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Methods of Synthesis of Compounds with Halogenoimidoyl Groups

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The available information about the methods of synthesis of compounds of different classes containing the halogeno-imidoyl group $-N=\overset{|}{C}-Hal$ are surveyed and the application of the known methods of synthesis of such compounds to new objects is examined. Data are presented on new methods of synthesis of compounds containing the $-N=\overset{|}{C}-Hal$ group which have been developed in recent years.
The bibliography includes 239 references.

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I. INTRODUCTION

Compounds containing the halogenoimidoyl group $-N=C-Hal$ are extremely varied and have continually attracted the interest of investigators as a consequence of the high reactivity of the group, which makes it possible to involve them in a large number of reactions with formation of various acyclic and heterocyclic substances.[1-3] Furthermore, the interest in such compounds is due to the broad spectrum of the physiological activity of either the compounds themselves or the products of their reactions.[4-7]

Monographs and reviews devoted to the methods of synthesis and reactions of compounds of this large class are now available but they were published more than 15 years ago.[1,2] Thorough reviews covering the work of recent years are concerned mainly with imidoyl fluoride and fluorinated imidoyl halides,[8-11] hydrazonohalides [halogenocarbonyl hydrazones (Ed.of Translation)], and halogenoazines.[12-14] Fragmentary data on compounds with halogenoimidoyl groups have been included in several monographs.[15-22]

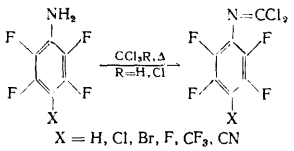
The aim of the present review is to survey data on the methods of synthesis of compounds containing the $-N=\overset{|}{C}-Hal$ group published between 1970 and 1986. It includes as a rule recent studies which have not been covered by the existing reviews. For this reason, few data are presented on imidoyl fluoride and difluorides and also on *N*-halogeno-compounds. In the case of hydrazonohalides and halogeno-azines, attention has been concentrated on studies published after 1974 and 1977 respectively. With the exception of a few examples, the review does not deal with heterocyclic compounds in which the halogenoimidoyl group forms part of the heterocycle or is attached to it.

Analysis of the literature data on the synthesis of various compounds with halogenoimidoyl groups up to 1970 permits the conclusion that, together with the development of the traditional methods of synthesis of such compounds, fundamentally new methods of their synthesis have been developed in the last 15 years and have expanded the range of these compounds and their possible applications.

II. SYNTHESES FROM AMINES, *N*-HALOGENOAMINES, AND HYDRAZINES

1. Thermolytic and Photochemical Reactions of Amines and *N*-Halogenoamines

A novel thermolytic method of synthesis of polyfluorinated *N*-(aryl)-carboimidoyl dichlorides not described previously, has been proposed comparatively recently. It consists in the copyrolysis of polyfluorinated primary aromatic amines with $CHCl_3$ or CCl_4 in a flow system at 600–670 °C:[23,24]



X = H, Cl, Br, F, CF_3, CN

The reaction is fairly general for polyfluorinated benzene derivatives and has been extended also to 2-aminohepta-fluoronaphthalene and 4-amino-2,3,5,6-tetrafluoropyridine. The yield of carboimidoyl dichloride is 14–34%. The copyrolysis with CCl_4 takes place at a lower temperature, with a smaller excess of the halogenomethane and with a higher yield than the reaction with $CHCl_3$. The polyfluorinated *N*-(aryl)carboimidoyl dichlorides are also formed on copyrolysis of *N*-chloroamines with $CHCl_3$.

The disadvantages of the method include the low yield of the carboimidoyl dichloride, the high content of the polychlorinated products of the thermolysis of $CHCl_3$ and CCl_4 in the reaction mixture, and in certain cases side reactions of the substituents in the initial amine.

The formation of carboimidoyl dichlorides from amines and $CHCl_3$ apparently includes the preliminary generation of dichlorocarbene. However, the available data do not formally

conflict with the participation in the reactions with $CHCl_3$ also of the trichloromethyl radical. The latter process is apparently the main one in the copyrolysis of amines with CCl_4.

The method of synthesis of carboimidoyl dichlorides indicated above has no analogies in the series of non-fluorinated compounds. The attempts to extend it to non-fluorinated amines, for example, aniline, was unsuccessful. The reason may be the thermal instability of the initial amines at high temperatures.

The copyrolysis of aromatic polyfluoroamines with pentafluorotrichloromethylbenzene at 500–520 °C leads to *N*-(polyfluoroaryl)pentafluorobenzimidoyl chlorides.[25] The yield is 50–77% in most cases. It has been suggested that the reaction proceeds via a radical pathway, although the possibility of the nucleophilic substitution of chlorine in pentachlorotrichloromethylbenzene under severe copyrolysis conditions is not ruled out.

The formation via a radical pathway of *N*-(pentafluorophenyl)carboimidoyl fluoride chloride as one of the products has been noted[26] in the pyrolysis of *N*-4-dichloroperfluorocyclohexa-2,5-dienylideneamine (550 °C, 1 mmHg) in a flow system.

Unstable *N*-chloroamines also having a chlorine atom at the α-carbon atom are very readily dechlorinated and are converted into the corresponding imidoyl chlorides even at room temperature:[27]

$$CF_3CON{-}\underset{Cl}{CF}(CF_3)_2 \xrightarrow{PCl_5} [CF_3CCl_2N{-}\underset{Cl}{CF}(CF_3)_2] \rightarrow CF_3\underset{Cl}{C}{=}N{-}CF(CF_3)_2 \quad .$$

In the photolysis of a mixture of t-butylamine with trifluoromethylbenzenes, *N*-(t-butyl)benzimidoyl fluorides are formed as the main products, but their yields are low and the process cannot be regarded as preparative.[28]

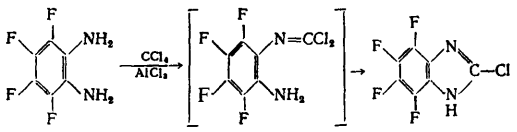
2. Reactions of Amines, *N*-Chloroamines, and Hydrazines in the Presence of Lewis Acids

A new method of synthesis of carboimidoyl dichlorides and chlorides involves the reaction of weakly basic amines with compounds of the type CCl_3R in the presence of $AlCl_3$. Thus heating of aromatic polyfluoroamines with CCl_4 and $AlCl_3$ at 40–80 °C leads to *N*-(polyfluoroaryl)carboimidoyl dichlorides in yields of 40–90%:[29,30]

$$Ar_FNH_2 \xrightarrow[AlCl_3]{CCl_4} Ar_FN{=}CCl_2$$

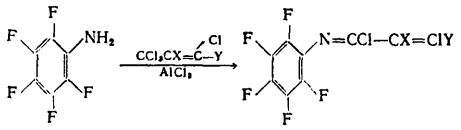
The reaction is fairly general for polyfluorinated benzene, biphenyl, naphthalene, and heterocyclic amine derivatives. The corresponding carboimidoyl dichlorides have been obtained in this way from pentafluoroaniline and *p*-substituted tetrafluoroanilines (the *p*-Br, *p*-Cl, *p*-NO_2, *p*-CN, and *p*-CH_3 derivatives and also the compound with H in the *p*-position), as well as pentachloroaniline. Compared with the pyrolytic method,[23,24] this procedure gives an increased yield and a greater range of products.

Tetrafluoro-*m*-phenylenediamines and tetrafluoro-*p*-phenylenediamines also enter into this reaction, which takes place in steps and leads to a mixture of mono- and di-carboimidoyl dichlorides with the latter predominating. On the other hand, the interaction of tetrafluoro-*o*-phenylenediamine with CCl_4 and $AlCl_3$ takes place in a more complex manner and leads to 2-chloro-4,5,6,7-tetrafluorobenzimidazole. It may be that the reaction proceeds via the intermediate *N*-(2-amino-3,4,5,6-tetrafluorophenyl)carboimidoyl dichloride, like the formation of benzimidoyl derivatives from the intermediate *o*-aminoarylamidoyl fluorides:[31]



The reaction with 4-amino-2,3,5,6-tetrachloropyridine takes place fairly smoothly.[32] In contrast to this, 4-amino-2,3,5,6-tetrafluoropyridine does not react.[30] Non-fluorinated amines react with CCl_4 and $AlCl_3$ to form carboimidoyl dichloride only if their basicity is sufficiently low. Thus *p*-nitroaniline is converted into *N*-(*p*-nitrophenyl)carboimidoyl dichloride, while aniline forms a high-melting salt-like product.[30]

Aluminium chloride is a specific catalyst in the process. Other Lewis acids proved to be virtually ineffective.[30] The replacement of CCl_4 by trichloromethylbenzene and its derivatives leads to the formation of the corresponding imidoyl chlorides even at room temperature.[30,33] Polyhalogenopropenes containing the CCl_3 group at the C=C aliphatic bond also react very readily with pentafluoroaniline, affording a high yield of the corresponding azadienes:[34]



X = F, Y = Cl; X = Y = Cl; X = F, Y = C_6F_5

Hexafluorobenzene, $CHCl_3$, and CH_2Cl_2 are inert solvents for these reactions. In the synthesis of carboimidoyl dichloride and chloride by the above method, account must be taken of the side processes due to the effect of $AlCl_3$, for example, the exchange of fluorine for chlorine in the fluoroalkyl groups.[30]

