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N-Functionally substituted imines of polychlorinated (brominated) aldehydes and ketones

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Abstract. Published data on the synthesis, structure and chemical transformations of *N*-acyl-, *N*-alkoxy(aryloxy)carbonyl-, *N*-carbamoyl-, *N*-sulfonyl- and *N*-phosphoryl-imines of chlorine-(and bromine)-containing ketones and aldehydes are surveyed and described systematically. The influence of polyhaloalkyl and functional substituents at the azomethine bond on their properties is considered. The bibliography includes 198 references.

I. Introduction

The chemistry of imines presents interest for both theoretical and applied organic chemistry.[1–21] On the one hand, azomethines are convenient models for the investigation of stereochemistry of organic compounds, tautomerism and isomerism phenomena, molecular rearrangements and mechanisms of radical, electrophilic and nucleophilic addition at the double bond and cycloaddition.[1–5] On the other hand, imines are used as the starting compounds for organic synthesis,[6] for the synthesis of biologically active[7–10] and natural products,[5] monomers [1] and various nitrogenous heterocycles.[1–5, 11] In addition, compounds containing an azomethine group are known to play an important role in living organisms.[1, 5]

N-Functionally substituted polyhalogenated aldimines and ketimines present special interest due to their enhanced reactivity imparted by electron-withdrawing polyhaloalkyl substituents and by acyl, alkoxy(or aryloxy)carbonyl, -carbamoyl, sulfonyl or phosphoryl group at the N atom.

The chemistry of polyhalogenated *N*-acyl aldimines and ketimines started to develop in the last two or three decades, because it was not until the early 1960s that preparative methods for their synthesis appeared. Quite a large number of review papers devoted to these interesting compounds have been published. The synthesis and properties of *N*-fluoro-, *N*-acyl-, *N*-sulfonyl- and *N*-phosphoryl-imines of polyfluorinated ketones and aldehydes have been considered in the literature fairly comprehensively;[12–17] therefore, they will not be discussed here.

However, known reviews [18–25] dealing with the corresponding polychloro(bromo)-containing derivatives do not cover adequately the chemistry of *N*-acyl-, *N*-carboxy-, *N*-carbamoyl-, *N*-sulfonyl- and *N*-phosphoryl-imines of polyhalogenated aldehydes and ketones.

Therefore, it appears pertinent to generalise and describe systematically the data concerning the methods of synthesis and chemical transformations of *N*-acyl-, *N*-alkoxy(aryloxy)carbonyl-, *N*-carbamoyl-, *N*-sulfonyl- and *N*-phosphoryl-imines of polychlorinated (brominated) aldehydes and ketones $R^1N=CXCHal_nR^2$, where R^1 = Alk(Ar)CO, Alk(Ar)OCO, Alk_2NCO, NH_2CO, Alk(Ar)NHCO, $Alk(Ar)SO_2$, Alk_2NSO_2, $(AlkO)_2P(O)$, $(AlkO)_2P(S)$, $Ar_2P(O)$, $(ArO)_2P(O)$; X = H, Ar, $COOR^3$, CCl_3, OAlk(Ar), CN, NR^4R^5, Cl, *etc.*; *n* = 2, 3; Hal = Cl, Br; R^2 = Alk, ArAlk, *etc.*

II. Synthesis of polychlorinated (brominated) aldimines and ketimines *N*-substituted by carboxylic, carbamic, sulfonic and phosphoric acid residues

The known methods for the synthesis of acid *N*-polychloro(bromo)alkylideneamides can be divided into several groups differing in the approach to the formation of the azomethine bond.

1. Preparation of *N*-acylated ketimines and aldimines from carboxamides and polyhalogenated aldehydes and ketones.

2. Syntheses based on amide derivatives — *N*-sulfinylsulfonamides and *N*-sulfonyl isocyanates — and carbonyl compounds.

3. Successive transformation of α,β-polyhaloalkyl isocyanates into amides and azomethines upon reactions with nucleophiles.

4. Creation of an azomethine bond by a free radical reaction of *N*,*N*-dihaloamides with 1,2-polyhaloethenes and alkynes.

5. Photochemical halogenation of *N*-alkyl(or aryl)amides.

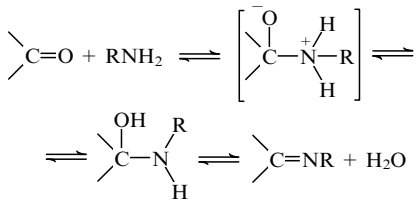
Other methods, which have not found wide application, are also known; they are considered at the end of this Section.

1. Preparation of polychlorinated (or brominated) aldimines and ketimines based on amides and carbonyl compounds

Condensation of carbonyl compounds with amines is a classical method used to introduce an azomethine bond into a molecule. This is a two-stage process involving the intermediate formation of an amino alcohol.

