with *N*-chloroamidines, imidazole derivatives are formed[189–191]:



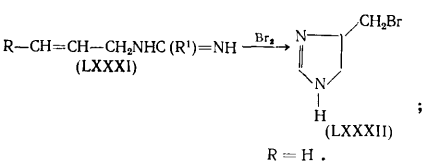
The imidazolones (LXXX) have been obtained by the reaction of α-carbamoyl (or ethoxycarbonyl)-β,β-dichloroenamides with amidines[192]:



Imidazole derivatives have also been synthesised from substituted azirines[193,194]:

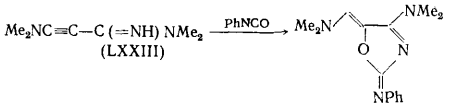


It has been established recently that the amidines (LXXXI), having an unsaturated group in the side chain, can be converted into the imidazolines (LXXXII):[195]

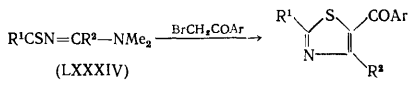


We may note that, when R = Ph in compound (LXXXI), tetrahydropyrimidine derivatives are formed[195].

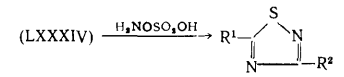
The reaction of ynaminoamidines (LXXXIII) with carbon dioxide or phenyl isocyanate has been used to synthesise oxazole derivatives[53]:



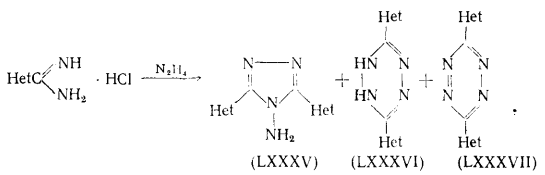
A preparatively convenient method of synthesis of substituted thiazoles is based on the reaction of thioacylamidines (LXXXIV) with α-bromoketones[196,197]:



The amidines (LXXXIV) are also used to synthesise thiadiazoles[48]:



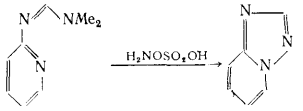
The same principle has been applied in the synthesis of triazole[47,52] and oxadiazole[47] derivatives: in these cases *N*-acylamidines[47] or *N*-ethoxycarbonylamidines[52] were made to react with hydrazine[47,52] and hydroxylamine[47]. An interesting synthesis of *N*-aminotetrazoles (LXXXV) and the tetrazines (LXXXVI) and (LXXXVII) is based on the interaction of heteroarylamidines with hydrazine[198]:



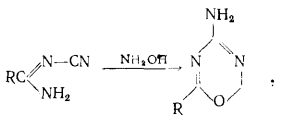
(LXXXV) (LXXXVI) (LXXXVII)

where Het = 2-furyl, 2-thienyl, 3-furyl, 3-thienyl, 2-selenophenyl, or 3-selenophenyl.

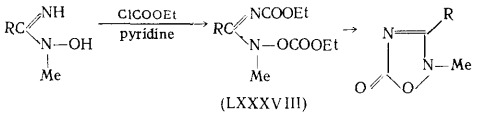
A new synthesis of condensed triazoles from *N*-(2-pyridyl)- and *N*-(1-isoquinolinyl)-formamidines has been published recently[199]:



N-Hydroxy- and *N*-cyano-amidines have been used in the synthesis of oxadiazoles[200]: in the former case amidines are made to react with bromocyanogen or trichloroacetic anhydride and in the latter with hydroxylamine:

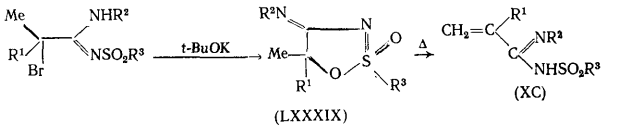


Another method of synthesis of oxadiazoles from *N*-hydroxyamidines consists in their interaction with chlorocarbonic ester and subsequent intramolecular cyclisation of the intermediate *O*,*N*-bisacyl derivative (LXXXVIII):[201]



(LXXXVIII)