One of the possible mechanisms of the formation of imidoyl chlorides and dichlorides from aromatic amines and compounds with the trichloromethyl group in the presence of $AlCl_3$ involves the formation of complexes by $AlCl_3$ with the trichloromethyl derivatives and the amine and subsequent conversion of the amine into the chloroalkyl derivative and further into the final product:[30]

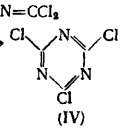
$$ArNH_2 + [R\overset{\delta+}{C}Cl_2 \ldots Cl \ldots \overset{\delta-}{Al}Cl_3] \rightarrow [Ar\overset{+}{N}H_2{-}CCl_2R] \xrightarrow[-H^+]{} [ArNHCCl_2R] \rightarrow \xrightarrow[-HCl]{} ArN{=}CClR$$

The reaction of nitrogen trichloride with CCl_4 in the presence of $AlCl_3$ also leads to carboimidoyl chlorides,[35,36] but in this case a mixture of compounds is formed, whose proportions can be changed by varying the reaction conditions. It is of interest that bis- and tris-(carboimidoyl dichlorides) (I) and (II) have been obtained in this way. Small amounts of compound (III) and cyanuric chloride (IV) were isolated from the reaction mixture together with the above compound. The following mechanism of the reactions has been proposed:

$$CCl_4 + NCl_3 \xrightarrow[-Cl_2]{AlCl_3} [CCl_3{-}NCl_2]$$

$$CCl_3{-}NCl_2 \xrightarrow{-Cl_2} ClN{=}CCl_2$$

$$ClN{=}CCl_2 \xrightarrow{-Cl_2} Cl{-}C{\equiv}N \rightarrow$$



(IV)

$$ClN{=}CCl_2 \xrightarrow[-Cl_2]{CCl_4} CCl_3N{=}CCl_2 \quad ,$$

(III)

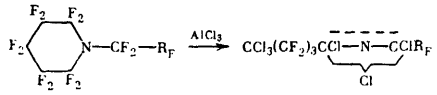
$$ClN{=}CCl_2 + CCl_3{-}N{=}CCl_2 \xrightarrow{-Cl_2} CCl_2(N{=}CCl_2)_2 \quad .$$

(I)

$$ClN{=}CCl_2 + CCl_2(N{=}CCl_2)_2 \xrightarrow{-Cl_2} ClC(N{=}CCl_2)_3 \quad .$$

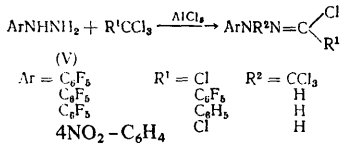
(II)

On treatment of perfluorinated cyclic tertiary amines with CCl_4 and $AlCl_3$, imidoyl chlorides with a linear structure are formed.[37,38] In this case, the mobile fluorine atoms in the α-position with respect to the nitrogen atom in the complex of the amine and $AlCl_3$ are exchanged for chlorine under the influence of the excess $AlCl_3$ with subsequent rearrangement of the αα'α"-polychloroamines, which are unstable under these conditions, to the sterically less hindered imidoyl chlorides. The rearrangement is accompanied by the dissociation of the C–N bond in the ring:



$R_F = (CF_3)_2CF-$, $CF_3CF_2CF_2-$

The weakly basic hydrazines (V) also react with compounds having trichloromethyl groups and $AlCl_3$.[39] Pentafluorophenylhydrazine and *p*-nitrophenylhydrazine react with CCl_4 or trichloromethylbenzene and $AlCl_3$ and are converted into the corresponding *N*-(aryl)hydrazonodichloromethanes or *N*-(aryl)phenylhydrazonochlorides:



(V)

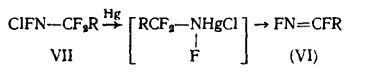
Ar =	$R^1 = Cl$	$R^2 = CCl_3$
C_6F_5	C_6F_5	H
C_6F_5	C_6H_5	H
$4NO_2-C_6H_4$	Cl	H

The direct conversion of arylhydrazine into arylhydrazonochlorides had not been noted earlier in the literature.

N-(Trifluoromethyl)carboimidoyl dibromide was obtained in 93% yield by the reaction of bis(trifluoromethyl)amine with CF_2Cl_2 and BBr_3.[40]

3. Other Reactions of Amines with *N*-Halogenoamines

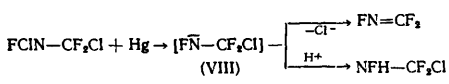
A method has been proposed for the synthesis of *N*-fluoroimidoyl fluorides (VI) in a satisfactory yield by dehalogenating amines of the type $NFClCF_2R$ (VII) by heating with mercury in the absence of a solvent.[41,42] The reaction mechanism has not been established accurately, but it has been suggested that it involves the insertion of mercury in the N–Cl bond and subsequent formation of the intermediate mercury compound:



VII (VI)

$R = CF_3, C_2F_5, CF_2NClF$

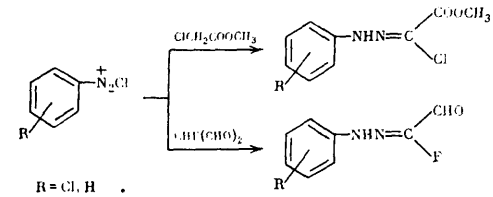
N-Fluorocarboimidoyl difluoride (VI, R = F) is formed in this way from the amine (VII, R = F) in yields up to 60%, but it cannot be separated from the impurities produced. A product which was readily purified was obtained in 90% yield by carrying out the reaction in trifluoroacetic anhydride. The use of trifluoroacetic acid as the solvent at 0 °C led to a mixture of the difluoride (VI, R = F) and *N*-(chlorodifluoromethyl)-*N*-fluoramine. Apparently the intermediate anion (VIII) is formed in the reaction in solvents and readily loses Cl^-, affording imidoyl difluoride, or abstracts a proton from the solvent and is converted into an amine:



(VIII)

Other amines of the type R_FNClF are converted only into *N*-(fluoroalkyl)-*N*-fluoramines under these conditions. *N*-(Chloro)trifluoroacetimidoyl fluoride has been obtained in a moderate yield from *NN*-dichloro-*N*-(perfluoroethyl)-amine on interaction with mercury in trifluoroacetic acid.

The coupling of diazotised anilines with methyl α-chloroacetate or fluoromalonaldehyde leads respectively to *N*-(aryl)-hydrazonochlorides or fluorides:[43–45]



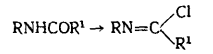
R = Cl, H .

III. SYNTHESES FROM COMPOUNDS WITH THE –NHCO OR –NHCS GROUP

The conversion of the –NHCO or –NHCS group into $-N=\overset{|}{C}-Hal$ on treatment with various halogen-containing reagents is the basis of well known and widely used methods of synthesis of halogenoimidoyl derivatives. Most of the studies in recent years on these lines have been associated with the involvement of new compounds in the reaction already described previously.

1. Reactions with Halogeno-derivatives of Phosphorus and Sulphur and with Halogens

One of the simplest and most convenient methods of synthesis of imidoyl halides is the halogenation of amides by phosphorus halides or $SOCl_2$. The following reactions have been carried out using PCl_5 and $SOCl_2$:



$R = CH_3$	$R^1 = C_6H_5$, 4-XC_6H_4, $COOC_2H_5$ (Refs.46–48)
$OCOCF_3$	CF_3 (Ref.49)
CCl_3CHOH, $CHClBrCHCl$	C_6H_5, 4-XC_6H_4, CH_3 (Refs.50–52)
CCl_3CHCl, $CCl_2=CH$	$CHCl_2$, CCl_3, $C(CH_3)_3$
SF_5	CF_3, CH_3 (Ref.53)
OCH_3, OC_2H_5, OC_3H_7-m	C_6H_5, 4-XC_6H_4 (Refs.54–57)
OC_3H_7-iso, OC_4H_9-n	2,4-XYC_6H_3
4-$XC_6H_4CH_2$, $C_6H_5CH_2$	C_6H_5, 4-$NO_2C_6H_4$ (Ref.58)
C_6H_5, 4-XC_6H_4	$2CF_3SO_2C_6H_4$, C_6H_5, 4-XC_6H_4 (Refs.59–60).