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However, in the general case, this reaction cannot be used to prepare imines of polyhalogenated compounds. The presence of electron-withdrawing groups in the molecule enhances the stability of the intermediate amino alcohol. Therefore, the rate of the synthesis of polyhalogenated aldimines and ketimines is limited by the second stage, that is, dehydration of hemiaminals. Thus it is known that condensation of carboxamides with aliphatic and aromatic aldehydes gives *N*,*N*-alkylidene- or *N*,*N*-arylidene-bisamides,[18] whereas polyhalogenated aldehydes and ketones react with amines and amides to give stable 1-hydroxyalkylamines.[18,26] In the case of aliphatic and aromatic amines and chlorinated aldehydes and ketones, the problem of transformation of amino alcohols into imines was solved by using $TiCl_4$.[27]

For the synthesis of acyl-, alkoxy(or aryloxy)carbonyl- and -carbamoyl-, sulfonyl- and phosphoryl-imines of polyhalocarbonyl compounds, methods based both on dehydration and on other chemical transformations of 1-hydroxypolyhaloalkylamides have been devised.

a. Dehydration of *N*-(1-hydroxypolyhaloalkyl)amides

In the earliest studies[28–30] devoted to *N*-trichloroethylideneamides, it was found that treatment of *N*-(1-hydroxy-2,2,2-trichloroethyl)acetamide, *N*-(1-hydroxy-2,2,2-trichloroethyl)chloro(bromo)benzamides and *N*-(1-methoxy-2,2,2-trichloroethyl)bromobenzamides with dehydrating agents gives bis(1-acylamino-2,2,2-trichloroethyl) ethers instead of the corresponding chloral imines.

An example of fairly easy thermal dehydration giving rise to the target imines has been reported. Chloroacetamide reacts with chloral and bromal[31] yielding *N*-(2,2,2-trichloroethylidene)- and *N*-(2,2,2-tribromoethylidene)chloroacetamides **1a**,**b**.

$$ClCH_2CONH_2 + CX_3CHO \xrightarrow{100\ ^\circ C} ClCH_2CON{=}CHCX_3$$
1a,b

X = Cl (**a**), Br (**b**).

Subsequently, synthetic expedients have been developed which permit dehydration of some chloral hemiaminals.

N-(2,2,2-Trichloroethylidene)-4-toluenesulfonamide **2a** has been prepared by dehydration of the corresponding *N*-(1-hydroxyalkyl) derivative induced by P_2O_5 at 200 °C in benzene or xylene.[32]

$$4\text{-}MeC_6H_4SO_2NHCH(OH)CCl_3 \xrightarrow{P_2O_5} 4\text{-}MeC_6H_4SO_2N{=}CHCCl_3$$
2a (71%)

In our opinion, the sulfonamide derivative is esterified in this reaction by phosphoric anhydride and then phosphoric acid splits off. However, phosphorylimines cannot be prepared by dehydration of *N*-(1-hydroxy-2,2,2-trichloroethyl) dialkyl phosphoramidates.[33] An attempt to dehydrate *N*-(1-hydroxy-2,2-dichloroalkyl)amides was also unsuccessful.[34]

Apparently, the limited scope of the method for the synthesis of imines based on dehydration of hemiaminals of polyhalogenated aldehydes and ketones is due to the fact that these compounds are unstable in the presence of dehydrating agents and decompose to give the initial components or condensation products (esters) under the reaction conditions (see, for example, Refs 28–30).

b. Dehydrochlorination of chloro(bromo)polyhaloalkylamides

Dehydrochlorination of *N*-(1-haloalkyl)amides, which are prepared by chlorination of the corresponding hydroxy derivatives by $SOCl_2$ or PCl_5, is a fairly general method for the synthesis of acyl-, alkoxy- and -carbamoylimines of polyhalogenated carbonyl compounds as well as their sulfonyl and phosphoryl analogues.

This synthetic route was first used[35] to prepare *N*-(2,2,2-trichloroethylidene)benzamide **3a** and *N*-(2,2,2-trichloroethylidene)-*N*-benzyloxycarbonylamine **3b**.

$$Cl_3CCH(OH)NHR \xrightarrow{PCl_5} Cl_3CCH(Cl)NHR \xrightarrow{Et_3N} Cl_3CCH{=}NR$$
3a,b

R = PhCO (**a**), $PhCH_2OCO$ (**b**).

The same method, except that thionyl chloride has been used as the chlorinating agent, has been employed to prepare trichloromethyl- and tribromomethyl-ethylidene-*N*-(alkoxycarbonyl)amines,[36] including various acyl- and alkoxy(aryloxy)-carbonylimines of chloral[37–41] and bromal,[42] acylimines and alkoxycarbonylimines of bromodichloroacetaldehyde,[43,44] and *N*-acetyl(benzoyl)imines and *N*-methoxycarbonylimines of 1,1,2-trichloro-2-phenylpropionaldehyde and 1,1,2-trichlorobutyraldehyde,[45] their yields ranging from 52% to 92%. Several *N*-(2,2,3-trichloropropylidene)amides and *N*-(2,2,3-trichloropropylidene)ethoxycarbonylamine have been prepared in the same way (yields 52%–72%).[46]

$$R_{Hal}C(O)H + RCONH_2 \longrightarrow R_{Hal}CH(OH)NHCOR \xrightarrow{SOCl_2} R_{Hal}CH(Cl)NHCOR \xrightarrow{Et_3N} R_{Hal}CH{=}NCOR$$

R_{Hal} = CCl_3, CBr_3, $CBrCl_2$, $PhCHClCCl_2$, CH_2ClCCl_2, $MeCHClCCl_2$, $AlkCCl_2$; R = Alk, Ar, $PhCH_2$, OEt, OMe.

