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The Reactions of Compounds with Halogenoimidoyl Groups

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New data on the reactions of compounds of different classes containing the halogenoimidoyl group -N = C-Hal, including the reactions of both the halogen atom and the N = C bond, are surveyed.
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I. INTRODUCTION

The reactions of compounds with halogenoimidoyl groups $-N=\overset{|}{C}-Hal$ are extremely varied. The high mobility of their halogen atom and the ability of the N=C bond to enter into various reactions determine the possibility of using these compounds as precursors of derivatives of almost any type, including heterocyclic compounds. The ability to serve as sources of reactive intermediate ions extends still further their synthetic possibilities. It is therefore not surprising that reviews and monographs have been devoted to the study of these reactions.[1-3] However, after 1970, data for only individual types of compounds, in particular imidoyl fluorides and difluorides as well as fluorinated imidoyl halides,[4-6] hydrazonohalides, and halogenoazines[7-9] have been treated systematically. Some information about other compounds with halogenoimidoyl groups can be found in a series of comparatively recently published monographs[10-14] and reviews (1971–1973),[15-17] but they are not complete.

It appeared useful to give a systematic account of the extensive data on the reactions of compounds with the $-N=\overset{|}{C}-Hal$ groups published after 1970 and not included in the publications quoted above. This attempt was made in the present review. Bearing in mind the available review articles on the reactions of imidoyl difluorides and fluorides, only new data obtained in recent years are included. In the case of hydrazonohalides and halogenoazines, attention has been concentrated on studies after 1974 and 1977 respectively. Only a few examples of the reactions of compounds in which the halogenoimidyl group enters into the composition of a heterocycle or is attached to a heterocycle are presented. All the information about the reactivity of compounds with halogenoimidoyl groups has been divided into three groups corresponding to three main types of reactions: nucleophilic substitution reactions at the N=C bond, elimination reactions, and addition reactions. A common feature of these reactions is that they frequently do not stop after the formation of the primary products but proceed further and lead to a wide variety of final compounds, including heterocyclic derivatives.

Only the chemical reactions of compounds with halogenoimidoyl groups are considered in this review. New data on some of their other properties can be found in other publications: ^{13}C and ^{15}N NMR spectra,[18-20] IR and Raman spectra,[10] data on the dipole moments, configurations, and conformations,[10,21-24] and quantum-chemical calculations.[10,25-28]

II. NUCLEOPHILIC SUBSTITUTION AT THE N=C BOND

In terms of its properties (bond length and bond energy, dipole moment), the N=C bond occupies an intermediate position between the C=O and C=C bonds. The reactions with nucleophiles have been investigated fairly adequately for activated vinyl halides and acyl halides, but simple azomethine systems have been investigated to a much lesser extent. However, by analogy with nucleophilic reactions of the C=O and C=C bonds, one can assume that nucleophilic attack on the N=C bond should lead to the formation of an anion or zwitter-ion, which can subsequently give rise to substitution, addition, and cleavage products. In halogenoimidoyl compounds there is in addition the possibility of the dissociation of the C–Hal bond and the formation of cationoid intermediates, which are also capable of undergoing various reactions.

1. Reactions with O-Nucleophiles

(a) Hydrolysis

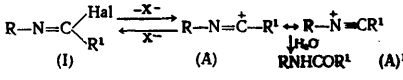
The hydrolysis of imidoyl halides with formation of amides is characteristic of compounds of this class.[29-39] Many imidoyl halides are extremely sensitive even to atmospheric moisture, as a result of which their isolation in a pure form is difficult and their formation in the course of reaction is inferred from the amide isolated. On the other hand, a convenient preparative method of synthesis of amides has been based on this finding.[40] However, this mode of the reaction is not unique. Thus the products of the hydrolysis of chloroformamidines are the corresponding ureas.[34,41-44] The hydrolysis of *N*- arylchloroformimidates or the corresponding chlorothioformimidates can lead to carbamates or their decomposition products—anilines, hydroxy-derivatives, and CO_2.[34] The hydrolysis of *N*-arylcarboimidoyl dichlorides takes place with formation of amino-derivatives of carbamates.[45] 4-Aminotetrachloropyridine is the only product of the acid hydrolysis of *N*-(2,3,5,6-tetrachloro-4-pyridyl)carboimidoyl dichloride.[46] *N*-(trichloromethyl)carboimidoyl dichloride reacts with water vigorously in a solvent or on heating until the decomposition is complete.[15]

At the same time, the reactions of imidoyl halides with water do not always take place readily. Thus certain *N*-(pentafluorothio)chloroformimidates and the corresponding chloroformamidines proved to be fairly resistant to hydrolysis.[47] *N*-(Pentafluorophenyl)halogenoacetimidoyl chlorides

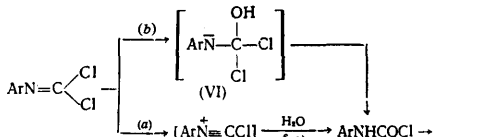
hardly interact with water even on being boiled.[37] Perfluoroalkylimidoyl iodides also do not hydrolyse under mild conditions.[48] Their conversion into the corresponding amides requires refluxing with 20% hydrochloric acid.

The hydrolysis of halogenoazines can afford various products, including ylidene hydrazides and heterocyclic derivatives, depending on their structure and the hydrolysis conditions.[8,49-52] On treatment with water, hydrazonohalides are converted into the corresponding hydrazides of cyclic products.[7,53-60]

The mechanism of the hydrolysis of compounds with halogenoimidoyl groups has so far been studied fairly completely. Kinetic studies on imidoyl chlorides and dichlorides,[34,45,61] halogenoazines,[8,51,62] and hydrazonohalides[8,55-58] have shown that the unimolecular S_N1 mechanism with the dissociation of the C–Hal bond as the rate-determining stage is most characteristic of the hydrolysis of these compounds. The nitrilium ion (A), for which the contribution by the octet resonance structure (A)[1] predominates, is then formed as an intermediate:

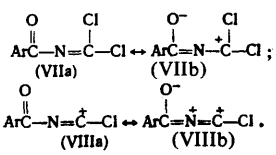


However, this mechanism is not unique and can vary depending on the structure of the substrate, the reagent, and the medium. Thus the hydrolysis of *N*-arylcarboimidoyl dichlorides (I, R = Ar, R^1 = Cl) in solution in the 1:4 dioxan–water mixture at 25 °C and a pH of the medium up to approximately 12 is characterised by the Hammett constant $\rho = -2.30$, which indicates the operation of the S_N1 mechanism via the intermediate nitrilium ion (II) (pathway *a*):



This results in the formation of the carbamoyl chloride (III), which is rapidly converted into the isocyanate (IV). The addition of water to the latter and the decomposition of the resulting carbamate (V) gives rise to the observed reaction products.[45] As the concentration of OH^- ions increases, there is a direct attack by the hydroxyl on the substrate (pathway *b*) with formation of the tetrahedral intermediate of type (VI) (S_N2 mechanism, $\rho = +1.26$). The observed influence of the substituents in the arene ring on the rate of hydrolysis confirms the above findings.

The hydrolysis of *N*-aroylcarboimidoyl dichlorides (I, R = COAr, R^1 = Cl) takes place 10^3 times faster under similar conditions, although the rate via the S_N1 mechanism diminishes by a factor of 10^6. Only the bimolecular mechanism operates. The observed facts can be accounted for by the greatest sensitivity of *N*-aroylcarboimidoyl dichlorides to nucleophilic attack [see the structure (VIIb)] and also by the stabilisation of their negative charge adjoining the carbonyl group in the type (VI) intermediate and the destabilisation of the nitrilium ion postulated for the S_N1 mechanism [see the structure (VIIIb)]:[45]

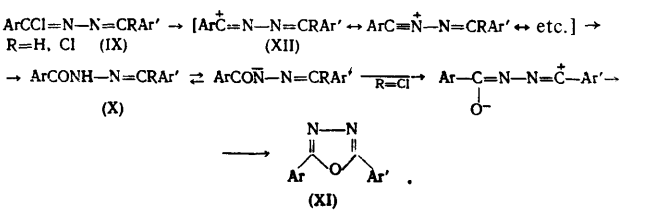


In aqueous dioxan, the hydrolysis of *N*-aryl- and *N*-aroylbenzimidoyl chlorides in the corresponding chlorothioimidates and chloroformamidines (I, R = Ar or COAr, R′ = Ar′, SAr′, or NMeAr′, Hal = Cl) proceeds via the S_N1 mechanism. Under these conditions, *N*-arylimidoyl chlorides are 10^6 times more reactive. On the other hand, the bimolecular mechanism of the hydrolysis reaction is more characteristic of the corresponding chloroformimidates (I, R = Ar or COAr, R′ = OAr′, Hal = Cl) under similar conditions.[35,45] The tendency of *N*-arylchloroformimidates to hydrolyse via the S_N2 mechanism, in contrast to other *N*-arylimidoyl chlorides, is attributed to the influence of substituents at the imidoyl carbon atom on the formation and stabilisation of the developing carbonium centre, which varies in the sequence Ar > NMeAr > SAr > OAr. Compared with the sulphur atom, the oxygen atom stabilises the carbonium centre to a lesser extent owing to the mesomeric effect and destabilises it more because of the greater negative inductive effect. In all cases, the degree of cooperation with the formation of the carbonium centre as a result of the delocalisation of the positive charge is greater for the aromatic ring linked to the nitrogen atom than for that linked to the carbon atom, because the contribution of the octet resonance structure to the nitrilium ion predominates.