The corresponding imidoyl bromide has been obtained from compound (IX, R = OCH_3, $R^1 = C_6H_5$) by reaction with PBr_3, but its yield was low;[56] an alternative method of synthesis with a yield of 51% involves the nitrosative deamination of *o*-methylbenzamide oxime in HBr.[57] *N*-Phenylbenzimidoyl bromide can be obtained from benzanilide and PBr_5 only in a mixture with the product of the bromination in the *p*-position of the aromatic ring attached to the nitrogen atom.[61]

It is of interest to note that the trichloroacetyl derivative of pentachloroaniline is converted into *N*-(pentachlorophenyl)trichloroacetimidoyl chloride on reaction with PCl_5,[62] while *N*-(pentafluorophenyl)trichloro- or -trifluoro-acetimidoyl chloride cannot be obtained from the corresponding anilides and PCl_5. Under the reaction conditions, they are converted into trichlorophosphazopentafluorophenyl.[63] The formation of organophosphorus compounds instead of the expected hydrazonochlorides has been observed also in the interaction of *N*-phenyl- and *N*-methyl-*N*-trifluoroacetohydrazides with PCl_5.[64]

In the case of the *o*-azidobenzanilides or *N*-(*o*-azidobenzoyl)anilides, the imidoyl chlorides formed rapidly cyclise to derivatives of 2*H*-indazole or benzimidazole, so that they

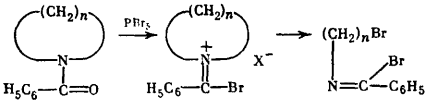
cannot be isolated, although there is no doubt about their intermediate formation.[65,66]

An *o*-allyl-substituted imidoyl chloride has been obtained from the *o*-allylbenzoyl derivative of *p*-nitrobenzylamine.[67] Various 2-phenylethylamides react with reagents of the type of PCl_5, $POCl_3$, and $SOCl_2$ under mild conditions to form imidoyl halides in high yields.[68,69] This finding proved to be extremely important for the understanding of the mechanism of the formation of derivatives of dihydroisoquinoline from amides and $POCl_3$ in the classical Bischler–Napieralski reaction. It permitted the conclusion that imidoyl chlorides are formed as intermediates in this reaction and made it possible to modify the conditions for its occurrence in order to attain the highest yield of the cyclisation product.

The chlorination of *NN'*-dichlorodimethylmalonamide with chlorine under UV irradiation proceeds differently to the reactions of amides described above, although it also leads to a compound with imidoyl dichloride groups:[70]

$$CH_3NHCOCCl_2CONHCH_3 \xrightarrow[h\nu]{Cl_2} CCl_2{=}N{-}\overset{O}{\overset{\|}{C}}{-}CCl_2{-}\overset{O}{\overset{\|}{C}}{-}N{=}CCl_2 \quad .$$

Amide groups forming part of the heterocyclic ring are converted into imidoyl chlorides on treatment with PCl_5 or $POCl_3$. Chlorine-containing quinazolines,[71] phthalazines,[72] 1,2,4-triazines,[73] pyrazines,[74] pyridazines,[75,76] isoindolenines,[77] and phenanthridines[78,79] have been synthesised in this way. Cyclic benzamides of type (X) react with PBr_5 with ring opening and the formation of *N*-(ω-bromoalkyl)imidoyl bromides (XI). The reaction proceeds via the intermediate iminium bromide (XII):[80]



(X) (XII) $X = Br_3^-; Br^-$. (XI)

A mixture of $SOCl_2$ and SO_2Cl_2 is as a rule used for the synthesis of carboimidoyl dichloride from amides. The corresponding *N*-arylcarboimidoyl dichlorides have been obtained in this way from formanilide and its 2,6-dichloro- and 2,4,5-trichloro-derivatives.[81] However, the attempt to use this method to synthesise *N*-pentafluorophenylcarboimidoyl dichloride was not very successful.[82]

The synthesis of *N*-pentafluorophenyl)perfluoropropylimidoyl fluoride by treating a tertiary amide with SF_4 in HF has been described:[83]

$$C_6F_5N(COC_2F_5)_2 + SF_4 \xrightarrow{HF} C_6F_5N{=}C\begin{matrix}F\\ C_2F_5\end{matrix} \quad .$$

The yield of the product is 73%. The proposed reaction pathway involves the rupture of the *N*-acyl bond by HF and the formation of a secondary amide which is then converted into the imidoyl fluoride. Thiobenzanilide reacts with SF_4 and is converted into *N*-phenylbenzimidoyl fluoride in 52% yield.[84]

Like amides, hydrazides are readily chlorinated by $SOCl_2$ or PCl_5, being converted into the corresponding hydrazonochlorides:

$$R^1CONHNR^2R^3 \rightarrow R^1{-}\overset{Cl}{\overset{|}{C}}{=}N{-}NR^2R^3$$

$R^1 = 2\text{-}BrC_6H_4$, $2\text{-}FC_6H_4$; $R^2 = H$; $R^3 = C_6H_5$ (Ref.85); $R^1 = C_6H_5$, $R^2 = H$, $R^3 = C_6F_5$ (Ref.86); $R^1 = R^3 = C_6F_5$; $R^2 = H$; $R^1 = t\text{-}C_4H_9$, C_6H_5; $R^2 = CH_3$; $R^3 = 2,4\text{-}(NO_2)_2C_6H_3$, $4\text{-}NO_2C_6H_4$, C_6H_5 (Ref.87); $R^1 = C_6H_5$; $R^2 = H$; $R^3 = Ts$ (Ref.13);

$$R{-}CO{-}NH{-}NH{-}COR \xrightarrow{PCl_5,POCl_3} R{-}\overset{Cl}{\overset{|}{C}}{=}N{-}N{=}\overset{Cl}{\overset{|}{C}}{-}R \text{ [88]}, \quad R = -N[CH_2CF(NO_2)_2]_2 .$$

A convenient modification of the method involves treating the hydrazides with the $POCl_3$.pyridine complex in an excess of $POCl_3$.[12,89–91] On treatment with PCl_5, certain hydrazides undergo a rearrangement in the course of which the intermediate formation of compounds with the imidoyl chloride functional groups is postulated.[92]

On treatment with PCl_5, arylureas are converted in high yields into *N*-arylbenzimidoyl chlorides,[93] while *N*-alkylideneureas are converted into chloro-1,3-diaza-1,3-dienes.[94] Compounds of a similar type with two conjugated imidoyl chloride groups are obtained by chlorinating *N*-thioaroyl-*N'*-arylthioureas.[95]

Chlorination of perfluoroalkylthioanilides leads to *N*-phenylimidoyl chlorides in high yields:[84]

$$C_6H_5NHCSCF_3 \xrightarrow{Cl_2} C_6H_5N{=}C\begin{matrix}Cl\\ CF_3\end{matrix}$$

The formation of a small amount (up to 10%) of relatively unstable *N*-pentafluorothioimidoyl chlorides, characterised spectroscopically, has been noted in the reactions of *N*-pentafluorothiourethanes or thiourethanes with PCl_5:[96]

$$SF_5NHCOR \rightarrow SF_5N{=}C\begin{matrix}Cl\\ R\end{matrix} \quad ,$$

$R = OC_6H_5$, SCH_3, SC_6H_5 .

2. Reactions with the Vilsmeier Reagent and Its Analogues

The reactions of amides with the Vilsmeier reagent proceed in a more complex manner. Thus, when acetanilides interact with this reagent, imidoyl chlorides are formed only as intermediates, which are subsequently converted into formamidines, 2-chloroquinolines, or other heterocyclic derivatives depending on the substituent in the acetanilide and the reaction conditions.[97–101] The interaction of the Vilsmeier reagent with 2- and 3-acetamidothiophens proceeds analogously.[98,102] The reaction of the Vilsmeier reagent with *NN*-dimethylurea has been described by Boyd et al.[103]

The intermediate formation of imidoyl chlorides has been postulated in the reactions of anilides of the type $ArNHCOCH_2R$ with the aza-analogues of the Vilsmeier reagent obtained from $POCl_3$ and *N*-nitrosodimethylamine or its homologues.[100] However, *N*-(*m*-tolyl)carboimidoyl dichloride is one of the side products in the case of 3-methylpropioanilide.

3. Reactions with Triphenylphosphine and Dihalogenophosphoranes

A new convenient method of synthesis of imidoyl chlorides and bromides in high yields has been proposed by Appel and co-workers[104,105] using secondary amides, the corresponding tetrahalogenomethane, and triphenylphosphine as the starting materials:

$$R^1CONHR^2 + (C_6H_5)_3P + CX_4 \rightarrow R^1CX{=}NR^2 + (C_6H_5)_3PO + CHX_3 \quad ;$$

$R^1 = CH_3$, C_6H_5; $R^2 = C_6H_5$, cyclo-C_6H_{11}; $X = Cl$, Br .

The study of the reaction mechanism suggested that the reaction proceeds via the intermediate *O*-phosphorylated compound formed from the amide on treatment with the complex of the tetrahalogenomethane and triphenylphosphine or the product of their reaction—a dihalogenophosphorane. Taking this into account, a method of synthesis of imidoyl chlorides and bromides from the corresponding dihalogenophosphoranes in the presence of bases (to bind the HHal formed) was developed. The yields of imidoyl halides

obtained by this method are also fairly high. The reaction with the less reactive dichlorophosphorane takes place at a higher temperature than the reaction with dibromophosphorane.

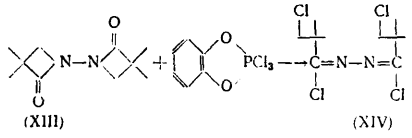
The mild conditions in the synthesis of imidoyl chlorides and bromides by this method make it possible to obtain even relatively unstable compounds, which can be used for further reactions without isolation. A convenient version of the reaction has been proposed[106] using triphenylphosphine on a support, which facilitates the separation of phosphorus compounds from imidoyl halides.