Synthesis of *N*-(2,2-dichloroalkylidene)acetamides by condensation of dichlorinated aldehydes with acetamide followed by chlorination and then dehydrochlorination of the resulting compounds has been reported.[34] In the same study,[34] dichloroethylidenebenzamide was prepared in a low yield and an attempt to prepare 2,2-dibromoaldimines failed, probably due to the instability of the intermediate hemiaminals formed from 2,2-dihaloaldehydes and amides.

The condensation of carboxamides with methyl trichloropyruvate gave the corresponding *N*-acylhemiaminals, which were then converted into methyl 2-acylimino- and 2-alkoxycarbonylimino-3,3,3-trichloropropionates **4a**–**d**.[47]

$$RCONH_2 + Cl_3CC(O)COOMe \longrightarrow RCONHC(OH)(CCl_3)COOMe \xrightarrow{SOCl_2} RCONHC(Cl)(CCl_3)COOMe \xrightarrow{Et_3N} RCON{=}C(CCl_3)COOMe$$
4a–d

R = Me (**a**), Et (**b**), OMe (**c**), OEt (**d**).

N-(2,2,2-Trichloroethylidene)-*N*′,*N*′-dimethylaminosulfonamide has been synthesised by a traditional multistage procedure based on the condensation of chloral with *N*,*N*-dimethylaminosulfonamide followed by chlorination by PCl_5. Dehydrochlorination of the intermediate compound was carried out on heating.[48]

$$Cl_3CCHO + H_2NSO_2NMe_2 \longrightarrow Cl_3CCH(OH)NHSO_2NMe_2 \xrightarrow{PCl_5} Cl_3CCHClNHSO_2NMe_2 \xrightarrow{\Delta} Cl_3CCH{=}NSO_2NMe_2$$
5

Preparation of the phosphoryl analogues of *N*-acylimines of halogenated aldehydes was first reported in 1965.[49] It was shown that the products of acidolysis of trichlorophosphazo com-

pounds — *N*-polychloroalkylaminophosphoryl dichlorides containing chlorine atoms at the α-position with respect to nitrogen — readily abstract an HCl molecule on treatment with triethylamine to give *N*-(2-chloro-2-methylpropylideneamino)- and *N*-(2,2-dichloro-3,3-dimethylbutylideneamino)phosphoryl dichlorides.[49]

$$RCHClNHPOCl_2 \xrightarrow{Et_3N} \underset{\mathbf{6a,b}}{RCH{=}NPOCl_2}$$

R = Me_2CCl (**a**), Bu^tCCl_2 (**b**).

Several dialkyl *N*-(2,2,2-trichloroethylidene) phosphoramidates have been prepared in 50% – 76% yields from chloral and dialkyl phosphoramidates using chlorination and dehydrochlorination of intermediate products.[33, 50]

$$Cl_3CC(O)H + H_2NP(O)(OR)_2 \longrightarrow Cl_3CCH(OH)NHP(O)(OR)_2 \xrightarrow{SOCl_2}$$

$$\longrightarrow Cl_3CCH(Cl)NHP(O)(OR)_2 \xrightarrow{Et_3N} \underset{\mathbf{7a-e}}{Cl_3CCH{=}NP(O)(OR)_2}$$

R = Me (**a**), Et (**b**), Pr^n (**c**), Pr^i (**d**), Bu^i (**e**).

Dimethyl *N*-(2,2,2-trichloroethylidene) phosphoramidothioate has been synthesised in a similar way.[51]

It has been shown [52, 53] that some tetrachloroalkanesulfonamides can be dehydrochlorinated thermally without using dehydrochlorinating agents. For instance, *N*-trichloroethylidenemethane- and -propane-sulfonamides were synthesised in 73% and 93% yields on distillation of the corresponding tetrachloroethylalkanesulfonamides.

Thus, this method is fairly versatile and permits the preparation of various *N*-functionally substituted imines of polychlorinated (or brominated) aldehydes and ketones. The drawbacks of this method include the large number of stages, the use of corrosive reagents and also the facts that the intermediate hemiaminals are relatively unstable and haloaldehydes with different halogen atoms are inaccessible.

c. Condensation of *N*-sulfinylsulfonamides and *N*-sulfonyl isocyanates with haloaldehydes

Chloral *N*-4-tolylsulfonylimine **2a** has been prepared in 91% yield by the reaction of chloral with unstable *N*-sulfinyl-4-toluenesulfonamide in the presence of $AlCl_3$;[32, 54, 55] the starting amide was synthesised by the reaction of 4-toluene sulfonamide with thionyl chloride in the presence of $AlCl_3$.[56] *N*-(Trichloroethylidene)benzenesulfonamide **2b** (yield 40%) and other chloral *N*-arylsulfonylimines (*e.g.*, **2c**,**d**) were prepared in a similar way.[57]

$$4\text{-}RC_6H_4SO_2N{=}S{=}O + Cl_3CCHO \xrightarrow[-SO_2]{} \underset{\mathbf{2a-d}}{4\text{-}RC_6H_4SO_2N{=}CHCCl_3}$$

R = Me (**a**), H (**b**), Cl (**c**), MeO (**d**).