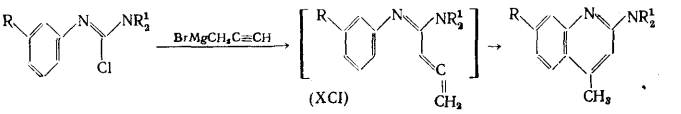
The conversion of α-bromo-*N*-sulphonylamidines into oxaisothiazolines (LXXXIX), which isomerise on heating to the enamidines (XC), has also been described[202]:



(LXXXIX) (XC)

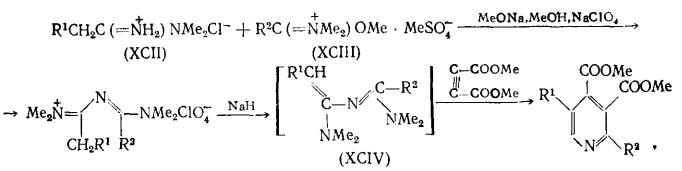
The employment of amidines in the synthesis of various six-membered, particularly pyridine, pyrimidine, and triazine, systems is even more promising.

The closure of the pyridine ring was achieved on reaction of chloroformamidines with ethynylmagnesium bromide or propargylmagnesium bromide[155]. In the latter case the process apparently proceeds via the intermediate formation of the allene (XCI):



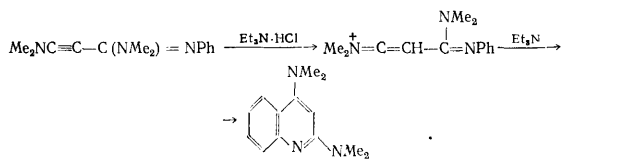
(XCI)

The reaction of the amidine salt (XCII) with the methyl sulphate complex (XCIII), followed by treatment of the intermediate enaminoamidine (XCIV) with acetylenedicarboxylic ester, also leads to the formation of a pyridine derivative[203]:

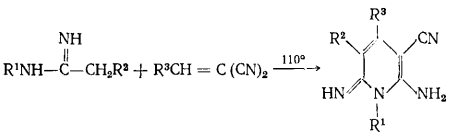


(XCII) (XCIII) (XCIV)

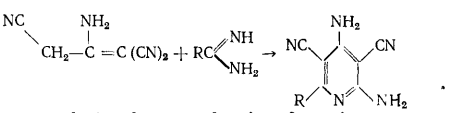
It has likewise been shown that the presence of the triple bond in the substituent at the meso-carbon atom of the amidine also makes it possible to achieve intramolecular cyclisation with formation of quinoline derivatives[204]:



A number of studies have been devoted to the synthesis of pyridines by the reactions of amidines with ylidenemalononitriles[205,206]:

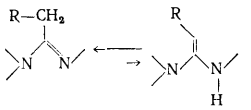


A reaction of a similar type also takes place between formamidine or acetamidine and the malononitrile dimer—in this case tetra- or penta-substituted pyridines are also formed[42]:

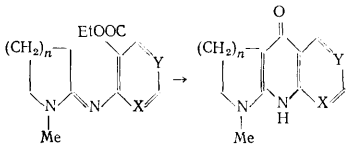


Another approach to the synthesis of various types of pyridine-containing heterocycles is based on the principle of potential "enaminisation" mentioned above (Section IV, subsection 1). The significance of this principle consists in the fact that the protons of the $CH_2(CH_3)$ groups attached to the amidine *meso*-carbon atom are fairly acidic and under certain conditions can be split off, creating thereby the basis for electrophilic substitution, for example, for deuterium exchange (see Section IV, subsection 1) or intramolecular cyclisations. There is then a possibility of the intermediate formation of enamines, although their appearance has not been detected experimentally#:

#In the study of the synthesis of pyridazines, definite evidence has been obtained quite recently in support of the occurrence of such amidine–enediamine tautomeric equilibrium (see below).

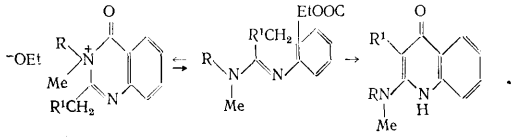


A number of syntheses of 4-pyridones, 4-quinolones and derivatives of pyrrolo-, pyrido-, and azepino-quinolines, pyrrolo-, pyrido-, and azepino-naphthyridines, and pyrrolo-, pyrido-, and azepino-pyrido[2,3-*d*]pyrimidines have been achieved using this approach[60,207-212]:

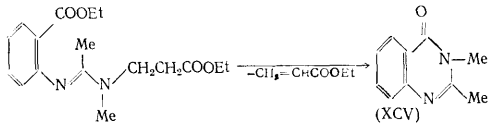


X=Y=CH; X=N, Y=CH, X=Y=N.