The S_N1 mechanism has been established for the hydrolysis in aqueous dioxan of the isomeric (*Z*)- and (*E*)-*O*-methylbenzohydroximoyl halides,[33] the (*Z*)-isomers hydrolysing almost 470 times faster than the (*E*)-isomers. This shows that the free electron pair at the nitrogen atom should be preferentially in the *trans*-position with respect to the leaving group in the formation of the intermediate nitrilium ion. The nature of this group affects the rate of hydrolysis. For bromine, the rate is much higher than for chlorine, which also confirms the S_N1 mechanism.

Compared with *N*-arylimidoyl halides, *O*-methylbenzohydroximoyl halides hydrolyse with more difficulty (at 120 °C compared with room temperature for imidoyl halides), which can be explained by the destabilisation of the intermediate nitrilium ion by the electronegative methoxy-group at the nitrogen atom.

It follows from kinetic data for the hydrolysis in an aqueous organic medium of halogenoimidoyl groups in halogenoazines[8,50,51] that for compounds of this type the mechanism can change, as for imidoyl halides, from the dissociative S_N1 mechanism to the associative S_N2 mechanism depending on the structure of the substrate and the medium. For example 1,4-diaryl-1-chloro, and 1,4-diaryl-1,4-dichloro-2,3-diazabuta-1,3-dienes (IX, R = H or Cl) are converted respectively into the hydrazides (X) and the oxadiazoles (XI) in aqueous dioxan; a similar slow stage, involving the unimolecular cleavage of the C–Cl bond and the formation of the stabilised nitrilium ion (XII), has been observed for compounds of both series:



In basic media, compounds of both series are subjected to direct S_N2 attack by hydroxide, but only provided that electron-accepting substituents are present in the arene rings. In other cases, the rate of reaction falls with increase in the concentration of OH^- ions.[50]

In the series of hydrazonohalides, studies have been made of the kinetics of the hydrolysis in an aqueous organic medium of *N*-arylhydrazonobromides[55-57] and *N*-amidinohydrazonobromides,[58] including those with the amidine group as part of the composition of the heterocycle.[59,60] It was shown that, as a rule, the hydrolysis proceeds in accordance with the S_N1 mechanism via the nitrilium ion (XIII):

$$R\overset{+}{C}{=}N{-}NR^1R^2 \longleftrightarrow RC{\equiv}\overset{+}{N}{-}NR^1R^2 \quad (XIII)$$

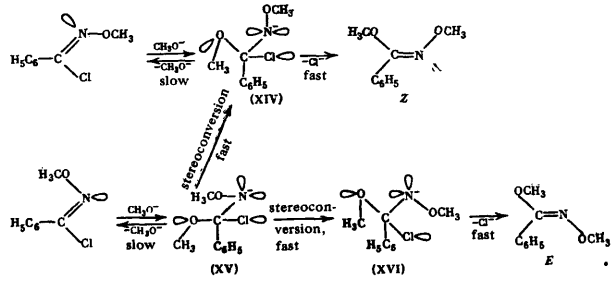
Electron-donating substituents at the imidoyl carbon atom (R) and the hydrazine nitrogen atom (R^1 and R^2) promote the formation of the nitrilium ion. Steric factors are also significant. Thus the rate of hydrolysis of *N*-arylhydrazonobromides with an alkyl group at the imidoyl carbon atom decreases with increase in the bulk of this group.[55] The hydrolysis of the hydrazonobromide group forming part of the composition of a heterocycle is difficult.[56]

(b) Reactions with Alcohols and Phenols

The familiar reaction involving the nucleophilic substitution of the halogen atoms in imidoyl halides and dihalides on treatment with alcohols or alkoxides, leading to the formation of the corresponding imidates, has been extended to new systems.[24,33,47,48,63-72] The interaction of *N*-(perfluoroisopropyl)acetimidoyl chloride with polyfluorinated alcohols has been carried out in the presence of trimethylamine,[66,72] while in the reactions of *N*-(pentafluorophenyl)carboimidoyl dichloride with alcohols and phenols, potassium carbonate has been used as the base.[64] It has been shown in relation to the interaction of *N*-arylbenzimidoyl chlorides and sodium phenoxides that aryl imidates can be obtained in satisfactory yields under the conditions of two-phase catalysis.[73,74] For a description of the reactions of *N*-trichloromethyl)carboimidoyle dichloride with alcohols and phenols, see Findeisen et al.[15]

The substitution of halogens by alkoxy- and aryloxy-groups has also been described for halogenoazines[51] and hydrazonohalides.[62,75-77] The reaction of *N*-arylhydrazonohalides with *o*-aminophenols leads to 1,4-benzoxazine derivatives.[78]

Not only a kinetic but also a stereochemical study has been made on the reactions involving alkoxide substitution at the N=C bond for benzohydroximoyl chlorides[71] and benzohydrazonochlorides,[75] although in many cases the configurational instability of the azomethine systems hinders such study. The reactions of the (*Z*)- and (*E*)-isomeric *O*-methylbenzohydroximoyl chlorides with sodium methoxide in solution in the 10% methanol–90% dimethyl sulphoxide (DMSO) mixture are characterised by the Hammett constant $\rho = 1.90$ and proceed with retention of configuration to the extent of ≥95% for the (*Z*)-isomer and 77–≥95% (depending on the substituents in the arene ring) for the (*E*)-isomer. The $E \rightarrow Z$ isomerisation of the initial chlorides does not then take place. The data obtained agree with a bimolecular mechanism for the addition–elimination reaction, in which the rate-determining stage is nucleophilic attack by the alkoxide ion on the initial chloride with formation of a tetrahedral intermediate:

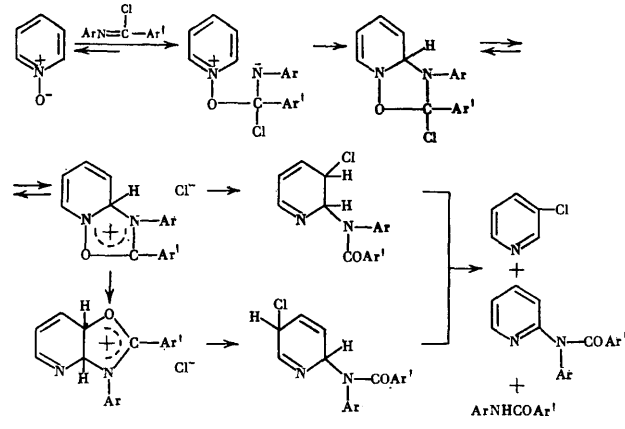


The stereochemistry and the relative rates of the reactions are interpreted in terms of the theory of the stereoelectronic control of the addition and elimination stages.[79] Accordingly, the loss of the chloride ion from the tetrahedral intermediate (XIV) is faster than the elimination of the methoxide ion with conversion into the initial compound or stereoconversion. The stereoconversion to the intermediates (XIV) and (XVI) proceeds more rapidly in the tetrahedral intermediate (XV).