The reaction with triphenylphosphine and CCl_4 has been successfully carried out for trihalogenoacetylpentafluoroanilines in order to synthesise *N*-(pentafluorophenyl)halogenoacetimidoyl chlorides:[107]

$$C_6F_5NHCOR \xrightarrow[(C_6H_5)_3P]{CCl_4} C_6F_5N{=}C(Cl)R$$

$R = CF_3, CCl_3$ $\qquad$ $R = CF_3, CCl_2H$

NNN'-Substituted ureas[105,108,109] and the *S*-esters of thiocarbamic acid[105] react with CCl_4 and $(C_6H_5)_3P$ like the amides. The dione (XIII) reacts with trichloro-1,2-phenylenedioxyphosphorane and is converted into the azine (XIV) in 70% yield:[110]



(XIII) (XIV)

IV. REACTIONS OF COMPOUNDS WITH A NITROGEN–CARBON MULTIPLE BOND

1. Reactions of Ketoximes and Aldoximes

Aromatic and aryl-substituted aliphatic ketoximes undergo the Beckmann rearrangement on treatment with CCl_4 and $(C_6H_5)_3P$, affording imidoyl chlorides. The unsubstituted aryl group then migrates in the diaromatic ketoximes, while in aryl-substituted aliphatic ketoximes the aryl group migrates. The yields are in the range 70–90%:[111]

$$(C_6H_5)_3P + CCl_4 + R^1R^2C{=}N{-}OH \rightarrow R^1{-}C(Cl){=}N{-}R^2 \ ;$$

$R^1 = C_2H_5, C_6H_5, 4\text{-}ClC_6H_4$; $R^2 = C_6H_5$.

Under these conditions, the dialiphatic ketoximes are apparently also converted into imidoyl chlorides, but the latter cannot be isolated.[112] Imidoyl chlorides are likewise obtained in the reactions of ketoximes with dichlorophosphorane in the presence of triethylamine.[111] The intermediate *N*-chloroketimines or their precursors, namely *O*-phosphorylated ketoximes, undergo the Beckmann rearrangement in these reactions.[111]

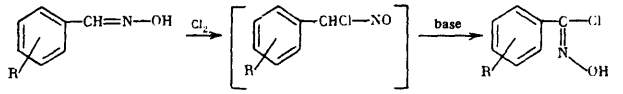
The Beckman rearrangement of *O*-substituted oxime derivatives on treatment with trimethylsilyl iodide or diethylaluminium iodide in an aprotic medium under mild conditions makes it possible to obtain high yields of imidoyl iodides, which can be used for further reactions with isolation in a pure form:[113]

$$R^1R^2C{=}N{-}OX \xrightarrow[\text{or } (C_2H_5)_2AlI]{(CH_3)_3SiI} R^1{-}N{=}C(R^2)I \ ;$$

$X = COCH_3, COC_6H_5, COOC_2H_5$

Derivatives of acetone, diethyl ketone, acetophenone, cyclohexanone, and cyclododecanone oximes have been investigated in these reactions.

Aldoximes are converted into compounds with the imidoyl chloride group on treatment with various chlorinating agents. The chlorination of benzaldoximes with chlorine in chloroform or methylene chloride, containing an admixture of ethanol or in the presence of triethylamine as the catalyst, makes it possible to obtain benzohydroximoyl chlorides in satisfactory yields.[114–122] The reaction intermediates are chloronitroso-compounds, which isomerise to hydroximoyl chlorides:



$R = 4\text{-}C_6H_5$; $4\text{-}NH_2$; $2,6\text{-}Cl_2$; H, $3\text{-}NO_2$ and $4\text{-}NO_2$; 2-, 3-, and 4-Cl; $2,6\text{-}Cl_2$.

The chlorination of pentachlorobenzaldoxime can be achieved without a catalyst. In order to obtain pentafluorobenzohydroximoyl chloride, nitrosyl chloride is used as the chlorinating agent since the reaction hardly occurs with chlorine.

A convenient and selective method of synthesis of benzohydroximoyl chlorides from the corresponding aldoximes on treatment with *N*-chlorosuccinimide has been described.[123,124] Chloral oxime is converted into trichloroacetohydroximoyl chloride on treatment with chlorine.[125]

2. Reactions of Aldimines and Aldazines

The formation of imidoyl chlorides has been postulated in the reaction of *N*-benzylideneanilines with PCl_5. Imidoyl chlorides were converted into the corresponding amides without isolation.[126] Satisfactory results have been obtained with *N*-benzylideneaniline, *N*-benzylidene-*p*-toluidine, and *N*-benzylidene-*p*-chloroaniline, but *N*-benzylidene-*p*-nitroaniline could not be made to undergo this reaction:

$$C_6H_5CH{=}N{-}R \xrightarrow{PCl_5} C_6H_5C(Cl){=}N{-}R \xrightarrow{H_2O} C_6H_5CONHR \ .$$

Aldazines of the type of 2,3-diazabuta-1,3-diene are converted into monochloro- or dichloro-azines on treatment with chlorine in inert solvents or in anhydrous acetic acid, while their bromination and iodination proceed in a more complex manner. These reactions have been described in detail by Buzykin and co-workers.[12,13] A convenient version of the synthesis of such chlorides involves the interaction of aroylhydrazones with thionyl chloride and subsequent chlorination of the 1-chloro-derivatives formed to 1,4-dichloro-2,3-diazabuta-1,3-dienes [127] [Pilgram and Skiles [128] described the more complex reaction of aroylhydrazones of aliphatic perfluoroaldehydes with $SOCl_2$ in the presence of dimethylformamide (DMF)]:

$$ArCONHN{=}CHR \xrightarrow{SOCl_2} ArCCl{=}N{-}N{=}CHR \xrightarrow[CH_3COOH]{Cl_2} Ar{-}C(Cl){=}N{-}N{=}C(Cl)R \ ,$$

$Ar = C_6H_5, 4\text{-}ClC_6H_4, 4\text{-}CH_3C_6H_4$; $R = C_6H_5, 4\text{-}NO_2C_6H_4, CF_3, C_2F_5, C_3F_7$.

The method makes it possible to obtain the compounds in satisfactory yields and free of isomers, which is especially important for asymmetric derivatives. However, when it is used, one must take into account the symmetrisation side reactions on treatment with $SOCl_2$.[13]

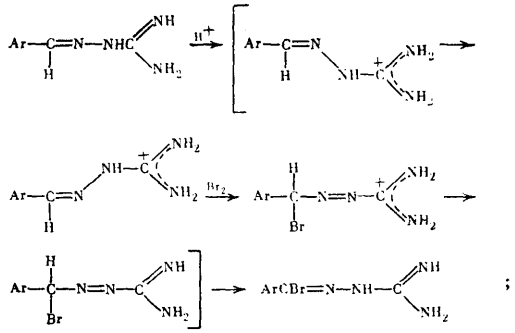
3. Reactions of Hydrazones

New *N*-arylhydrazonobromides have been obtained by the usual methods for the synthesis of compounds of this kind involving treatment with the arylhydrazones of aromatic and

aliphatic aldehydes with bromine in acetic acid. The reaction kinetics has been investigated and the role of the electronic steric factors in the formation of the product has been discovered.[12,89,129-131]

N-(Phenyl)trifluoroacetohydrazonobromide and the corresponding chloride can be synthesised in yields up to 70% on halogenation of the phenylhydrazone of trifluoroacetaldehyde with *N*-bromo- and *N*-chloro-succinimide in DMF.[132]

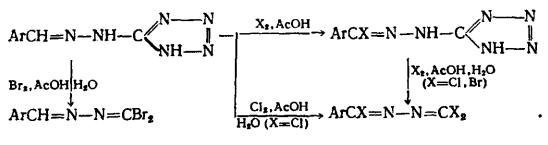
A new group of reactive *N*-amidinohydrazonobromides have been synthesised by brominating amidinohydrazones with bromine in aqueous acetic acid.[133] The compounds were isolated in the form of stable hydrobromides. The kinetic data obtained agree with the reaction mechanism in which the slow rate-determining step is the geometrical isomerisation of the protonated form of the initial thermodynamically stable (*E*)-isomer of the amidinohydrazone to the protonated form of the (*Z*)-isomer followed by the rapid stage involving the bromination of this form:



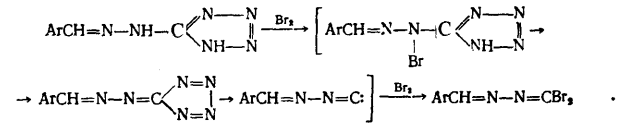
Ar = 4-XC_6H_4; X = OCH_3, CH_3, $(CH_3)_2CH$, H, Cl, Br.