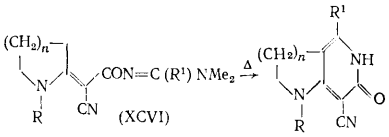
Reversible cyclisation at a nitrogen atom of the amidine system apparently takes place initially and the equilibrium is then displaced to the right as a result of the irreversible formation of a pyridone:



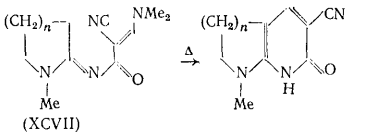
This hypothesis has been confirmed by the observation[209] that, when the substituent R can be split off in the form of a stable molecule, the only reaction product formed is a quinazolone derivative (XCV):[209]



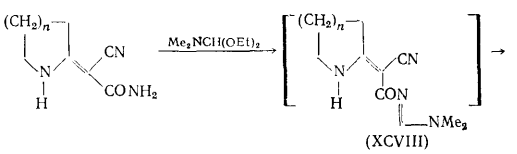
Enaminoacylamidines (XCVI) and (XCVII) proved to be an extremely promising class of compounds for the synthesis of various condensed pyridines[213-218]:



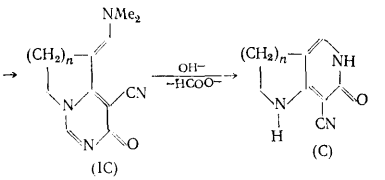
R=Me, $PhCH_2$, R¹=H, Me



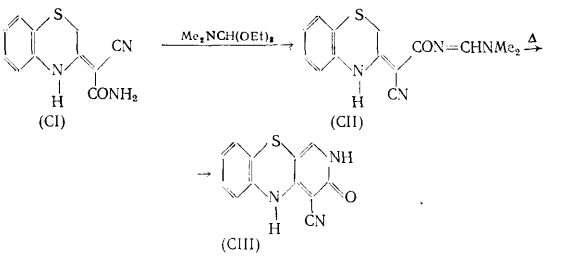
A study of the kinetics of both types of reaction showed that the rate of cyclisation is many times higher for compounds (XCVI) than for compounds (XCVII),[216] which corresponds to a more effective delocalisation of the positive charge in the amidine system compared with the enamine system. Enaminoacylamidines (XCVIII) are intermediates also in a new pyrimidine synthesis[215,217,219-223]:



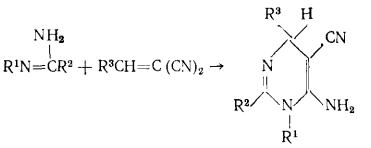
(XCVIII)



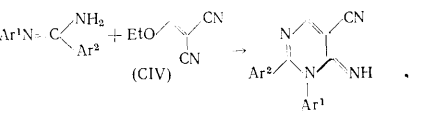
It is of interest that condensed pyrimidines (XCIV) behave similarly to cyclic amidines (see Section IV, subsection 1) and readily hydrolyse in an alkaline medium with elimination of formic acid[219,220] and recyclisation to 2-pyridone derivatives (C).[217,219-222] When the enaminoamide (CI) obtained from 2-benzothiazinone was used in the reaction, it was found that the intermediate acylamidine (CII) cyclises on heating to pyridobenzothiazine (CIII) and not to a pyrimidine derivative[223]:



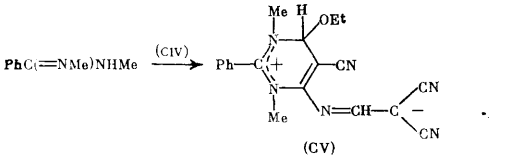
Pyrimidine derivatives are formed smoothly on interaction of amidines with various three-carbon components, such as dicarbonyl[224] and enaminocarbonyl[225,226] compounds as well as acetylenedicarboxylic ester[64]. Substituted pyrimidines are also formed when amidines react with various derivatives of 4-benzopyrone[227-229] or pyrylium salts[230]§. The reaction of amidines with ylidenemalononitriles leads to dihydropyrimidines[232,233]:



It has been shown[174] that the reaction of amidines having a primary amino-group with ethoxymethylenemalononitrile (CIV) takes place in the usual manner with formation of 4-iminopyrimidines:



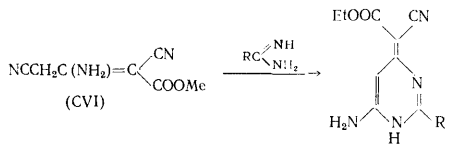
However, compound (CIV) reacts differently with *N*,*N'*-disubstituted amidines and the reaction product is in this case the zwitterionic 1:2 adduct (CV):[172]



(CV)

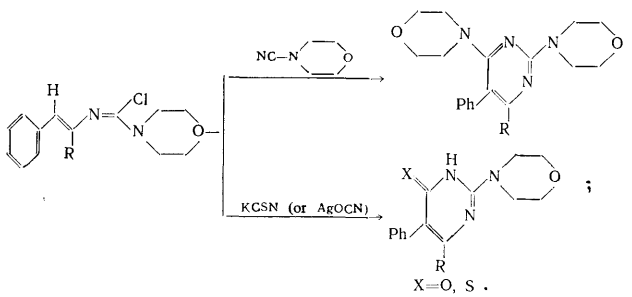
§For a review of the transformations of oxygen-containing rings into pyrimidines under the influence of amidines (and guanidines), see Takagi and Hubert-Hebart[231].

The interaction of the codimer of malononitrile and cyanoacetic ester (CVI) with benzamidines and acetamidines (but not with formamidine—pyridines are formed in this instance) leads to derivatives of 4-methylenepyrimidine (CVII):[42]



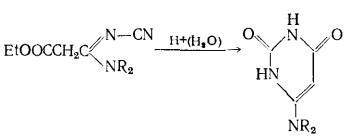
(CVI) (CVII)

Substituted chloroformamidines can be used successfully to synthesise substituted pyrimidine derivatives[234]. For this purpose, they are made to react with derivatives of cyanamide, silver isocyanate, or potassium isothiocyanate:

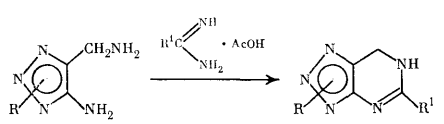


X=O, S.

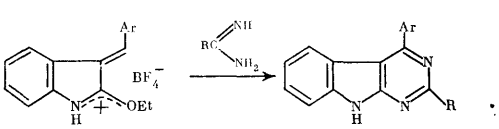
The salts of enaminoamidines can also serve as a source of pyrimidines, both directly (via their reaction with amidines[6]) and after their conversion into enaminoamidines of type (XCIV) (see above) followed by treatment with phenyl isothiocyanate[203]. A new synthesis of pyrimidine-2,4-diones by the intramolecular cyclisation of *N*-cyanoamidines has been published recently[235]:



Certain amidines have been used recently[236] as single-carbon components in the synthesis of condensed pyrimidines:

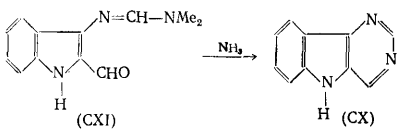


The presence of the amidine and carbamide functional groups in neighbouring positions ensures the possibility of the closure of the pyrimidine ring on interaction with formamide[237]. Pyrimidoindoles (CVIII) have been synthesised successfully by the reaction of amidines with tetrafluoroborate complexes (CIX):[238,239]



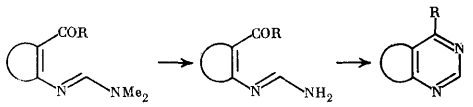
(CIX) (CVIII)

Pyrimidoindoles of another type (CX) have been synthesised by the reaction of the indolylamidine (CXI) with ammonia, primary amines, and hydroxylamine[240], for example:

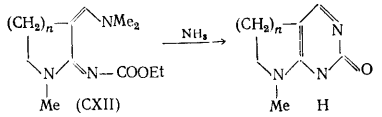


(CXI) (CX)

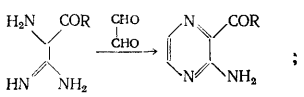
The first stage in pyrimidine synthesis of this type is usually transamination with subsequent cyclisation involving the participation of the adjacent carbonyl-containing group:



Anthrapyrimidines[151], pyrazolopyrimidines[152], and pyridopyrimidines[211] have been obtained by this method. A new synthesis of pyrimidines and derivatives of pyrrolo-, pyrido-, and azepino-[2,3-*d*]pyrimidines is based on the reaction of enaminoamidines of type (CXII) with ammonia[52]:



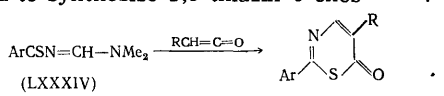
The aminoamidines (CXIII) have proved to be convenient starting materials for the synthesis of 2-amino-3-ethoxycarbonylpyrazines—important intermediates in the synthesis of pteridines[241,242].