A similar mechanism and stereochemistry have been established also for the reactions of *N*-arylbenzohydrazonohalides with the methoxide ion in methanol.[75]

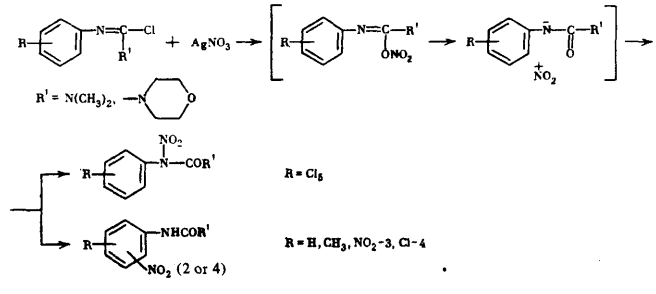
(c) Reactions with *N*-Oxides and Silver Nitrate

The *N*-oxides of nitrogen heterocycles interact with benzimidoyl chlorides to form heterocyclic derivatives containing 2-acylamino-groups, which readily hydrolyse to 2-amino-derivatives without being isolated.[80-83] Apart from the acylamination reaction, the chlorination of the heterocyclic ring and in certain cases the formation of hydroxy-derivatives are observed. In the presence of bases, the yield of the acylamination products increases. The reactions with pyridine *N*-oxides have been most fully investigated.[80,81] One of the reaction schemes is presented below:



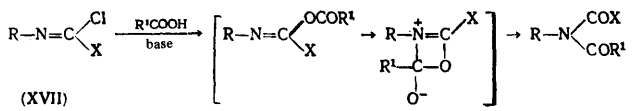
Ar = C_6H_5; Ar' = C_6H_5, $C_6H_4CH_3$-2, -3 and -4 etc.

Nucleophilic attack by the *N*-oxide oxygen on the electrophilic carbon atom of the imidoyl chloride and subsequent intramolecular addition of nitrogen in the 2-position in the pyridine ring leads to the intermediate, 1,2-dihydropyridine, which aromatises or undergoes a successive 1,5-sigmatropic shift and aromatisation. The primary products of the substitution of chlorine by the $-ONO_2$ group rearrange to nitroureas in the reaction of *N*-arylchloroformamidines with silver nitrate:[41]



(d) Reactions with Organic Acids

The reactions of salts of aromatic and aliphatic carxobylic acids or of the acids themselves with benzimidoyl chlorides or aryliminochloromethyl sulphides having the general formula (XVII) in the presence of bases take place via the nucleophilic substitution of the chlorine atom and the subsequent 1,3-migration of the acyl group from the oxygen to the nitrogen atom.[73,84] Satisfactory results have been obtained also under the conditions of two-phase catalysis:



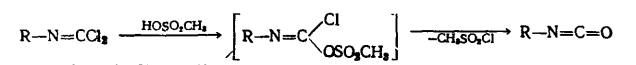
(XVII)

R=Ar, Alk; R'=Ar, Alk; X=C_6H_5, SC(Hal)$_3$

N-(Trichloromethyl)carboimidoyl dichloride reacts with aromatic, aliphatic, alicyclic, and heterocyclic carboxylic acids via the intermediate *N*-(chloroformyl) carboimidoyl dichloride in accordance with the scheme[15]

$$CCl_3{-}N{=}CCl_2 + R{-}COOH \rightarrow RCOCl + CO_2 + ClCN + HCl$$

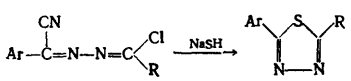
In the reactions involving aliphatic sulphonic acids, the final product is *N*-chloroformyl isocyanate. Isocyanates are obtained also in the reactions of carboimidoyl dichlorides with methanesulphonic acid:[17,85-87]



R=ClCH$_2$, CHCl$_2$, COCl

2. Reactions with *S*-Nucleophiles

The reactions of compounds containing halogenoimidoyl groups with aromatic and aliphatic thiols or their salts take place readily, leading to products of the substitution of the imidoyl halogen atom by a thio-group.[66,68,73,75,88-91] In many instances the reaction does not stop at the thioimidate formation stage and proceeds further, affording cyclisation products, 2,5-Disubstituted 1,3,4-thiadiazoles have been obtained in this way from, for example, 4-chloro-1-cyano-2,3-diazabuta-1,3-dienes:[2]



Ar=C_6H_5, $C_6H_4CH_3$-2, C_6H_4Cl-4; R=CH_3, C_6H_4Cl-2.

N-(Trifluoromethylthio)trifluoroacetimidoyl chloride, having two centres susceptible to nucleophilic attack (the imidoyl carbon atom and the sulphur atom), reacts with thiols as soft nucleophiles exclusively via the sulphenyl sulphur atom (the carbon atom is sensitive to attack by hard nucleophiles).[72]

Among other sulphur-containing reagents, phosphorus pentasulphide has been involved in the reaction, converting *N*-(dichloromethylthio)carboimidoyl dichloride into the corresponding isothiocyanate with a low yield.[93] The reactions of hydrazonohalides with various sulphur-containing reagents have been described by Shawali[9] and Hassaneen et al.[77]

3. Reactions with *N*-Nucleophiles

(a) Reactions with Amines

Primary and secondary amines. The reactions of compounds containing halogenoimidoyl groups with primary and secondary amines lead to the products of successive substitution of the halogen atoms at the imidoyl carbon atom by amino-groups. The compounds then formed are either entirely stable and can be isolated and characterised or they are unstable and undergo various conversions, in particular, carbodiimides or their tautomers (amidonitriles) and heterocyclic derivatives.

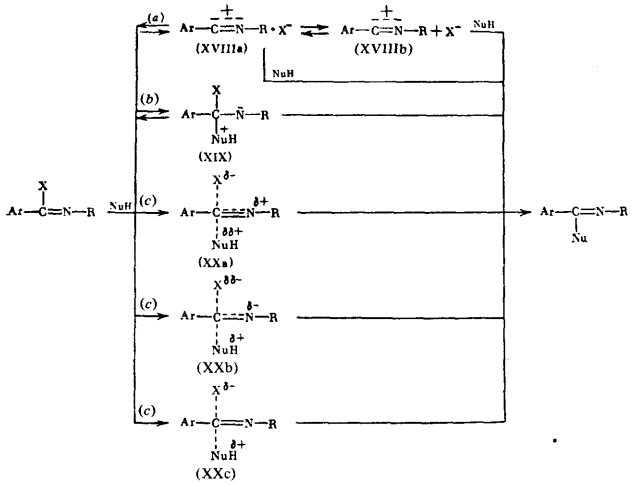
Stable substitution products have been isolated in the reactions of carboimidoyl dihalides,[41,45-97] imidoyl halides[37,48,65,72,95-109] hydrazonohalides,[59,77,91,110,111] and halogenoazines.[8] In certain cases trimethylsilyl derivatives of the amine were used for the reactions.[49,107]

It is noteworthy that, in the reactions of carboimidoyl dichlorides with aromatic amines, it is frequently not possible to obtain the products of the substitution of one chlorine atom and guanidines are formed.[17,46] They are present in the reaction mixture even when the degree of reaction of the initial dichloride is low.

Amidonitriles are formed in the reactions of *N*-(*p*-chlorophenyl)- and *N*-(pentachlorophenyl)-carboimidoyl dichlorides with ammonia.[3] Conversion into a carbodiimide has been noted in the reaction of 2,4,6,6-tetrachloro-1,1,1-trifluoro-2-phenyl-3,5-diazahexa-3,5-diene with t-butylamine. In the analogous reaction with isopropylamine or primary aromatic amines, derivatives of 1,2-dihydro-1,3,5-triazine were obtained.[112] Heterocyclic compounds have also been synthesised from carboimidoyl dichlorides and chlorides by reaction with ethylenediamine,[113] anilines,[15,108,114] and *o*-phenylenediamines[30,94,115-117] and also in the reactions of halogenoazines with amines.[8,35]

Kinetic data have been obtained for the formation of amidines in the reactions of diarylamidoyl halides with aliphatic[100,105,106] and aromatic[98,99] amines in non-aqueous solvents of different polarity and also in the reactions of isomeric *O*-methylbenzohydroximoyl halides with aliphatic amines.[109] Analysis of the influence of the nature of the substituents in the diarylimidoyl halide, the structure and basicity of the amine, the nature of the solvent, salt effects, and the effect of the leaving group and of the activation parameters supports bimolecular nucleophilic substitution at the imidoyl carbon atom with participation of the C=N bond. The substitution takes place via different pathways: (a) the nucleophilic elimination–addition mechanism characterised by negative values of the Hammett constant ρ in which the attack by the nucleophile on the nitrilium cation intermediate (XVIII) formed initially, which can exist either as the ion pair (XVIIIa) [the S_N2(IP) mechanism] or as the ion (XVIIIb) [the $S_N2(C^+)$ mechanism], is rate determining;† (b) the nucleophilic addition–elimination mechanism ($Ad_N - E$ or S_AN) involving the formation of the tetrahedral intermediate (XIX) and characterised by a positive value of ρ; (c) a concerted S_N2 mechanism which is differentiated in terms of the degree of involvement of the C=N bond (in terms of the relative contributions of the degree of dissociation of the C–Hal bond and the degree of formation of the C–Nu bond) into a dissociative bimolecular S_N2 mechanism with a transition state of type (XXa), where the degree of loosening of the C–Hal bond predominates over the degree of formation of the C–Nu bond (negative ρ), an associative mechanism where the opposite relative contributions obtain (the state (XXb), and a mechanism with a symmetrical transition state (XXc) with identical degrees of formation and loosening of the bond.