The formation of hydrazonobromides is also postulated in the bromination of arylidenesemicarbazones with bromine in anhydrous acetic acid, but the final products are triazolones.[134]

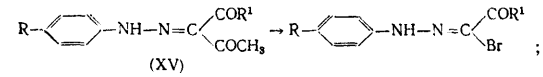
The pathway followed in the reactions of the tetrazolylhydrazones of aromatic aldehydes with chlorine or bromine in acetic acid depends on the conditions.[13] On treatment with halogens in glacial acetic acid, the methylidyne proton of the hydrazone is slowly substituted by the halogen and tetrazolylbenzohydrazonochlorides or the corresponding bromides are obtained respectively. On treatment with halogens in aqueous acetic acid, these compounds undergo oxidative cleavage on the tetrazole ring and are converted into 1,1,4-trihalogeno-2,3-diazabutadienes. Treatment of the initial tetrazolylhydrazones with halogens in aqueous acetic acid also leads to the cleavage of the tetrazole ring. The 1,1-dibromo- and 1,1,4-trichloro-derivatives are then formed in the reactions with bromine and chlorine respectively. The bromination of the 1,1-dibromo-derivative to the 1,1,4-tribromo-derivative does not take place. Thus, in order to obtain the 1,1,4-trihalogeno-derivatives of 2,3-diazadienes, it is necessary that the methylidyne position be halogenated before the cleavage of the tetrazole ring:



The study of the bromination kinetics suggested the following mechanism of the formation of 1,1-dibromo-derivatives:



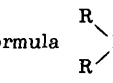
The bromination of the 5-phenyltetrazolylhydrazones of aromatic aldehydes has been described by Hegarty et al.[135] The attempts to involve ketone tetrazolylhydrazones in the bromination reaction were unsuccessful with the exception of benzophenone tetrazolylhydrazone.[136] On the other hand, *C*-alkoxycarbonyl derivatives of *N*-arylhydrazonobromides have been obtained[137] by brominating hydrazones (XV) in a mixture of glacial acetic acid and acetic anhydride in the presence of sodium acetate:

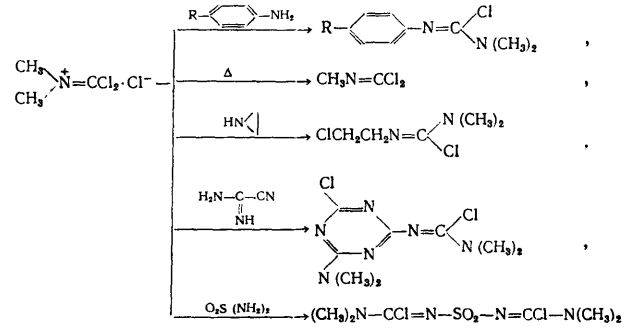


(XV)

R = Br, CH_3; R^1 = OC_2H_5, OCH_3.

4. Reactions of Dichloromethyleneammonium Salts

The highly reactive dichloromethyleneammonium salts having the general formula , which have been vigorously investigated in recent years, can serve as starting materials in the synthesis of carboimidoyl dichlorides and chlorides. Thus thermolysis of dichloromethylenedimethylammonium chloride above 100 °C leads to *N*-methylcarboimidoyl dichloride and its reaction with compounds containing the amino-group makes it possible to obtain smoothly chloroformamidines:

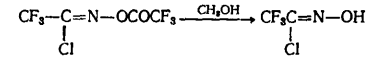


The reactions of dichloromethyleneammonium salts are described in greater detail in Refs.138–141.

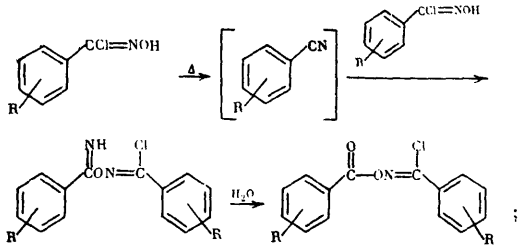
5. Reactions of Imidoyl Halides

For the synthesis of new imidoyl halides, it is possible to use the reactions of the compounds themselves involving the substitution of the halogen atom at the N=C bond, the reactions of other substituents, and also isomerisation not involving the N=C–Hal group. The methods associated with the reactions of the first type have been examined in a review.[142] The reactions of the second type are extremely varied. Thus difluoroacetohydroximoyl chloride can be obtained from *O*-(trifluoroacetyl)trifluoroacetohydroximoyl chloride with methanol.[46-49,143] The reverse reaction makes it possible to synthesise *O*-acylhydroximoyl chlorides from

hydroximoyl chlorides:[122,144,145]

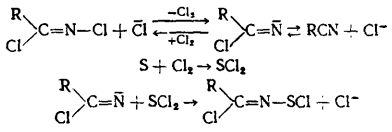


Pyrolysis of benzohydroximoyl chlorides containing electron-accepting substituents in the ring leads to *O*-benzoylbenzohydroximoyl chlorides, but the yields of the products are low.[146] The reaction mechanism involves the reactions of intermediate benzonitriles:



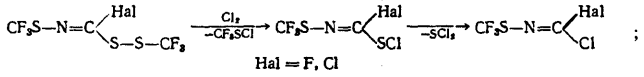
R = 3-NO_2, 4-NO_2, 4-Cl.

On interaction with sulphur in the presence of a chloride ion donor (tetrabutyl or tetraethyl-ammonium chloride), *N*-chloroformimidoyl chlorides are converted into *N*-chlorothioformimidoyl chlorides.[147] The proposed reaction mechanism is presented below:

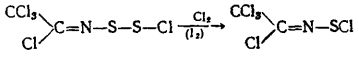


When R = Cl or CCl_3, the products can be isolated, but, when R = CN or $-CCl_2-CN$, further reactions take place. *N*-Alkylthio- or *N*-phenylthio-formimidoyl chlorides are formed in the reactions with disulphides.[148] Bis-*N*-chloroformimidoyl chlorides react with disulphides analogously.

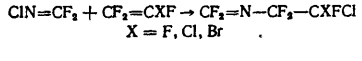
The chlorination of *N*-(trifluoromethylthio)trifluoromethyldithioimidoyl fluoride or chloride takes place with cleavage of the S–S bonds:[149]



Another example of reactions with cleavage of the S–S bond has been described:[150]



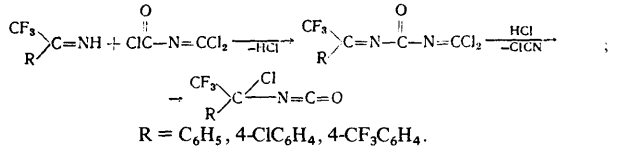
N-Chlorocarboimidoyl difluoride reacts via a radical mechanism with fluoro-olefins at a high temperature affording *N*-halogenoalkylcarboimidoyl difluorides.[151,152] The degree of conversion of the initial imidoyl difluoride reaches 75–95%:



The reaction does not take place with hydrogen-containing olefins.

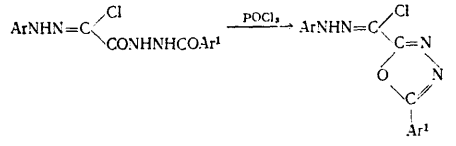
The conversion of *N*-trichloromethylcarboimidoyl dichloride into *N*-chloroformylcarboimidoyl dichloride in a high yield in reactions with aliphatic aldehydes and acid anhydrides has been described.[153]

NN'-Bisalkylideneureas have been isolated in the reactions of ketimines with trichloromethyl isocyanate, which exists preferentially in the form of *N*-chloroformylcarboimidoyl dichloride, under mild conditions in the absence of HCl.[154] In the presence of HCl and on heating, the reaction proceeds further and α-chloroalkyl isocyanates are formed in 75–80% yields:



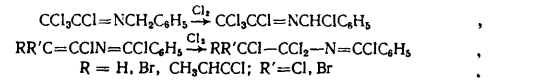
R = C_6H_5, 4-ClC_6H_4, 4-$CF_3C_6H_4$.

The reaction of a substituent, accompanied by intramolecular cyclisation, has been observed on treating *N*-arylhydrazonochloroacetyl-*N*-benzoylhydrazines with $POCl_3$:[155]



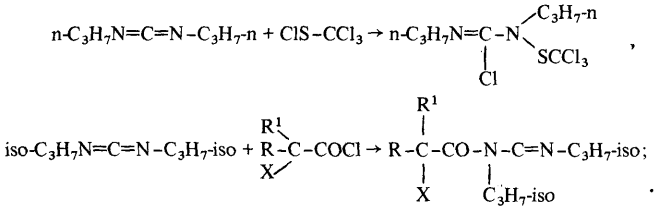
The isomerisation of (*Z*)-isomers of *O*-alkylbenzohydroximoyl chlorides to the (*E*)-isomers takes place on irradiation with UV light or under the conditions of acid catalysis.[55,56,156]

The reactions of substituents in imidoyl chlorides involving chlorination have been described.[51,52,157] Some examples are presented below:



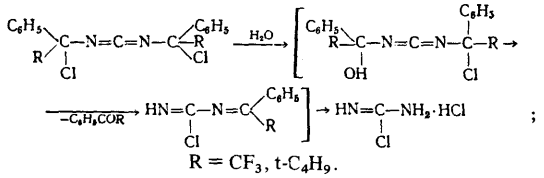
6. Reactions of Carbodiimides

Trichloromethanesulphenyl chloride or α-halogenoacid chlorides add under mild conditions to the C=N bond in carbodiimides affording the corresponding chloroformamidines:[20,158]



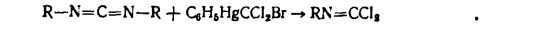
X = Cl, Br; R, R^1 = H, CH_3

On treatment with water, chloroalkylcarbodiimides are converted into the hydrochloride of chloroformamidine:[159]



R = CF_3, t-C_4H_9.