(CXIII)

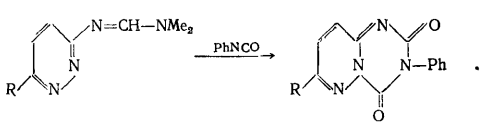
R=OEt, NH_2.

The *N*-thioacylamidines (LXXXIV) already mentioned above have been used to synthesise 1,3-thiazin-6-ones[197,243]:

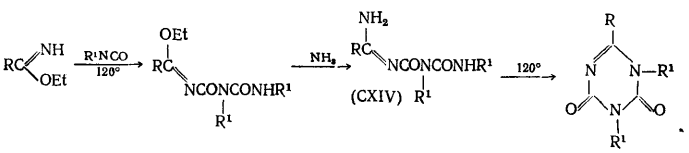


(LXXXIV)

Numerous studies have been devoted to the synthesis of triazine derivatives from amidines. The main bulk of these syntheses are associated with the use of various isocyanates and isothiocyanates, for example, phenyl isocyanates, as the second reaction component[150,244]—in these cases *N*-heteroarylamidines were introduced into the reaction:

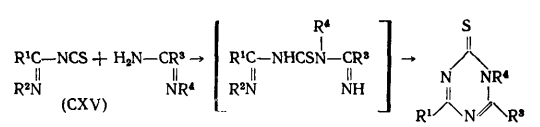


[1,2]-Adducts (triazinediones or triazinedithiones) are also formed when amidines react with benzenesulphonyl isocyanate[168] or methyl isothiocyanate[168,169]. The study of the synthesis of triazine derivatives by the intramolecular cyclisation of the amidine (CXIV), obtained by treating the corresponding iminoester with R^1CNO and then with ammonia[245], is related to these investigations:



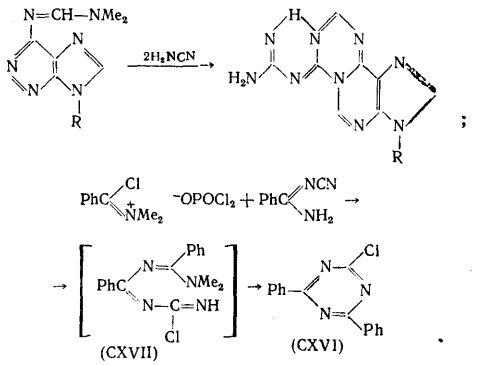
(CXIV)

sym-Triazinethiones have also been obtained by the reaction of iminoisothiocyanates (CXV) with amidines[246,247]:



(CXV)

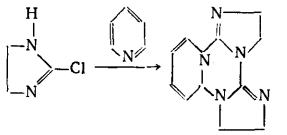
The reactions of amidines with cyanamide[43] and the reaction of *N*-cyanoamidines and complexes of amides with phosphoryl chloride[248] belong to another class of methods of synthesis of triazines:



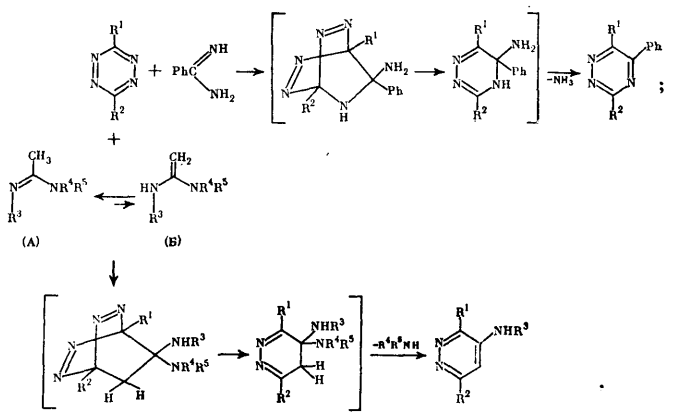
(CXVII) (CXVI)

The author does not explain why chlorotriazine (CXVI) is formed, but one can suppose that the intermediate chloroimide (CXVII) cyclises.