†The notation S_N2(IP) and $S_C2(C^+)$ represents respectively the ion-pair bimolecular nucleophilic substitution mechanism and the bimolecular nucleophilic subsitution mechanism with participation of the free ion and has been taken from Ta-Shma and Rapport.[105]



Pathways in which base, electrophilic, or bifunctional catalysis by an amine operates are also manifested, but their contribution to the overall process is small.

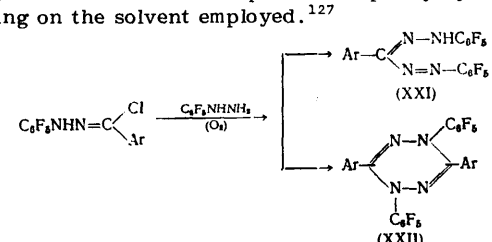
The $S_N2(IP)$ mechanism is preferable for the reactions of imidoyl halides having electron-donating substituents at the nitrogen atom with moderate nucleophiles and in solvents with a high solvating power, the version $S_N2(C^+)$ (pathway *a*) occurring for sterically strained nucleophiles. Pathway *b* is more characteristic of the reactions of substrates with electron-accepting substituents and strong nucleophiles. In intermediate cases, the diminution of the withdrawal of electron density from the azomethine linkage can be accompanied by the simultaneous operation of pathways *a* and *b*. Pathway *c* is less probable, but it cannot be rejected altogether especially since kinetic data do not always permit a clear-cut determination of the mechanism. For example, it is difficult to distinguish pathway *a* and pathway *c* with a transition state of type (XXa).[98]

The (*Z*)-isomers of *O*-methylhydroximoyl halides react with amines via an addition – elimination mechanism, while the (*E*)-isomers do not react.[109]

Tertiary amines are frequently used in the reactions of halogenoimidoyl compounds with nucleophiles in order to bind the HHal evolved or to generate ions (see below). However, instances of the addition of tertiary amines to halogenoimidoyl derivatives with formation of imidoylammonium salts are known. These reactions and their kinetics and mechanisms are described in detail elsewhere.[118–122]

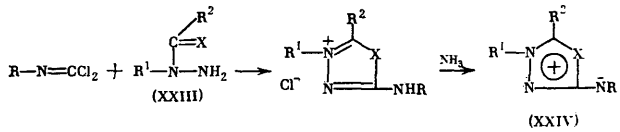
(b) The Reactions with Hydrazines and Their Derivatives

Hydrazines and their derivatives react with compounds containing halogenoimidoyl groups, forming stable primary products of the substitution of the halogen atom by the hydrazine residue[123–126] or the products of their further reactions. Thus mainly formazans (XXI) or tetrazines (XXII) are formed in the reactions of *N*-(pentafluorophenyl)-benzohydrazonochlorides with pentafluorophenylhydrazine depending on the solvent employed.[127]



Ar=C_6H_5, C_6F_5 .

Tetrazines are the products of the reaction of *N*-(arenesulphonyl)carboimidoyl dichloride with methylhydrazine in the presence of methyl orthobenzoate.[128] Substituted 1,2,4-triazoles or 2,5-diaryltetrazoles have been obtained by the reaction of *N*-(polychlorovinyl)imidoyl chlorides[108,114] and 1,3-dichloro-1-dimethylamino-4-fluoro-2-azabutadiene[129] or *N*-(benzenesulphonyl)benzohydrazonochlorides[130] respectively with arylhydrazines. The primary products of the reactions of *N*-(aryl)- or *N*-(alkyl)-carboimidoyl dichlorides with α-acyl- or α-thioacyl-hydrazines (XXIII) are converted into cyclic mesoionic compounds of type (XXIV) on treatment with ammonia:[131–134]



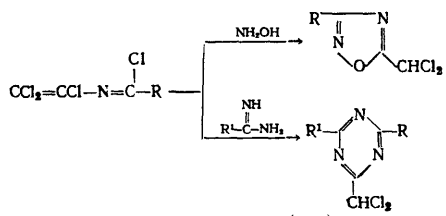
X = O, S

R^1 = CH_3; R^2 = C_6H_5; R = $C_6H_4CH_3$-4, C_6H_4Cl-4, CH_3 .

Mesoionic structures are also formed in the analogous reactions of 1,1-dibromo-2,3-diazadienes and *N*-aminobenzamidines.[125,134,135]

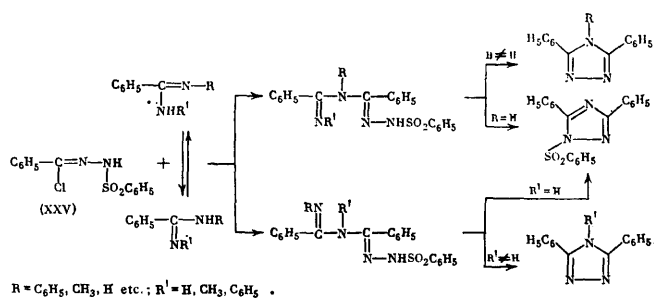
(c) Reactions with Hydroxylamine and Amidines

Carboimidoyl dichlorides and chlorides containing *N*-chloroalkenyl groups having α-chlorine atoms react with bifunctional nucleophiles, in particular, with hydroxylamine or amidines involving the substitution of an α-chlorine atom or the chlorine atom at the imidoyl carbon atom and affording various heterocyclic derivatives,[15,17,108,114] for example:



R=C_6H_5, C_6H_4Cl-4, $C_6H_4CH_3$-4, CCl_3 (etc.).

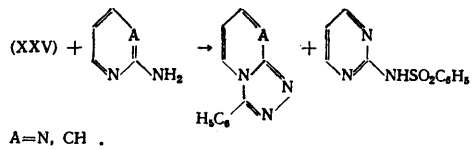
The reactions of *N*-(benzenesulphonyl)benzohydrazonochloride (XXV) with *N*-substituted amidines take place via a two-step mechanism involving the nucleophilic attack on compound (XXV) by two tautomeric forms of the amidine and subsequent cyclisation as a result of the nucleophilic attack by the amino-group on the iminocarbonyl carbon atom of the initial amidine in the intermediate compound. The final products are substituted 1,2,4-triazoles:[136]



R = C_6H_5, CH_3, H etc.; R^1 = H, CH_3, C_6H_5 .

2-Aminopyridine or 2-aminopyrimidine, which can be regarded as heterocyclic amidines, react analogously; the initial nucleophilic attack on the hydrazonochloride is by a ring nitrogen atom. This results in the formation of tri-

azolopyridines or triazolopyrimidines;



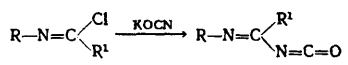
A=N, CH .

The reactions of other hydrazonohalides are similar,[137] Both linear and cyclic products are formed in the reactions of α-ketohydroximoyl chlorides with heterocyclic amidines.[138]

(d) Reactions with Azides and Cyanates

When compounds with a halogenoimidoyl group are acted upon by sodium azide, the halogen is replaced by the azido-group[57,139–143] and tetrazoles are formed.[51,84,139,144,145] The study of the kinetics of the reactions of isomeric acylbenzohydroximoyl chlorides with sodium azide in water showed that the reaction is bimolecular. When the (*Z*)-isomer is involved it takes place with retention of configuration, while in the case of the (*E*)-isomer it is ten times slower and the inversion of configuration is observed.[143]

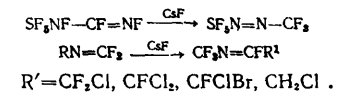
Open-chain imidoyl isocyanates, which have been little investigated, can be obtained by the reaction of imidoyl chlorides with potassium cyanates in the presence of crown-ether:[146]



R = iso-C_3H_7, C_6H_5 etc., R^1 = t-C_4H_9 .

4. Reactions with Halide Anions

The interaction of halogenoimidoyl compounds with the fluoride anion, whose source is as a rule caesium, potassium or sodium fluoride, has been most widely investigated. One of the reaction pathways involves the substitution of the imidoyl halogen atom by fluorine.[16,37,38,72,147–149] Under these conditions, other halogen atoms present in the molecule can also be substituted by fluorine[150,151] or these atoms alone are substituted if their mobility is higher than that of the halogen at the carbon atom of the N=C bond.[152] Another pathway in the reaction with alkali metal fluorides is isomerisation:[153,154]



R′=CF_2Cl, $CFCl_2$, CFClBr, CH_2Cl .