However, an attempt to prepare (*N*-2,2-dichloroethylidene)arenesulfonamides from *N*-sulfinyl-4-toluenesulfonamide and dichloroacetaldehyde [32] resulted in the isolation of 1,1-bis-(4-tolylsulfonylamino)-2,2-dichloroethane.

$$4\text{-}MeC_6H_4SO_2N{=}S{=}O + Cl_2CHCHO \longrightarrow$$

$$\longrightarrow (4\text{-}MeC_6H_4SO_2NH)_2CHCHCl_2$$

An attempt to synthesise 1-chloroimines by condensation of *N*-sulfinylarenesulfonamides with acid chlorides was also unsuccessful because the condensation products proved to be unstable under the reaction conditions.[58]

Thus, the applicability of this method is quite limited. For example, it is impossible to prepare *N*-trichloroethylidene dialkyl phosphoramidates by the condensation of the corresponding sulfinylamides with chloral.[33]

A general method for the synthesis of chloral sulfonylimines consists in the interaction of chloral with sulfonyl isocyanates in the presence of amines and quaternary ammonium bases.[59]

$$Cl_3CCHO + RSO_2NCO \xrightarrow{C_{16}H_{33}CH(NMe_2)COMe} \underset{\mathbf{2e,g}}{Cl_3CCH{=}NSO_2R}$$

R = Cl (**e**), F (**g**), Alk(C_1 – C_{20}), ArAlk(C_7 – C_{12}), Ar(C_6 – C_{10}).

The method for the synthesis of acyl-, X-carbonyl- and phosphoryl-imines of polyhalogenated aldehydes and ketones based on condensation of *N*-derivatives of amides with carbonyl compounds has not been further developed. However, a large number of sulfonylimines of aromatic and aliphatic aldehydes and ketones [60] and *N*-*tert*-butyl- and *N*-fluoroalkyl-imines of alkyl, aryl, polyfluoro and chloro aldehydes and ketones have been prepared from sulfinylimines.[61]

2. Preparation of imines of polychlorinated aldehydes and ketones from isocyanates

Methods for the synthesis of halo-containing imines based on 1-R-1,2,2,2-tetrahaloethyl isocyanates and perchlorinated isocyanates have found wide application.

Thus the reaction of 1-aryl-1,2,2,2-tetrachloroethyl isocyanates with alcohols, phenols, benzenethiols and amines taken in equimolar amounts affords *N*-(1-aryl-1,2,2,2-tetrachloroethyl)amides. These compounds are dehydrogenated on heating or on treatment with bases. *N*-R-Oxycarbonyl-, arylthiocarbonyl- and carbamoyl-imines of trichloromethyl phenyl ketone, *N*-R-oxycarbonylimines of trichloromethyl 4-methylphenyl ketone and phenoxycarbonylimines of trichloromethyl aryl ketones were prepared in this way.[62]

$$Cl_3CCAr(Cl)NCO \xrightarrow{HX} Cl_3CCAr(Cl)NHCOX \xrightarrow[-HCl]{}$$

$$\longrightarrow Cl_3CC(Ar){=}NCOX$$

Ar = Ph: X = MeO, PhO, 4-MeC_6H_4O, 3,5-$Me_2C_6H_3O$, 4-BrC_6H_4, $O(CH_2CH_2)_2N$, Ph_2N, PhNH, 3-CF_3-4-$NO_2C_6H_3NH$;
Ar = 4-MeC_6H_4: X = MeO, PhO;
X = PhO: Ar = 4-ClC_6H_4, 4-$Cl_3CC_6H_4$, 4-FC_6H_4.

Later,[63, 64] *N*-Alkyl(aryl)-*N*′-(perchloroethylidene)ureas **8a**–**d** were synthesised by the reaction of perchloroethyl isocyanate with primary amines at −20 °C.

$$Cl_3CCl_2CN{=}C{=}O \xrightarrow{RNH_2} [Cl_3CCl_2CNHC(O)NHR] \xrightarrow{RNH_2}$$

$$\longrightarrow \underset{\mathbf{8a-d}\ (20\%-70\%)}{Cl_3CClC{=}NC(O)NHR}$$

R = Pr^i (**a**), Bu^t (**b**), Ph (**c**), 2,4,6-$Me_3C_6H_2$ (**d**).

Tetrachloroethyl isocyanate was prepared by treatment of *N*-(1-hydroxy-2,2,2-trichloroethyl)alkoxycarbonylamide with PCl_5 [39] and pentachloroethyl isocyanate was obtained by its photochemical chlorination.[63]

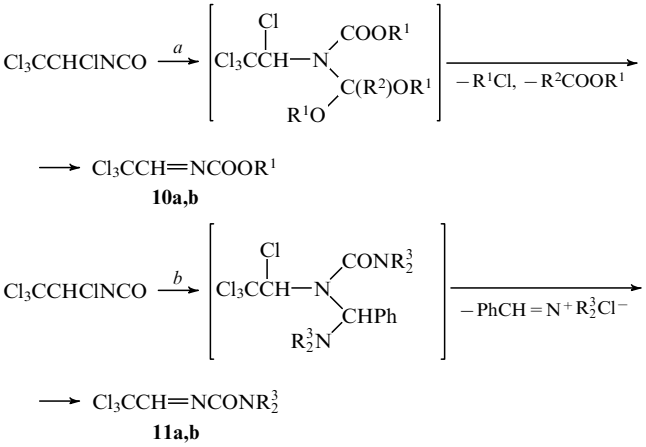
The readily available ylide $Ph_3P{=}CHCN$ easily adds to 1,2,2,2-tetrachloroethyl isocyanate giving rise to a new biphilic reagent, which contains the clearly electrophilic group $CClNHCO^-$, apart from the nucleophilic centre of the ylide fragment. This new reagent was used to create biphilic phosphonium ylide **9**.[65]