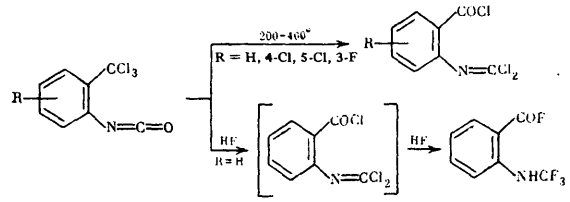
Diisopropyl- or dicyclohexyl-carbodiimide reacts with bromodichloromethylphenylmercury, as a source of dichlorocarbene, giving rise to the corresponding carboimidoyl dichloride:[160]



7. The Synthesis from Isocyanates and Isothiocyanates

An unusual intramolecular rearrangement with oxygen transfer in a series of *o*-trichloromethylphenyl isocyanates leads to *N*-phenylcarboimidoyl dichlorides.[161,162] It has

been detected in the high temperature thermolysis of these compounds and, in addition, apparently also when the latter were treated with HF:



Chloro-1,3-diaza-1,3-dienes can be obtained from perchloroethyl isocyanate and triphenylphosphazo-compounds as a result of the 1,3-chlorotropic shift in the $-C-N=C-$ triad in the carbodiimides formed initially:[94]

$$CCl_3CCl_2N=C=O + (C_6H_5)_3P=NR \rightarrow [CCl_3CCl_2N=C=N-R] \rightarrow CCl_3CCl=N-CCl=NR\ ;$$
$$R = \text{iso-}C_3H_7,\ C_6H_5.$$

Carboimidoyl dichlorides can be obtained by chlorinating isocyanates or isothiocyanates:

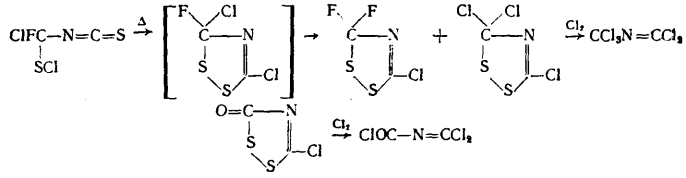
$$SF_5-N=C=O \xrightarrow{PCl_5} SF_5-N=CCl_2 \text{ (Ref.163)},$$

$$R-N=C=S \xrightarrow{Cl_2} \left[RN=C\begin{matrix}Cl\\SCl\end{matrix}\right] \rightarrow R-N=CCl_2 \text{ (Refs.164, 165)};$$

$$R=CH_3,\ CH_2C_6H_5,\ C_6H_5,\ CF_2Cl,\ CF_3\ ,$$

$$F(S)C-N=C=S \xrightarrow{Cl_2} CFCl_2-N=CCl_2 \text{ (Ref.165)}.$$

An unusual pathway leading to carboimidoyl dichloride has been discovered in the case of the chloride of chlorofluoroisothiocyanatomethanesulphenic acid.[165] On heating, this compound undergoes intramolecular cyclisation to a 1,2,4-dithiazole derivative. Such dithiazoles or their hydrolysis products afford carboimidoyl dichlorides on treatment with chlorine:

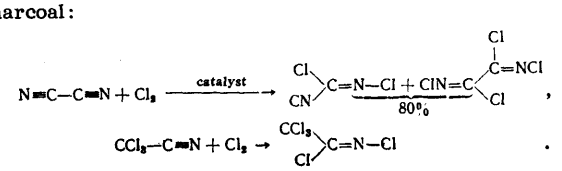


8. Addition to Nitriles, Cyanates, and Isonitriles

A large number of various imidoyl chlorides and dichlorides have been obtained by adding chlorine, sulphenyl chlorides, disulphides, sulphur dichloride, thionyl chloride, and sulphuryl chloride to the C ≡ N bonds of various nitriles. The chlorination of nitriles with electron-accepting substituents leads to substituted *N*-chloroformimidoyl chlorides.[166,167] The addition of chlorine to the activated C ≡ N bond in sulphonyl cyanides takes place readily and with a quantitative yield:

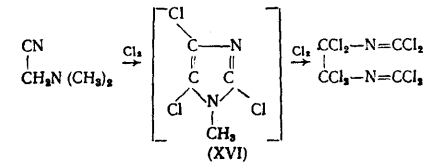
$$RSO_2C{\equiv}N + Cl_2 \rightarrow RSO_2C(Cl)=N-Cl\ .$$

In the case of less activated nitriles, such as, for example, cyanogen or trichloroacetonitrile, the reaction is performed in the presence of catalysts—tetramethylammonium chloride or charcoal:



The first stage of the chlorination reaction is nucleophilic attack by the chloride ion on the electron-deficient carbon atom of the cyano-group.

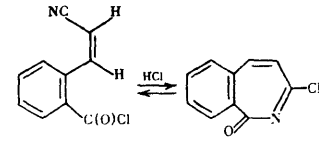
The high-temperature chlorination of dimethylaminoacetonitrile to biscarboimidoyl dichloride (XVI) proceeds via the intermediate formation of an *N*-methylimidazole derivative and subsequent ring opening:



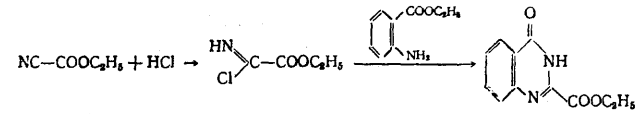
(XVI)

The reactions of nitriles with chloro-derivatives of sulphur proceed in the presence of catalysts (sources of chloride ions) and make it possible to obtain sulphur-containing imidoyl chlorides and dichlorides.[148,149,168-171]

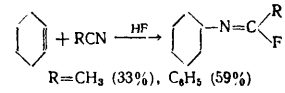
Cyclic imidoyl chlorides are formed in satisfactory yields in the reactions involving the addition of HCl to nitriles, accompanied by intramolecular cyclisation,[172] for example:



The interaction of ethyl cyanoformate and HCl in acetic acid leads to the unstable ethoxycarbonylformimidoyl chloride, which has been detected from the presence of products of its reactions with nucleophiles added to the system. Ethyl 4-quinazolone-2-carboxylate has been obtained in this way in 50% yield in the presence of *o*-ethoxycarbonylaniline:[173]



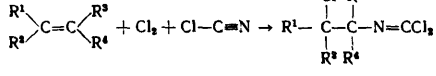
The Ritter condensation of nitriles with olefins in the presence of HF led to imidoyl fluorides, which were isolated in a pure form.[174,175] This reaction made it possible to obtain imidoyl fluorides, little known hitherto, and to investigate their properties:



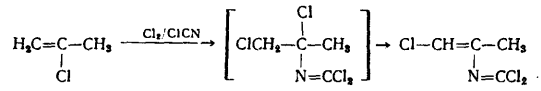
R=CH$_3$ (33%), C$_6$H$_5$ (59%)

The use in these reactions of not only cyclic but also linear olefins with branched and unbranched chains at the C=C bond showed that alkenes with branched alkyl groups do not form imidoyl fluorides, while those with unbranched groups react normally. For example, pent-1-ene reacts with benzonitrile to form a mixture of *N*-(2-pentyl)benzimidoyl fluoride and the corresponding 3-pentyl derivative in 62% yield. The different behaviour in these processes of the two types of olefins is determined by the possibility of further reactions of the ions formed as intermediates in the addition of HF to olefins.

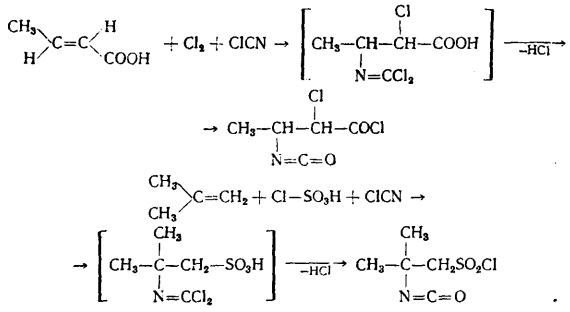
A preparative method of synthesis of aliphatic *N*-(β-chloroalkyl)carboimidoyl dichlorides consists in the electrophilic addition of chlorine to olefins in the presence of chlorocyanogen:[176]



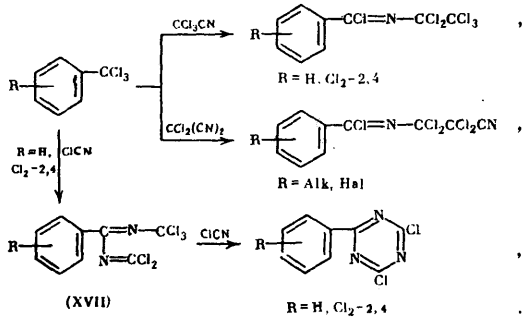
Especially satisfactory yields have been obtained with vinyl chloride or butadiene. When α-halogenocarboimidoyl chlorides are formed, dehydrohalogenation, which takes place readily, makes it possible to obtain at once αβ-unsaturated carboimidoyl dichlorides:



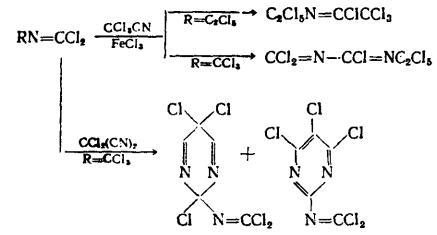
However, in those cases where the olefin contains an acid group or an electrophile capable of introducing such groups is used, the reaction does not stop with formation of carboimidoyl dichloride:



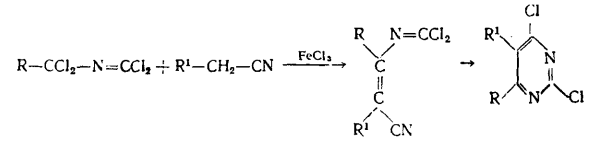
N-Polychloroalkylimidoyl chlorides or dichlorides are formed on interaction of activated nitriles, such as chlorocyanogen, trichloroacetonitrile, 2,2,3-trichloropropionitrile, and dichloromalonidinitrile with compounds having the CCl_3 or CCl_2H groups.[177,178] The reactions are catalysed by $FeCl_3$ or $AlCl_3$. The addition of chlorine-containing compounds to the activated nitrile group takes place in the first stage and is followed by the migration of chlorine (chlorotropism), which results in the formation of imidoyl chlorides or dichlorides. In a number of instances at low temperatures, the processes can be arrested at this stage. In other cases the formation of heterocyclic compounds is observed. Thus imidoyl chlorides are the main products of the reaction of dichloroacetonitrile with trichloromethylbenzenes,[177] but in the reaction with chlorocyanogen cyclisation to substituted triazines takes place readily and the intermediate carboimidoyl dichloride (XVII) could be isolated in small amounts only in the case of 2,4-dichloro-1-trichloromethylbenzene:[178]



Imidoyl chlorides have also been isolated in the reactions of trichloromethylbenzenes with dichloromalonodinitrile,[177] while the reaction with benzylidenechloro-derivatives gave rise to pyrimidine derivatives.[178] Trichloromethoxybenzenes and carboimidoyl dichlorides with perchloroalkyl groups have also been used as the polychloroalkyl component:[177-179]

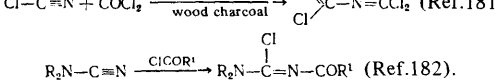


It has also been found that, in the presence of Lewis acids and at elevated temperatures, carboimidoyl dichlorides of the type $RCCl_2N{=}CCl_2$ react with nitriles having two hydrogen atoms in the α-position, affording chloropyrimidines.[180] The elimination of HCl is rate determining in this two-stage reaction. In most cases the reaction can be stopped at the first stage involving the formation of carboimidoyl dichloride:

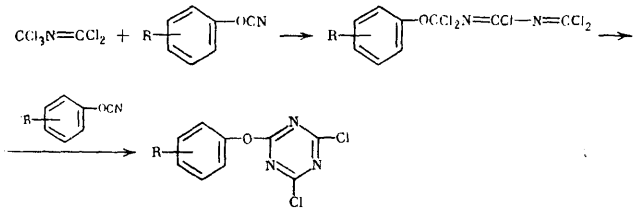


R=Cl, CCl_3, C_6H_5; R^1=H, Cl, CH_3, C_6H_5 etc.

The reaction proceeds analogously also when the α-chlorine atoms in carboimidoyl dichloride have been substituted by hydrogen and the α-hydrogen atoms of the nitrile have been substituted by chlorine. *N*-Acylimidoyl chlorides and dichlorides can be obtained from nitriles and acyl chlorides:



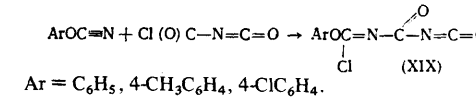
Like nitriles, phenyl isocyanates react with *N*-trichloromethylcarboimidoyl dichloride, giving rise to heterocyclic derivatives.[178] In some cases it is possible to isolate small amounts of the primary products of the chlorotropic rearrangement:



R = H, Cl-4, Cl_2-2, 4, $(CH_3)_2$-2, 4

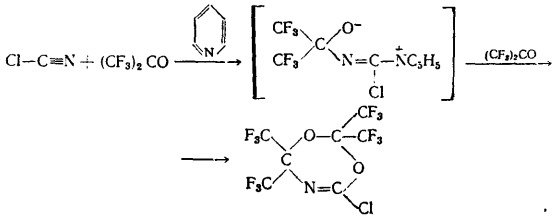
Cyanates react with acyl chlorides similarly to nitriles.[182] The reaction is carried out by heating in inert solvents, the yield of products being 45–90%. Phosgene reacts at 0–20 °C.

The electrophilic addition of chloroformyl isocyanate to aromatic cyanates leads to compounds of type (XIX):[181,183]



Ar = C_6H_5, 4-$CH_3C_6H_4$, 4-ClC_6H_4.

The interaction of chlorocyanogen with hexafluoroacetone in the presence of pyridine results in the formation of chlorodioxazine:[184]



N-Bromocarboimidoyl difluoride has been obtained by brominating fluorocyanogen in the presence of alkali metal fluorides:[185]

$$FC{\equiv}N + Br_2 \xrightarrow{MF} [CF_2{=}\bar{N}\,\dot{M}] \xrightarrow{Br_2} CF_2{=}N{-}Br$$
$$M{=}K,\ Cs,\ Rb$$

It has been suggested that *N*-pentafluorotelluroimidoyl chloride and dichloride be obtained by the photolysis of chlorocyanogen or trifluoromethylcyanogen with TeF_5Cl. Up to 10% of tetrachloro-2,3-diazabuta-1,4-diene is then obtained as a side product.[186]

The radical addition of perfluoroalkyl iodides to isonitriles with primary or secondary alkyl groups is a method of synthesis of imidoyl iodides with perfluoroalkyl groups:[187,188]

$$RNC + R_FI \rightarrow RN{=}C\!\!<^{I}_{R_F}$$
$$R = n\text{-}C_4H_9,\ \text{cyclo-}C_6H_{11};\ R_FCF_3(CF_2)_n\ (n = 3, 5, 7).$$

However, there is no condensation with t-alkyl or aromatic isonitriles under these conditions. By carrying out the reactions in the presence of copper, it has been possible to involve in them also the nitriles indicated above. The yields of imidoyl iodides are mainly 70–90%. The mechanism of the copper-catalysed reaction involves the oxidative addition of R_FI to the copper complex of the isonitrile and the subsequent migration of the perfluoroalkyl group and iodine to the isonitrile ligand.

Direct fluorination of isonitriles by a stream of elemental fluorine diluted with argon or nitrogen makes it possible to obtain carboimidoyl difluoride:[189]

$$RNC + F_2 \rightarrow RN{=}CF_2\ ,$$
$$R = t\text{-}C_4H_9,\ C_6H_5,\ 2\text{-}FC_6H_4,\ 4\text{-}ClC_6H_4.$$

N-Trifluoromethylimidoyl halides are formed in the reactions of *N*-trifluoromethylisonitrile with HHal or SF_5Br.[190]

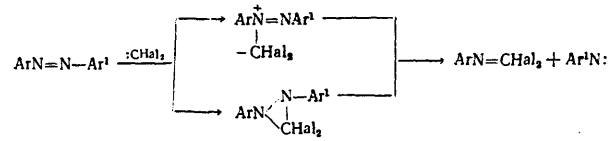
V. REACTIONS OF COMPOUNDS WITH A NITROGEN–NITROGEN MULTIPLE BOND

Azides, azo-compounds, and azoxy-compounds react with dichlorocarbene, generated in the course of the reaction from phenyltrihalogenomethylmercury, giving rise to carboimidoyl dichlorides.[191,192] Thus the decomposition of phenyl azide in the presence of phenyltrichloromethylmercury leads to *N*-phenylcarboimidoyl dichloride in 70% yield. Sodium trichloroacetate or ethyl trichloroacetate can also serve as a source of dichlorocarbene. The reaction kinetics has been investigated for phenyl, *p*-methoxyphenyl, and *p*-chlorophenyl azides.[192]

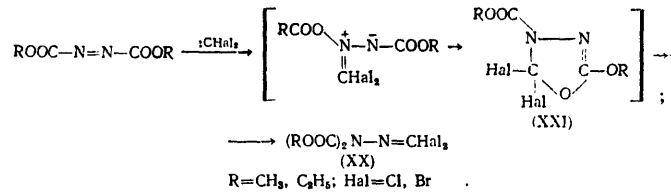
The reaction of an excess of azo- and azoxy-benzenes with bromodichloromethylphenylmercury results in the formation of a mixture of the same carboimidoyl chlorides. The azoxy-compounds are apparently initially deoxygenated by the organomercury derivative and the resulting azobenzenes react with dichlorocarbene. The overall yield of the products is low:[191]

$$\left.\begin{matrix} ArN{=}NAr^1 \\ ArN{=}N{-}Ar^1 \\ \quad\downarrow O \end{matrix}\right] \xrightarrow{C_6H_5HgCCl_2Br} ArN{=}CCl_2 + Ar^1N{=}CCl_2\ ;$$
$$Ar = C_6H_5,\ 4\text{-}ClC_6H_4,\ 4\text{-}CH_3C_6H_4;\ Ar^1 = C_6H_5,\ 4\text{-}ClC_6H_4.$$

The mechanism of the formation of carboimidoyl dichloride can include the participation of open-chain or cyclic intermediates, for example:



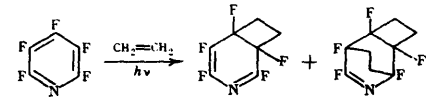
The reaction of trihalogenomethylmercury derivatives with aliphatic azo-compounds proceeds differently.[193] Depending on the mercury compound, azodicarboxylate esters afford dichloro-, dibromo-, or bromochloro-derivatives of compound (XX):



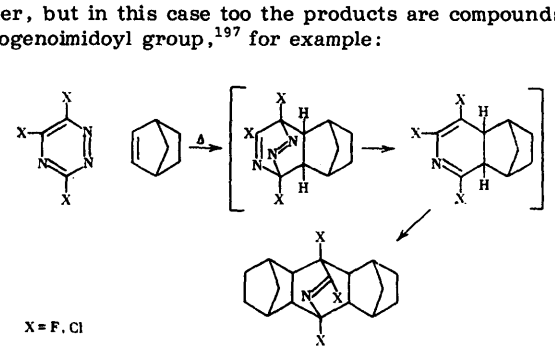
The reaction begins with the electrophilic attack by the nitrogen atom on the dihalogenocarbene with subsequent formation of intermediate 1,3,4-oxadiazolines (XXI), which have been detected spectroscopically.