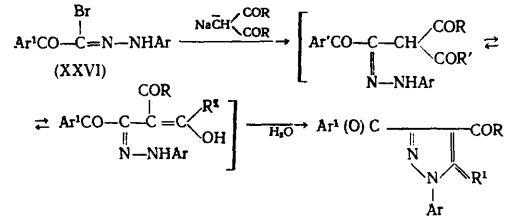
Finally, the addition of the fluoride anion to the N=C bond leads to the formation of *N*-anions, which can be inferred either from direct spectroscopic observations[155,156] and the isolation of stable salts[157] or from the reaction products. The anions can undergo intramolecular rearrangements and cyclisations[150,158,159] or they can participate in intermolecular reactions, functioning as active nucleophiles.[137,160] Dimerisation processes also belong to the class of intramolecular reactions.[159,161,162]

A study[159] of the interaction of the fluoride anion with perfluoro-2,5-diazahexa-2,4-diene established that the formation of a particular product is influenced by the source of the fluoride anion and the reaction conditions, which determine the formation of products resulting from kinetic or thermodynamic control.

The *N*-anion CF_3NF^-, formed by the reaction of $FN=CF_2$ with caesium, potassium, or mercury fluorides, behaves as an active nucleophile in reactions with the initial compound or its *N*-chloro-analogue and also with perfluorocarbonyl fluorides, giving rise to different products.[163,164] The less stable and nucleophilic *N*-anion CF_3NCl^-, formed by the reaction of $ClN=CF_2$ with potassium or caesium fluoride, is oxidised by chlorine to CF_3NCl_2.[164] The reactions of the *N*-anions derived from perfluoroazacyclohexene and perfluorocyclohexadienes have also been described.[155,156]

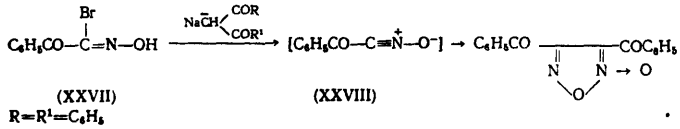
5. Reactions with *C*-Nucleophiles

The interaction of imidoyl chlorides or hydrazonohalides with KCN leads to the products of the substitution of the halogen by the CN group.[91,165,166] Carbanions generated from compounds with active methylene groups can also function as *C*-nucleophiles:[167]



R=R^1=CH_3, C_6H_5; Ar=C_6H_5; Ar^1=C_6H_5; $C_6H_4NO_2$-4 .

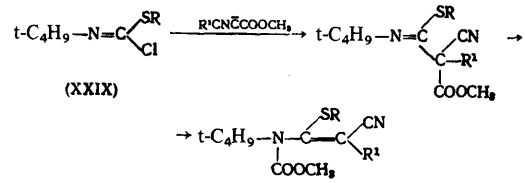
In contrast to this, in the reaction of hydroximoyl bromide (XXVII) with a carbanion, the latter acts only on the base, which promotes the formation of the intermediate nitrile oxide (XXVIII):[88]



R=R^1=C_6H_5 .

The difference in the behaviour of the two types of compounds, (XXVII) and (XXVI), can be attributed to the different acidities of the O–H and N–H bonds and to the ease of formation of the nitrile oxide from compound (XXVII) and the nitrile imine from compound (XXVI).

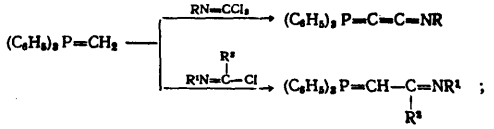
The interaction of chlorothioformimidates (XXIX) with carbanions derived from cyanomalonic esters leads to thioimidates which rearrange even at room temperature to the (*E*)- and (*Z*)-isomers of *N*-vinylcarbamates as a result of the 1,3-migration of the alkoxycarbonyl group:[168]



R=CH_3, C_6H_5; R^1=C_6H_5, $C_6H_4CH_3$-4 etc.

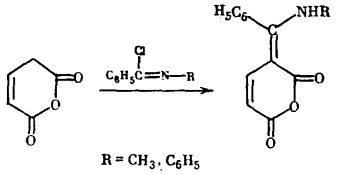
In the reaction of phenyl-lithium with *N*-(pentafluorothio)-chloroformamidine, the chlorine atom is substituted by the phenyl group.[47] Reactions with vinyl- and ethyl-magnesium bromides and also with aromatic and aliphatic magnesium bromide derivatives are described elsewhere.[42,89,171]

Carboimidoyl dichlorides react with methylenetriphenylphosphorane:[169,170]

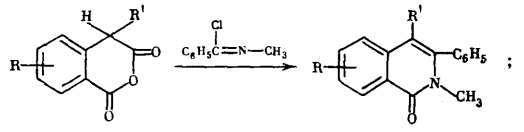


R=C_6H_5, CH_3, C_6H_{11} etc.; R^1=C_6H_5, $C_6H_4CH_3$-4;
R^2=C_6H_5, OCH_3, SCH_3 .

In reactions of glutaconic or homophthalic anhydrides with imidoyl chlorides, the initial nucleophilic attack on the imidoyl carbon ion is by the C(4) atom of the anhydride. The intermediate compounds of the aldol type are converted into the final products with and without the involvement of the anhydride component of the molecule:[172–174]



R = CH_3, C_6H_5



R = H, OCH_3 etc.; R' = H, CH_3.

6. Reactions with Other Nucleophiles

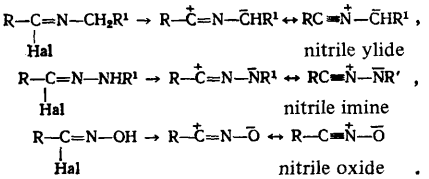
The reactions of imidoyl chlorides and hydrazonohalides with selenium compounds, leading to selenium heterocycles, have been described.[175,176] The mode of the reactions of imidoyl chlorides with di- and tri-alkyl phosphites[177,178] and also with phosphorus acid ester amides[179] depends unambiguously on the structure of the initial compounds and the reaction conditions. Imidoyl chlorides are converted into imines and amines on treatment with the $HFe(CO)_4^-$ anion in high yields,[180] while the reaction with the $C_6H_5COFe(CO)_4^-$ anion affords mesoionic 1,3-oxazol-5-ones.[181]

III. ELIMINATION REACTIONS

The elimination reactions of compounds with halogenoimidoyl groups have been fairly thoroughly investigated, particularly those which lead to highly reactive intermediate dipolar ions capable of interacting with various reagents to form new compound of many types. The wide scale use of halogenoimidoyl derivatives in organic synthesis, especially in the synthesis of heterocyclic compounds, is associated with precisely this feature.

1. The Formation of Ions and Their Reactions

When comounds with the halogenoimidoyl group are acted upon by strong bases, hydrogen halide is split off and dipolar ions of the following main types are formed:



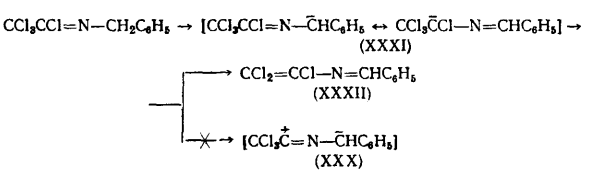
nitrile ylide

nitrile imine

nitrile oxide .

As a rule, these ions are formed only *in situ* and, depending on their structure and the reaction conditions, rapidly undergo intramolecular reactions or enter into intermolecular reactions with formation of dimers or the products of the reactions with other reagents present in the system.