The triazine ring is also formed in the reaction of cyclic chloroformamidines with pyridine or quinoline[249]:

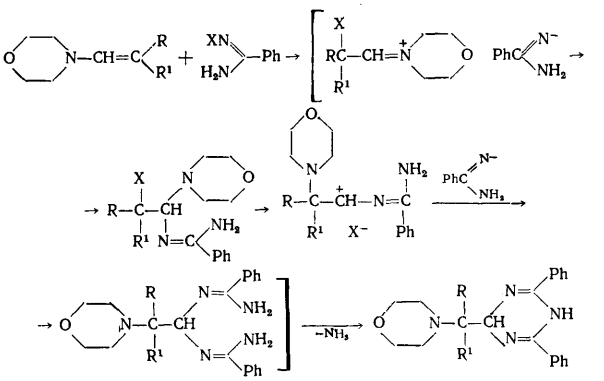


Amidines behave as dienophiles in reactions with tetrazines, which result in the formation of 1,2,4-triazines[250]. It is significant that, when *N*,*N*,*N'*-trisubstituted amidines are made to undergo an analogous reaction, pyridazines are produced[251]. The authors believe that this process is a consequence of the amidine–enediamine equilibrium (A ⇌ B) [215] (see also above):

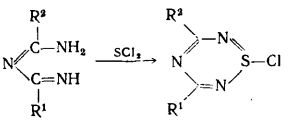


(A) (Б)

Finally we may note the interesting reaction of *N*-halogenoamidines with enamines via the mechanism[252]



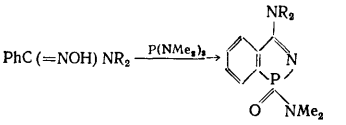
The 1,2,4,6-thiatriazine derivative (CXVIII) has been obtained by the reaction of imidoylamidines with sulphur dichloride[253]:



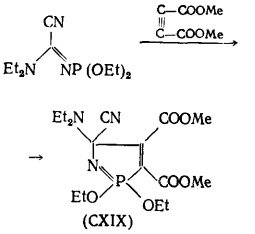
(CXVIII)

If *N*-arylamidines are introduced into a reaction of this kind, derivatives of 4-chloro-4-thiaquinazolines are formed[254].

In conclusion of this section, we may note studies devoted to the synthesis of phosphorus- and boron-containing heterocycles. The largest number of such studies have been made on phosphatriazines, which have been obtained by the reaction of *N*-cyanoamidines[255] or *N*-imidoylamidines[256] with phosphorus pentachloride, of trichlorophosphazo-compounds with amidines or *N*-dichlorophosphonylamidines[94], and also of *N*-hydroxyamidines with phosphines[257]. The last reaction involves *N*-hydroxyamidines unsubstituted at the second nitrogen atom. The reaction of the *N*-substituted compounds proceeds differently and a five-membered and not six-membered ring is formed[257]:

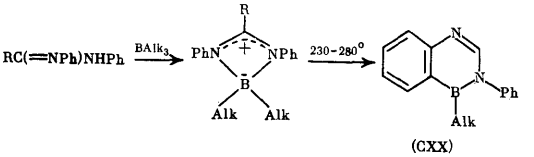


Phosphorus-containing amidines have been used in the synthesis of derivatives of azaphospholes (CXIX):[166]



(CXIX)

Since the review mentioned above[7] was devoted to boramidines, we shall mention only one recently published study on the synthesis of boraquinazolines (CXX):[258]



(CXX)

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This review has dealt with the literature data on the chemistry of amidines and was not concerned with the results of studies on related systems, such as those comprising derivatives of guanidine, *O*- and *S*-substituted ureas, and thioureas. Only in a few instances does the review deal with the chemistry of amidinium salts, because a series of recently published reviews have described their properties[6,259]. Examination of data on the above types of compounds together with those on the chemistry of amidines is hardly possible within the framework of a single article.

Summarising the literature data, one may claim that the development of the chemistry of amidines has been responsible for the development of various fields of organic chemistry, in the first place the chemistry of heterocycles, and has proved extremely fruitful in both theoretical and practical respects.

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