VI. REACTIONS OF COMPOUNDS WITH A CARBON–CARBON MULTIPLE BOND

Compounds with the imidoyl chloride or imidoyl fluoride groups incorporated in a ring are formed in the photochemical Diels–Alder addition of unsaturated hydrocarbons to nitrogen-containing heterocycles. Thus the reactions of pentafluoropyridine with linear and cyclic olefins and also with acetylenic derivatives give rise to 1:1 and 2:1 adducts containing the imidoyl fluoride group:[194–196]



The thermal reactions of 3,5,6-trifluoro- or 3,5,6-trichloro-1,2,4-triazines with olefins proceed in a more complex manner, but in this case too the products are compounds with a halogenoimidoyl group,[197] for example:



VII. THERMOLYSIS OF 3,3-DIHALOGENOAZIRIDINES

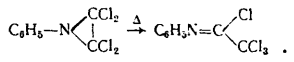
3,3-Dihalogeno-1,2-diphenylaziridines are converted into *N*-phenylimidoyl halides in various solvents at 80–100 °C:[198]



X=Y=Cl, Br; X=Cl, Y=Br; X=F, Y=Br; X=F, Y=Cl .

This thermal isomerisation involves the 1,2-migration of the halogen and the dissociation of the adjoining C–N bond with the opening of the aziridine ring. The study of the reaction kinetics and analysis of the calculated data made it possible to establish the reaction mechanism. The series based on the capacity of the halogens for migration, namely Br > Cl > F, found is consistent with the C–Hal bond energies. The rate of isomerisation depends not only on the nature of the migrating halogen but also on the halogen which remains. Fluorine significantly facilitates migration compared with chlorine and bromine.

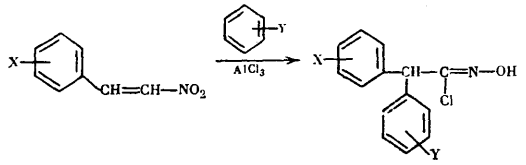
The yields of the imidoyl halides are fairly high. 3,3-Dibromo-1,2-diphenylaziridine is thermally less stable than the corresponding dichloro-derivative. Tetrachloroaziridines are thermally more stable than dichloroaziridines, but at 180 °C the two isomerise to imidoyl chlorides:[191]



The rearrangement of tetrachloro-*N*-isopropylaziridine does not take place even on prolonged heating.

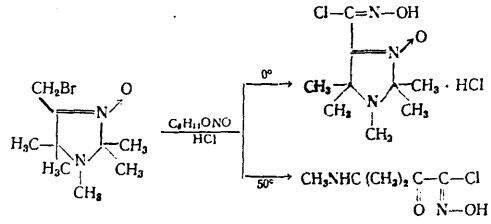
VIII. OTHER METHODS

New diarylacetohydroximoyl chlorides have been obtained by the reaction, already known previously, of β-nitrostyrenes with aromatic hydrocarbons in the presence of Lewis acids, which proceeds via 1,4-addition to the conjugated nitro-olefin chain:[199,200]

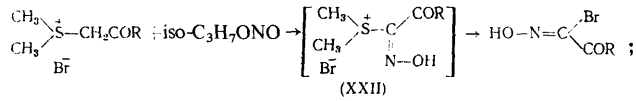


X = 2-Br; 2,4-Cl_2; 2,6-Cl_2; 2-Cl, 6-F;
Y = H, 4-CH_3, 4-C_2H_5, 4-iso-C_3H_7, 4-Br, 4-F, 4-Cl.

The reactions of β-nitrostyrenes with acetyl chloride form under these conditions, together with other products, *N*-acetoxyphenylchloroacetotrihydroximoyl chlorides, whose yield depends significantly on the Lewis acid employed (it is a maximum for $TiCl_4$) and the substituents in the nitrostyrene molecule.[201,202] In the reaction with benzoyl chloride in the presence of triethylamine, trifluoronitroethane is converted into trifluoroacetohydroximoyl chloride (yield 30%).[203] Certain heterocyclic hydroximoyl chlorides have been obtained by the conversion of the corresponding halogenomethyl derivatives into oximes by treatment with isopentyl nitrite in hydrochloric acid.[204,205] In a series of 3-imidazoline 3-oxides, the formation of the hydroximoyl chloride at an elevated temperature is accompanied by the opening of the heterocyclic ring:



Hydroximoyl bromides have been obtained in satisfactory yields by the reactions of isopropyl nitrite with sulphonium bromides.[206] Under these conditions, the salt (XXII) is apparently formed initially and then undergoes intramolecular nucleophilic substitution by the bromide ion with formation of a sulphide:

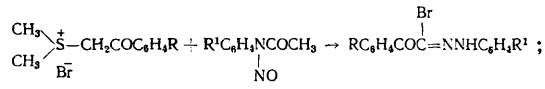


(XXII)

R=C_6H_5, CH_3, OC_2H_5 .

The nitrosation of dimethylphenylacylsulphonium bromide with sodium nitrite and HCl in aqueous dioxan leads to benzoylhydroximoyl chloride, also in a high yield.[207] Similar chlorides are formed effectively also in the nitrosation of β-ketosulphoxides with sodium nitrite in HCl, which is a fairly convenient and general method of synthesis of hydroximoyl chlorides of this kind.[208]

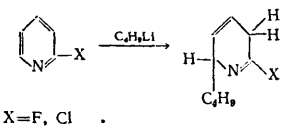
The azo-coupling reaction between sulphonium bromides and *N*-nitrosoacetanilides, which is similar to their nitrosation reaction, in non-aqueous solvents leads to hydrazonobromides:[209]



R = H, 4-CH_3, 4-Br, 4-NO_2; R^1 = H, 4-CH_3, 4-OCH_3, 4-Cl.

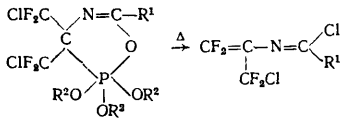
Imidoyl fluorides and difluorides are also formed in the photolysis of various polyfluoro-compounds. Thus perfluoroimidoyl fluorides and difluorides with a linear structure have been obtained in this way from perfluoroaza- and perfluorodiaza-cyclohexadienes;[210] *N*-(1-Chloro-octafluorobutyl)carboimidoyl difluoride has been obtained in 22% yield from *N*-chloroperfluoropiperidine.[211] The low-temperature photolysis of 1-adamantyl nitrite in the presence of trichloronitrosomethane results in the formation of up to 5% of *N*-[*O*-(1-adamantyl)]carboimidoyl chloride, which was isolated and characterised.[212]

Relatively unstable cyclic imidoyl fluorides and chlorides are formed from 2-fluoro and 2-chloro-pyridines by their reaction with butyl-lithium:[213]



X=F, Cl .

The thermolysis of 2,3-dihydro-1,4,2,λ^5-oxazaphosphole derivatives leads to reactive *N*-vinylimidoyl chlorides:[214]



R^1 = t-C_4H_9, C_6H_5, 4-$CH_3C_6H_4$, 4-ClC_6H_4, CH =CH-C_6H_5; R^2 = CH_3, C_6H_5.

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During the preparation of the manuscript for printing, new data were published on the synthesis of various compounds with halogenoimidoyl groups or on their formation as intermediates. Most of these communications are concerned with the reactions of nitriles and isonitriles with acyl halides,[215-219] sulphenyl chlorides or sulphur dichloride,[220-222] and the halogens (chlorine and bromine) in the presence of mercury difluoride,[223] and also with the reactions of amide groups on treatment with PCl_5.[224-227] Halogenoimidoyl derivatives have also been obtained or have been postulated in the chlorination of aldoximes,[228] in the interaction of perhalogenoalkylamines with SbF_5 [229] or in their thermolysis,[223] in the reactions of substituents in compounds already containing the halogenoimidoyl group,[222,230] and in certain other reactions.[231-237]

The main trend in these investigations has been the study of the configurations of different halogenoimidoyl groups by spectroscopic methods and the synthesis of the individual isomers and their interconversions.[228,237-239]

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