In the course of development of early research into nitrile ylides, the mechanism of the tautomeric transformation of *N*-(4-nitrobenzyl)benzimidoyl chloride, *N*-(benzyl)-4-nitrobenzimidoyl chloride, and of the nitrile ylides formed from them on treatment with triethylamine has been studied in greater detail and confirmed experimentally.[182] Treatment of *N*-(benzyl)trichloroacetimidoyl chloride with triethylamine does not lead to the expected nitrile ylide (XXX), because the mesomeric carbanion (XXXI) formed initially is converted into *N*-(benzylidene)perchlorovinylamine (XXXII):[183]



(XXXI)

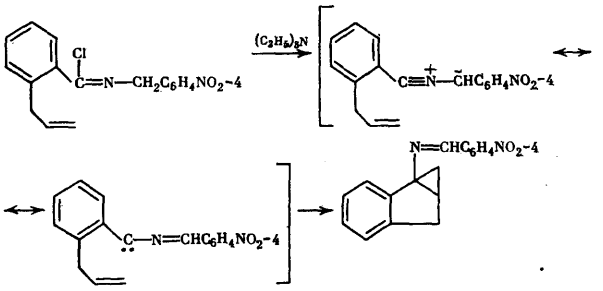
(XXXII)

(XXX)

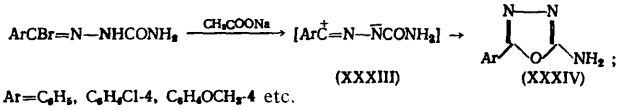
When the corresponding hydroximoyl chlorides were treated with triethylamine, acetonitrile oxide[184] and diphenylacetonitrile oxide[185] were obtained, the latter proving so stable that they could be isolated and characterised. Pentachlorobenzonitrile oxide is also extremely stable,[96] while pentafluorobenzonitrile oxide is unstable and readily dimerises. Silver nitrate has been used successfully to obtain the nitrile oxide from dichloroformaldoxime.[186] The attempt to obtain a nitrile imine from *N*-(benzenesulphonyl)benzohydrazonochloride was unsuccessful, which may be associated with the stability of the *N*-anion formed initially owing to the delocalisation of the negative charge on the electron-accepting benzenesulphonyl group.[136]

(a) Intramolecular Transformations of the Ions

The conversion of the nitrile ylide obtained from *o*-allyl-*N*-(*p*-nitrobenzyl)benzimidoyl chloride into a tricyclic compound as a result of the 1,1-cycloaddition of the carbene form of the nitrile ylide to the double bond may serve as an example of an intramolecular transformation:[187]



The intramolecular attack by the oxygen in the nitrile imine (XXXIII), which takes place as 1,5-dipolar addition, leads to the oxadiazole derivative (XXXIV):[188]



(XXXIII) (XXXIV)

Ar = C_6H_5, C_6H_4Cl-4, $C_6H_4OCH_3$-4 etc.

The nitronitrile imines formed as intermediates when the arylhydrazones of bromonitroformaldehyde are acted upon by sodium acetate in acetic acid isomerise to *N*-nitrosoaminoisocyanate, which is stable in the tautomeric cyclic mesoionic form of 3-aryl-1,2,3,4-oxatriazolate.[189,190]

The nitrile oxides formed from benzohydroximoyl chlorides on treatment with iron pentacarbonyl are deoxygenated further to nitriles.[191]

(b) Intermolecular Reactions of the Ions

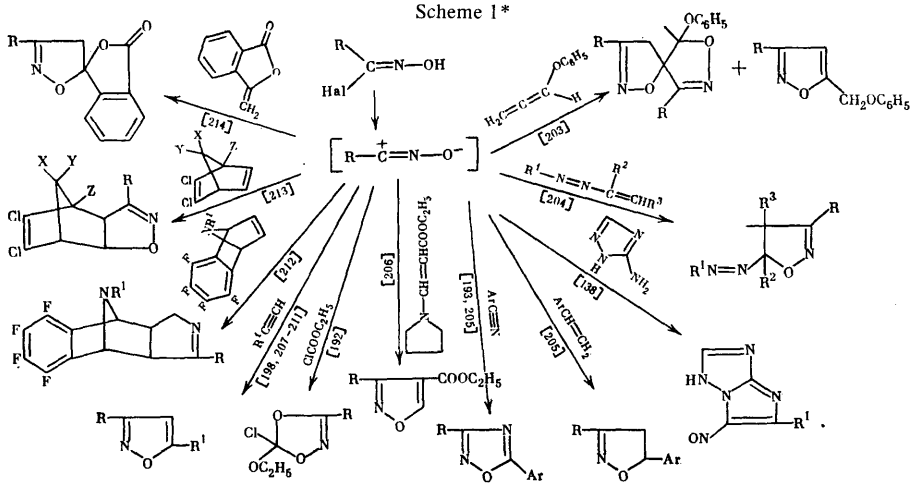
Dimerisation. The unstable nitrile oxides obtained from benzoylhydroximoyl halides[88,192] as well as acetonitrile oxide[184] and pentafluorobenzonitrile oxide[96] are converted into furoxan derivatives as a result of the 1,3-dipolar cycloaddition of one nitrile oxide molecule to the C≡N bond of another. Depending on the conditions under which trifluoroacetonitrile oxide is generated, its dimers are the corresponding dioxadiazine or furoxan.[193] Nitrile imines of the type $ArN^{-}-N=\overset{+}{C}-R$, where R = $COCH_3$, $COOC_2H_5$, or $COAr^1$, obtained from *N*-arylhydrazonohalides, dimerise to derivatives of 1,4-dihydro-1,2,4,5-tetrazine.[165,194]

Interaction with dipolarophiles and other reactions. The important and widely investigated reactions of the intermediate nitrile ylides, nitrile imines, and nitrile oxides involve their dipolar [3 + 2]cycloaddition interaction with various dipolarophiles occurring with the closure of a five-membered heterocycle ring and leading to the formation of a wide range of a wide variety of heterocyclic systems. At the present time the range of dipolarophiles used is extremely wide. The cycloaddition reactions proceed with participation of the C=C, C≡C, C=N, C≡N, C=O, C=S, and N=O bonds. Some examples of the 1,3-dipolar cycloaddition reactions of nitrile oxides are presented in Scheme 1.

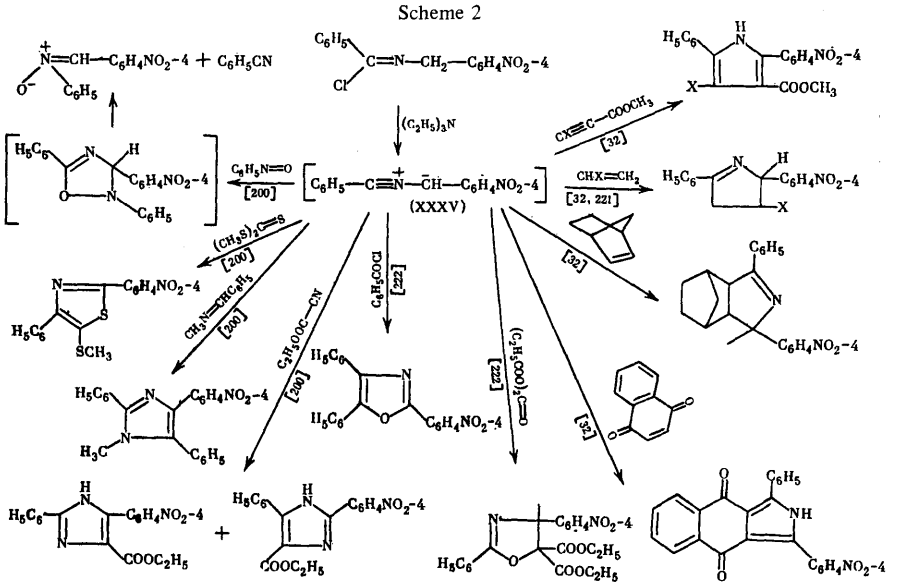
The reactions of nitrile oxides with other dipolarophiles have been described in a number of publications.[96,186,192,201,206,215–220] The 1,3-dipolar cycloaddition reactions of benzonitrile 4-nitrobenzylide are presented in Scheme 2. The reactions of the nitrile ylide (XXXV) with other dipolarophiles have been described by Huisgen and co-workers[32,222] and those of other nitrile ylides with dipolarophiles have been described by Padwa et al.[187] Scheme 3 presents the 1,3-dipolar cycloaddition reactions of nitrile imines. The reactions of nitrile imines with other dipolarophiles have been described in a series of publications.[194,199,202,212,228,230–232]

The mechanisms of these reactions have been described in a number of studies.[195–201] The most generally accepted point of view is that they take place via a concerted 1,3-di-

Scheme 1*



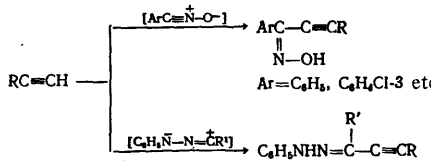
Scheme 2



Note. Numbers in square brackets denote references (Ed. of Translation).

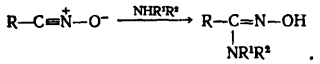
polar cycloaddition mechanism. The dipolarophile activity and mode of addition have been considered within the framework of the molecular orbital theory. The regioselectivity of the reactions is attributed to the ambident nucleophilic character of the 1,3-dipoles.