$$Cl_3CCHClN{=}C{=}O + NCCH{=}PPh_3 \longrightarrow$$

$$\longrightarrow Cl_3CCHClNHC(O)\underset{CN}{\underset{|}{C}}{=}PPh_3 \xrightarrow{Et_3N} \underset{\mathbf{9}}{Cl_3CCH{=}NC(O)\underset{CN}{\underset{|}{C}}{=}PPh_3}$$

The reactions of 1,2,2,2-tetrachloroethyl isocyanate with orthoesters of carboxylic acids and with benzaldehyde aminals

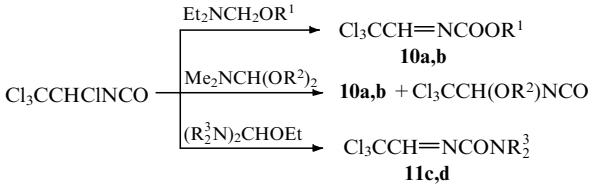
result in the formation of chloral *N*-alkoxycarbonylimines **10a**,**b** and *N*,*N*′-substituted dialkoxyureas **11a**,**b**.[66]



(*a*) $(R^1O)_3CR^2$; (*b*) $PhCH(NR^3_2)_2$; R^1 = Me (**10a**), Et (**10b**); R^2 = H, Ph, 4-ClC_6H_4; R^3_2 = $(CH_2)_2O(CH_2)_2$ (**11a**); $(CH_2)_5$ (**11b**).

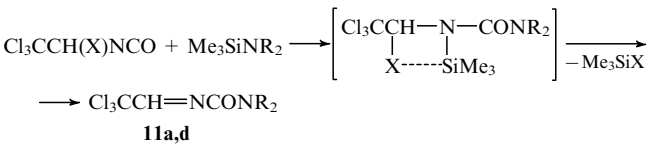
It was found [66] that acetals do not enter into similar reactions with tetrachloroethyl isocyanate.

1,2,2,2-Tetrachloroethyl isocyanate reacts with (dialkylamino)alkoxymethanes and bis(dialkylamino)ethoxymethanes giving rise to the chloral *N*-alkoxycarbonylimines **10a**,**b** and the *N*,*N*′-substituted ureas **11c**,**d**.[67] The reactions with dimethylformamide acetals afford a mixture of chloral imines and 1-alkoxy-2,2,2-trichloroethyl isocyanates.



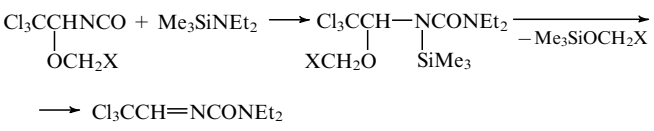
R^3 = Me (**11c**), Et (**11d**).

Apart from tetrachloroethyl isocyanate, the products resulting from replacement of one chlorine by an aryloxy or alkoxy group are also employed in the synthesis of imines. Thus the reaction of 1,2,2,2-tetrachloroethyl isocyanate and 1-aryloxy-2,2,2-trichloroethyl isocyanate with trimethylsilylamines gives the *N*,*N*′-substituted ureas **11a**,**d**.[68]



X = Cl, PhO, 4-ClC_6H_4O; R = Et, R^2 = $(CH_2)_2O(CH_2)_2$.

The compound **11a** was obtained in the reaction of diethyl(trimethylsilyl)amine with 1-alkoxytrichloroethyl isocyanates; the first stage of the reaction yields silylated ureas, which decompose on heating to give the imine **11d** and the corresponding alkoxysilanes.[69]



X = Cl_2CH, $H(CF_2)_2$, $H(CF_2)_4$, COOMe.

This method was used to synthesise a large number of acyl-, alkoxy(aryloxy)(thio)carbonyl- and *N*′-substituted carbamoylimines of chloral and trichloromethyl aryl ketones.

In conclusion, we would like to note that, despite the fact that these imines are produced from polychloroethyl isocyanates in preparative yields, isocyanates themselves are synthesised from polyhalogenated amides, nitriles, *etc*., using PCl_5, $COCl_2$ and other similar reagents, which restricts the scope of application of this method.

3. Reactions of *N*,*N*-dihaloamides with 1,2-polyhaloethenes as a new pathway to azomethines

The reactions of 1,2-polyhaloethenes with sulfonic, carboxylic, alkoxycarboxylic and phosphoric acid *N*,*N*-dichloroamides have been vigorously studied for about 20 years. These reactions were found to give azomethines rather than saturated adducts. They provide the basis for one-stage procedures for the preparation of polyhaloaldehyde imines and their derivatives. Studies dealing with the synthesis of acyl-, ethoxycarbonyl- and sulfonyl-imines of chloral and other haloaldehydes, *N*-(2-bromo-2,2-dichloroethylidene)benzenesulfonamide, *N*-(2,2-dibromo-2-chloroethylidene)-benzenesulfonamide and *N*-(2,2-dichloroethylidene)arenesulfonamides from *N*,*N*-dichloro- and *N*,*N*-dibromo-amides and 1,2-polyhaloethenes (trichloro-, tribromo- and dichloro-ethenes) published before 1989 have been surveyed in several reviews.[23–25] Here we consider the studies that have not been covered in these reviews.

For instance, when *N*,*N*-dichloronitrobenzenesulfonamide, aminobenzenesulfonamide and *N*,*N*-dichloroamides of perfluoroalkanesulfonic acids are made to react with trichloroethene (TCE), the chloral sulfonylimines **2e**–**h** are formed;[70,71] the reaction of *N*,*N*-dichlorourethanes with TCE affords chloral *N*-alkoxycarbonylimines **10a**–**c** in preparative yields.[72,73]

$$RSO_2NCl_2 + 2CHCl{=}CCl_2 \xrightarrow[-Cl_2]{} \underset{\mathbf{2a-c,\,e-h}}{Cl_3CCH{=}NSO_2R} + Cl_2CHCCl_3$$

R = 4-$MeOC_6H_4$ (**a**), Ph (**b**), 4-ClC_6H_4 (**c**), 3-$NO_2C_6H_4$ (**e**), 4-$NO_2C_6H_4$ (**f**), 4-MeOCONHC$_6H_4$ (**g**), Alk_F (**h**).

$$Cl_2NCOOR + 2CHCl{=}CCl_2 \xrightarrow[-Cl_2]{} \underset{\mathbf{10a-c}}{Cl_3CCH{=}NCOOR} + Cl_2CHCCl_3$$

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

The reactions of TCE with *N*,*N*-dichloroarenesulfonamides in the presence of Lewis acids ($SnCl_4$, $AlCl_3$) also afford the sulfonylimines **2a**–**c**, which are formed, however, in lower yields (up to 47%); *N*-(1-arylsulfonylamino-2,2,2-trichloroethyl)arenesulfonamides are formed as side products.[74]

It has been reported previously [23] that TCE reacts with *N*,*N*-dibromobenzenesulfamide or *N*,*N*-dibromourethane giving rise to the corresponding imines of 2-bromo-2,2-dichloroacetaldehyde $BrCl_2CCH{=}NSO_2Ph$ and $BrCl_2CCH{=}NCOOMe$.

The reaction of TCE with *N*-bromourethane, which is known to disproportionate to give amide and dibromoamide, results in the formation of 2-bromo-2,2-dichloro-1,1-di(ethoxycarbonylamino)ethane.[75]

The reactions of *N*,*N*-dichlorourethane and *N*,*N*-dichlorobenzenesulfonamide with tribromoethene (TBE) follow a similar route. *N*,*N*-Dichlorourethane is converted into ethyl *N*-(2,2-dibromo-2-chloroethylidene)carbamate **12**.[76] The reaction is accompanied by evolution of chlorine, bromine and 1,1,2-tribromo-1,2-dichloroethane.

$$EtOCONCl_2 + CHBr{=}CBr_2 \xrightarrow[-Cl_2,\ -Br_2]{} \underset{\mathbf{12}}{EtOCON{=}CHCClBr_2} + CHClBrCClBr_2$$

It has been reported in studies cited in a review [23] that *N*,*N*-dichloroarenesulfonamides react with 1,2-dichloroethene (DCE) to give *N*-(2,2-dichloroethylidene)arenesulfonamides **13a**–**c**; the formation of these products was proved by physico-chemical methods and by chemical transformations. In another study,[77] they were isolated and characterised for the first time. The relative

yields of the compounds **13**, **14** and **2** depend on the reaction conditions.[76, 77]

$$RNCl_2 + CHCl{=}CHCl \longrightarrow$$

$$\longrightarrow \underset{\mathbf{13a-c}}{RN{=}CHCHCl_2} + \underset{\mathbf{14a-c}}{(RNH)_2CHCHCl_2} + \underset{\mathbf{2a-c}}{RN{=}CHCCl_3}$$

R = $PhSO_2$ (**a**), 4-$MeC_6H_4SO_2$ (**b**), 4-$ClC_6H_4SO_2$ (**c**).

The reaction of *N*,*N*-dichlorourethane with DCE was found [76] to afford highly reactive ethyl *N*-(2,2-dichloroethylidene)carbamate **15**. However, like the reaction of *N*,*N*-dichloroarenesulfonamides with DCE, this process yields the imine **10b** and the product of addition of dichlorourethane to the C=N bond of this imine, namely, 2,2,2-trichloro-1,1-bis(ethoxycarbonylamino)-ethane **16**, together with the target imine **15**. This is due to the fact that the process is accompanied by the chlorination of DCE giving rise to trichloroethene, tetrachloroethane, tetrachloroethene and urethane.

$$EtOOCNCl_2 + CHCl{=}CHCl \longrightarrow \underset{\mathbf{15}}{EtOOCN{=}CHCHCl_2} +$$

$$+ \underset{\mathbf{16}}{(EtOOCNH)_2CHCHCl_3} + \underset{\mathbf{10b}}{EtOOCN{=}CHCCl_3}$$

N,*N*-Dichloroarenesulfonamides have been found to react readily with 1-bromo-1,2-dichloroethene yielding *N*-(2-bromo-2,2-dichloroethylidene)arenesulfonamides **17a**,**b**.[78]

$$ArSO_2NCl_2 + CHCl{=}CClBr \longrightarrow \underset{\mathbf{17a,b}}{ArSO_2N{=}CHCCl_2Br}$$

Ar = Ph (**a**), 4-ClC_6H_4 (**b**).