Nitrile imines and nitrile oxides are capable of entering not only into 1,3-dipolar cycloaddition but also into two-step 1,3-addition reactions with dienophiles, leading to acyclic products. For example, the reaction with acetylenes involves both processes and the second one leads respectively to acetylenic oximes or hydrazones:[195,198,202]

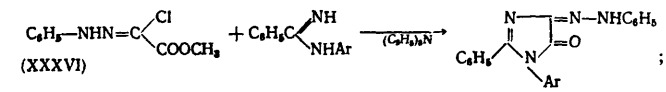


$R=C_6H_5$, $CH_2OC_6H_5$, $COOCH_3$; $R^1=CF_3$.

The reaction of nitrile imines and nitrile oxides with nucleophiles of different types (*N*-, *O*-, *S*-, and *C*-, and halogeno-nucleophiles) have also been investigated. The greatest number of publications refer to the reactions with *N*-nucleophiles. Primary and seconary amines react with nitrile oxides, affording amidoximes:[193,233,234]



Nitrogen-containing heterocyclic amino-derivatives are alkylated by nitrile imines at the most basic NH group of the ring and, if such a group is absent, at the NH_2 group.[226-228] Apart from the main product of cycloaddition to the C=N bond, 5-imidazolinones have been isolated in the reactions of the hydrazonochloride (XXXVI) with *N*-arylbenzamidines. Their formation is due to nucleophilic attack by the more basic amidine nitrogen atom (NHAr) of the electrophilic centre of the 1,3-dipole with subsequent ring closure involving a prototropic shift:[225]

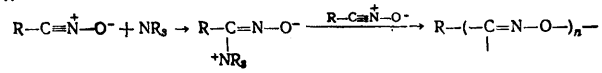


(XXXVI)

Ar=C_6H_5, $C_6H_4CH_3$-4 etc.

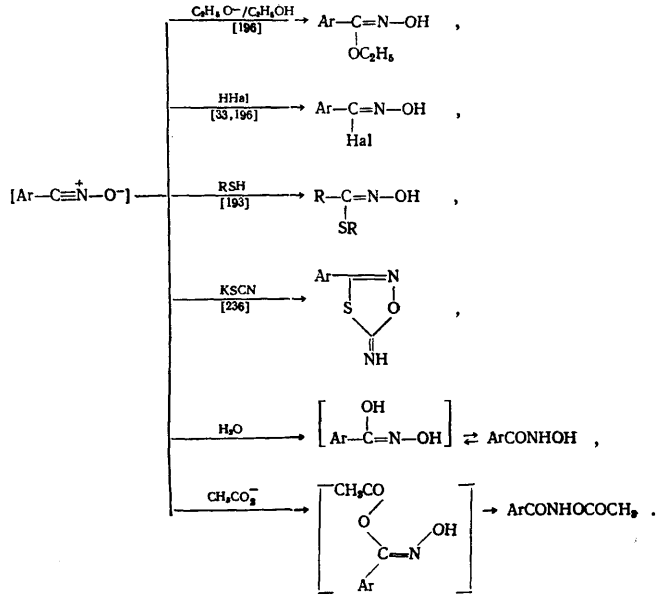
The reaction of nitrile imines with 1,1-diphenylhydrazine, carbohydrazides of the type $RCONHNH_2$, and the hydrazones of aromatic aldehydes and ketones involve the amino-group or proceed as 1,3-dipolar addition and lead to compounds of various types.[235]

Tertiary amines catalyse the polymerisation of nitrile oxides. They add to the nitrile oxides, giving rise to a zwitter-ion, which acts as a nucleophile on a second nitrile oxide molecule, etc.:[184,196]

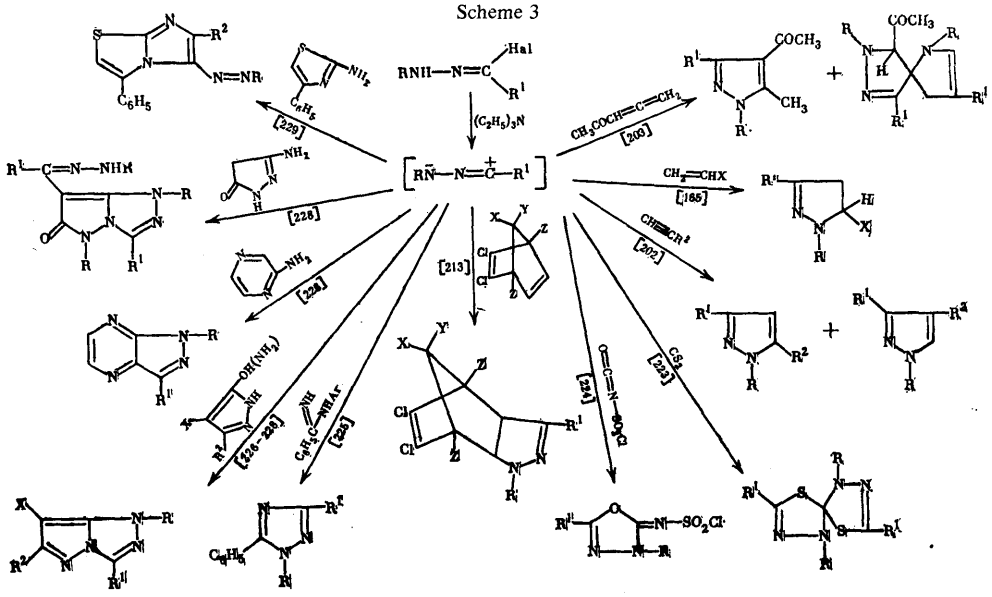


Hydroximoyl azides are formed as a result of the reaction of nitrile oxides with the azide ion.[196]

The interaction of nitrile oxides with *O*-, *S*-, *C*-, and halogeno-nucleophiles has been discussed in a number of studies.[33,193,196,197,233,236] "Open" oximes or the products of their further reactions are formed in these processes. Some of the reactions are presented below:



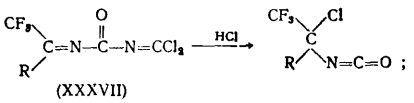
Scheme 3



2. Other Elimination Reactions

The familiar reaction involving the partial reduction of imidoyl chlorides to imines by treatment with tin dichloride has been used to convert a number of *N*-arylbenzimidoyl chlorides into aldehyde anils, from which aldehydes can be readily obtained in an acid medium.[237] In those cases where such a reductant cannot be applied, one can carry out the partial reduction under significantly milder conditions with the tris(t-butoxy)-derivatives of lithium aluminium hydride at a low temperature.[238] The reduction of imidoyl iodides with sodium tetrahydroborate leads to amines.[48] On treatment with magnesium in tetrahydrofuran (THF), *N*-(polyfluoroalkyl)- or *N*-(polyfluoroaryl)carboimidoyl dichlorides undergo reductive elimination of chlorine and the corresponding isocyanides are formed.[239]

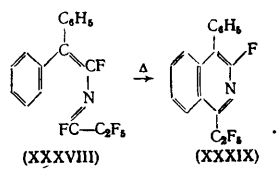
On heating with HCl, *NN'*-bisalkylideneureas of the type (XXXVII) split off chlorocyanogen with formation of α-chloroalkyl isocyanates:[240]



(XXXVII)

R=C_6H_5, C_6H_4Cl-4; $C_6H_4CF_3$-4 .

On thermolysis, imidoyl halides are converted into nitriles.[38,152,241] The high thermal stability of *N*-(pentafluorophenyl)carboimidoyl dichloride[161] and *N*-(pentafluorophenyl)chloroacetimidoyl chlorides[37] has been noted. Depending on the nature of the ring substituent, the thermolysis of benzohydroximoyl chlorides leads to nitriles, aryl isocyanates, or O-benzoylhydroximoyl chlorides.[242] *N*-(ω-bromopentyl)-benzimidoyl chloride undergoes fragmentation to ωω-dibromoalkane and benzonitrile on heating.[243] The azabutadiene (XXXVIII) splits off HF at 180–200 °C and is converted into the isoquinoline derivative (XXXIX):[244]



(XXXVIII) (XXXIX)

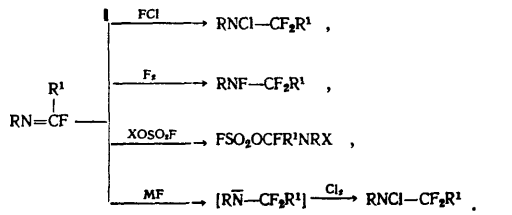
The thermolysis of compounds of the type $(RO_2C)_2N{=}N{-}CBrX$ (R = CH_3 or C_2H_5; X = Br or Cl) provides a new pathway to 2-halogen-1,3,4-oxadiazolin-5-ones which are difficult to obtain otherwise.[245]