Systematic studies dealing with the influence of the natures of the polyhaloethene and dihaloamide used on the structure of the imine $RN{=}CHCCl_nBr_{3-n}$ made it possible to refine the scheme proposed previously[23] for this reaction. It was demonstrated that the radical adducts formed either from *N*,*N*-dibromoamides and polychloroethenes or from *N*,*N*-dichloroamides and TBE do not undergo 1,2-halotropic rearrangement because these reactions afford neither polychloroaldehyde imines nor bromal imines.[23, 75-78]

The method for the synthesis of polyhaloaldehyde imines based on the reaction of amidyl radicals with polyhaloethenes permits polychlorinated (or polybrominated) azomethines including those with different halogen atoms to be prepared from available initial compounds and to be used subsequently without isolation for synthetic purposes. However, the process of the preparation of halo-containing acyl- and phosphoryl-imines requires optimisation. The applicability of this method to the preparation of carbamoylimines and fluorinated imines containing residues of various types of acids also has to be studied.

4. Synthesis of *N*-arylsylfonylimines of polyhaloaldehydes by the reaction of *N*,*N*-dihaloamides with acetylene derivatives

The method for the synthesis of imines from acid dichloroamides and acetylene derivatives was developed in the last decade.

It has been shown [79, 80] that the reaction of *N*,*N*-dichloroarenesulfonamides with phenylacetylene occurs by a free radical mechanism and results in the formation of *N*-(2,2-dichloro-2-phenylethylidene)arenesulfonamides **18a**,**b**. A detailed study of the process [80] demonstrated that *N*,*N*-dichlorobenzenesulfonamide reacts with phenylacetylene giving rise to a mixture of compounds, the imine **18a** being the major product (yield up to 75%); adduct **19a**, resulting from the addition of benzenesulfonamide to the C=N bond of **18a**, is also formed in a noticeable amount.

$$ArSO_2NCl_2 + PhC{\equiv}CH \longrightarrow \begin{cases} \underset{\mathbf{18a,b}}{ArSO_2N{=}CHCCl_2Ph} \\ \underset{\mathbf{19a}}{(ArSO_2NH)_2CHCCl_2Ph} \\ [ArSO_2NClCH{=}CClPh] \downarrow \\ ArSO_2NHCH{=}CClPh \end{cases}$$

Ar = Ph (**a**), 4-ClC_6H_4 (**b**).

The reaction of phenylacetylene with *N*,*N*-dibromoarenesulfonamides gives 2,2-dibromo-2-phenyl-1,1-di(phenylsulfonylamino)ethane and benzenesulfonamide.[80]

The reactions of *N*,*N*-dichlorourethanes and *N*,*N*-dichloroamides with phenylacetylene have also been studied.[81, 82] However, the results obtained are contradictory and require more precise determination of the structures and transformations of the reaction products.

The reaction of *N*,*N*-dichloroarenesulfonamides with propargyl alcohol and 3-chloroprop-1-yne [83, 84] gave the products of the subsequent addition of arenesulfonamides to the imines formed, namely, 3-chloro- and 3-hydroxy-2,2-dichloro-1,1-di(phenylsulfonylamino)propanes or 1,1-di(4-chlorophenylsulfonylamino)propanes.

$$ArSO_2NCl_2 + CH{\equiv}CCH_2X \longrightarrow (ArSO_2NH)_2CHCCl_2CH_2X$$

X = Cl, OH; Ar = Ph, 4-ClC_6H_4.

5. Chlorination and bromination of amide derivatives

Among the methods for the synthesis of polyhaloaldehyde imines, mention should be made of chlorination of *N*-alkyl(aryl)amides; however, this method has already been considered in several reviews.[17-21] We would only like to emphasise that chlorination of *N*-acylamides has been shown [85] to give products resulting from chlorination of both the aldehyde and the amide fragments. Photochemical high-temperature chlorination of isopropylamides of benzoic and 4-chlorobenzoic acids affords the corresponding acylimines of hexachloroacetone.

The transformation of *N*-(1-phenyl-2,2,2-trichloroethyl)-amides under conditions of photochemical chlorination [86] and the transformation of *N*-(1-diethoxyphosphoryl-2,2,2-trichloroethyl)benzamide on treatment with the chlorine complex of pyridine [87] yield *N*-(1-phenyltrichloroethylidene)trichloroacet(or benz)amides **19a**,**b** [86] and *N*-(1-diethoxyphosphoryltrichloroethylidene)benzamide **19c** (yield 68%).[87] It was shown [87] that the latter product is more convenient to prepare by the chlorination of the silyl derivative $CCl_2{=}C[P(O)(OEt)_2]$.$N(SiMe_3)COPh$ (yield 84%).

$$CCl_3CH(X)NHCOR \xrightarrow{Cl_2,\ h\nu} CCl_3CCl(X)NHCOR \xrightarrow[-HCl]{\Delta}$$

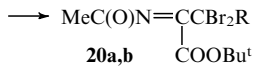
$$\longrightarrow \underset{\mathbf{19a-c}}{CCl_3C(X){=}NCOR}$$

X = Ph, R = CCl_3 (**a**, 58%), Ph (**b**, 62%); X = $(EtO)_2P(O)$, R = Ph (**c**).