Various chlorinated *SN*-heterocyclic systems are formed in the thermal dehalogenation reactions of polychlorinated imidoyl dichlorides and chlorides on treatment with sulphur.[246]

IV. ADDITION REACTIONS

1. The Action of Electrophiles and Radical Reagents

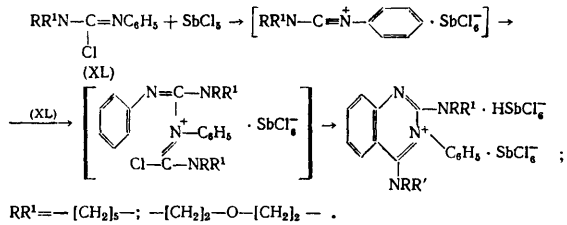
The reactions with electrophiles are less characteristic of compounds containing the halogenoimidoyl group than those with nucleophiles because of the electron-accepting properties of this group ($\sigma_m = 0.21$, $\sigma_p = 0.13$, $\sigma_I = 0.29$, $\sigma R = -0.08$[247]). However, such reactions are also known and in recent years their range has been appreciably extended. The interaction of halogenoimidoyl derivatives with the halogens,[248] including elemental fluorine,[249,250] chlorine monofluoride,[250–253] the highly electrophilic halogeno-derivatives of fluorosulphonic acid of the type $XOSO_2F$ (X = Cl, Br, or OSO_2F), the pseudohalogen $S_2O_6F_2$, and also moderately electrophilic halogeno-derivatives such as CF_3OCl and CF_3OF[164,148] has been investigated. These reactions involve the electrophilic or free radical addition of the reactants to the C=N bond. In many instances the reactions take place in the presence of alkali metal fluorides which promote the formation of the corresponding readily oxidisable *N*-anions:



The products of addition to the C=N bond are also formed in the oxidation of *N*-halogeno-, *N*-halogenoalkyl-, or *N*-pentafluorothio-imidoyl difluorides by trifluoromethyl hydroperoxide:[154,254,255]

$$RN{=}CF_2 + CF_3OOH \rightarrow CF_3OOCF_2{-}NHR$$

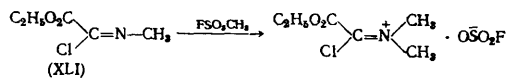
Lewis acids also enter into the addition reactions. This results in the formation of nitrilium salts,[243,256–259] which have been either isolated in a pure form or identified from the reaction products:



RR^1=—$[CH_2]_5$—; —$[CH_2]_2$—O—$[CH_2]_2$— .

The interaction of SbF_3 with *N*-(chlorodifluoromethylthiosulphenyl)carboimidoyl dichloride is accompanied by the decomposition of the latter to chlorocyanogen and a disulphide.[260,261]

The imidoyl chloride (XLI) is alkylated by methyl fluorosulphonate to a reactive salt, whose formation has been detected from the ^1H NMR spectra and numerous reactions:[97]



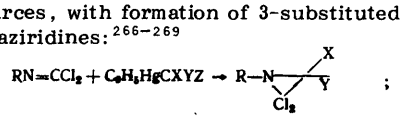
(XLI)

Treatment of imidoyl dichlorides with HF leads to the substitution of chlorine atoms by fluorine and addition to the C=N bond with formation of *N*-(trifluoromethyl)amino-derivatives.[157,262–264]

In the reaction of *N*-(t-butyl)carboimidoyl dichloride with bis(bistrifluoromethylamino-oxy)mercury, the final products resulted from the substitution of one or two chlorine atoms by the bistrifluoromethylamino-oxy-radical; the monosubstituted product can be converted into the disubstituted product by additional treatment with the mercury derivative.[264]

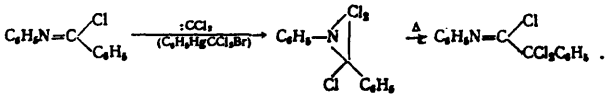
2. Cycloaddition

Aromatic and aliphatic carboimidoyl dichlorides enter into cycloaddition reactions with halogenocarbenes, obtained from mercury sources, with formation of 3-substituted 2,2-dichloro-1-phenylaziridines:[266–269]



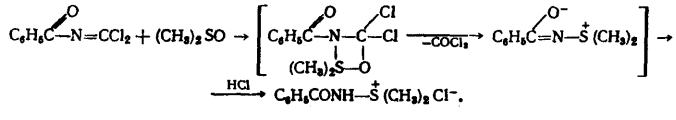
R=C_6H_5 Z=Cl or Br X=F; Y=$COOC_2H_5$
X=Y=Cl
X=F; Y=Cl .

The aziridine derivative of *N*-phenylbenzimidoyl chloride isomerises to the corresponding imidoyl chloride already during isolation:[266]



N-Phenyltrichloroacetimidoyl chloride does not react with dichlorocarbene.[266] Nor could *N*-pentafluorophenylcarboimidoyl dichloride be made to react with high-temperature sources of dichloro- and difluoro-carbenes.[161]

The cycloaddition to the N=C bond takes place in the reaction of *N*-benzoylcarboimidoyl dichloride with dimethyl sulphoxide; however, the cyclic adduct if unstable and decomposes under the reaction conditions with elimination of phosgene:[270]



During the preparation of the manuscript for publication, kinetic data were obtained for the arylaminolysis reactions of *N*-methane- and *N*-benzene-sulphonylbenzimidoyl chlorides in acetonitrile which are consistent respectively with the ion-pair and addition-elimination mechanisms.[271,272] The mechanism of the salt formation reactions of *N*-alkylbenzimidoyl chlorides with pyridine bases has been investigated.[273] It has been shown that the salt formation reaction of *N*-phenylcarboimidoyl dichloride and cyclic tertiary amines is accompanied by dealkylation with ring opening in the case of small rings.[274] The interaction of *N*-arylcarboimidoyl dichloride with cyclic secondary amines has been described.[275] The hydrolysis of chloroformamidines, the reactions of imidoyl chlorides and thioimidates with thiocyanates, and substitution of the chlorine atom in hydroximoyl chlorides on treatment with various nucleophiles have also been described.[275-279] The products of the reactions of perfluoroisopropylacetimidoyl chloride with *S*-, *P*-, and *N*-nucleophiles have been obtained in order to investigate the stereochemical isomerisation at the N=C bond.[280] 1,3-Prototropic migrations have been noted in the phosphorylation of imidoyl chlorides containing a hydrogen atom at the α-carbon atom. Bases also promote the migration of the chlorine atom.[281] In the reactions of *N*-phenylchloroformimidates, *N*-phenylthioformimidates, and *N*-phenylamidines with salts of phosphorus(IV) thio-acids, the 1,3-migration of the $X=P(OR)_2$ group from the sulphur atom to the nitrogen atom has been observed in the imidoyl phosphorothioates formed initially. Thiocarbamates, dithiocarbamates, or thioureas were then obtained as the products.[282] In contrast to other *P*-nucleophiles, dialkyl phosphites react with imidoyl chlorides at the oxygen atom, affording imidoyl phosphites.[283] The 2,2-dichloromalonamides having the general formula $(R_2N-CCl=N-CO)_2CCl_2$, which have been little investigated, react with monofunctional nucleophiles to give the products of the substitution of two chlorine atoms at the amidine carbon atoms. In the reactions with bifunctional reagents, cyclisation to heterocyclic spiro-compounds takes place.[284] The use of halogenoimidoyl derivatives as promising starting materials for the synthesis of a wide variety of heterocyclic compounds, formed directly in the reaction with nucleophiles or via further reactions of the products, has been demonstrated in studies on the reactions with azides,[285-287] with amines and hydrazines,[288-290] with carbanions,[291] and with copper and silver acetylides.[292] The synthesis of heterocyclic compounds with the aid of reactions involving the [2 + 4] cycloaddition of dicyclopentadiene to perfluoroimidoyl fluorides[293] and the reactions of the intermediate dipolar ions—either via their intramolecular cyclisations[294-296] or via their 1,3-dipolar cycloaddition to polarophiles[297-312]—has also been described. New data on the characteristics of the formation of dipolar ions and their structure and reactivity have likewise been published.[297,305-307] Problems concerning the formation, structure, and stereospecificity of the reactions of nitrilium ions have been considered.[307,308] Data concerning a convenient method of reduction of imidoyl chlorides to aldimines by treatment with hydrogen in the presence of palladium complexes and the reactions of these compounds with organotin compounds have been published.[309,310]

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