Yet another study deserves special attention[88] in which it was reported that *N*-acetyl-(1-*tert*-butoxycarbonyl-2,2-dibromo)-propan- and -butanimines **20a**,**b** are formed upon successive bromination of the corresponding enamides with *N*-bromosuccinimide (NBS).

$$MeC(O)NHC(COOBu^t){=}CHR \xrightarrow{NBS} MeC(O)NBrC(COOBu^t){=}CHR \longrightarrow$$

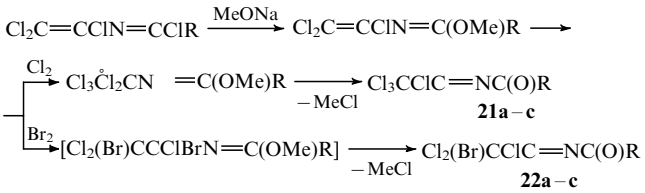
$$\longrightarrow MeC(O)NHC(COOBu^t){=}CBrR \xrightarrow{NBS} MeC(O)NBrC(COOBu^t){=}CBrR \longrightarrow$$



20a,b

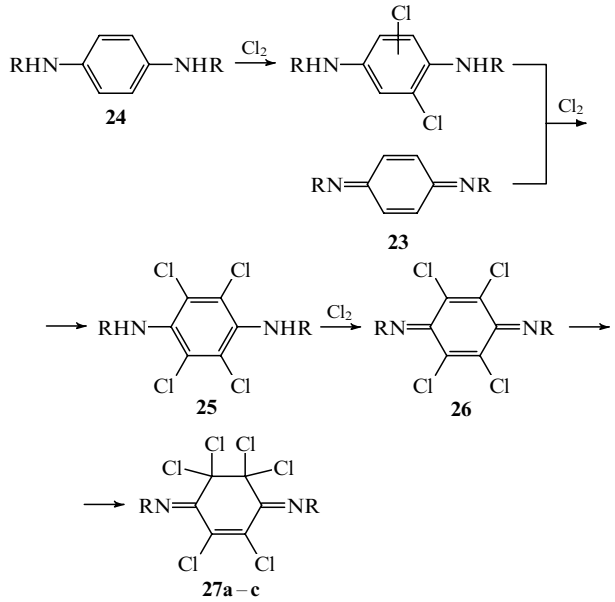
R = Me (**a**), Et (**b**).

Finally, some polyhalogenated ketimines have been prepared by halogenation of compounds with C=N bonds. Thus *N*-perchlorovinylcarboximidoyl chlorides were used to synthesise *N*-substituted imino esters with a perchlorovinyl group.[89] When these compounds are subjected to chlorination, the perchlorovinyl group is converted into a perchloroethyl group. Methyl *N*-perchloroethylbenzimidates eliminate chloromethane on heating to give *N*-(tetrachloroethylidene)benzamides **21a–c** in high yields. Bromination of esters of *N*-perchlorovinylimidic acids under mild conditions is accompanied by elimination of MeBr and gives rise to *N*-(2-bromotrichloroethylidene)benzamides **22a–c**.



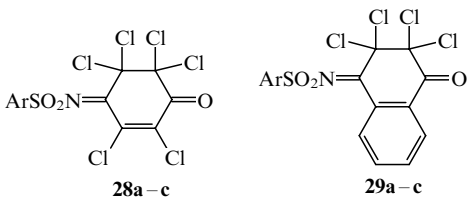
R = 4-XC_6H_4; X = H (**a**), Cl (**b**), NO_2 (**c**).

Chlorination has been employed to prepare imines of cyclic halogen-containing ketones.[90] Thus chlorination of both *N*,*N*′-bis(arylsulfonyl)-1,4-benzoquinonediimines **23** and *N*-arylsulfonyl-substituted *p*-phenylenediamines **24** in dimethylformamide results in the isolation of the same products, 2,3,5,6-tetrachloro-*N*,*N*′-bis(arylsulfonyl)-1,4-phenylenediamines **25**. Further chlorination affords tetrachlorobis(arylsulfonyl)benzoquinonediimines **26**, which, in turn, add a chlorine molecule at a double bond of the quinone ring to give the final products, 1,4-bis(arylsulfonylimino)-2,3,5,5,6,6-hexachlorocyclohex-2-enes **27a–c**.[90]



R = $PhSO_2$ (**a**), 4-$MeC_6H_4SO_2$ (**b**), 4-$ClC_6H_4SO_2$ (**c**).

Similarly, 4-arylsulfonylimino-2,3,5,5,6,6-hexachlorocyclohex-2-en-1-ones **28a–c**[91] and 4-arylsulfonylimino-2,3,5,5,6,6-hexachloro-1-oxo-1,2,3,4-tetrahydronaphthalenes **29a–c**[92] were obtained by chlorination of *N*-arylsulfonyl-1,4-aminophenols and *N*-arylsulfonyl-1,4-aminonaphthols.



28a–c **29a–c**

Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**c**).

6. The use of organophosphorus compounds and PCl_5 for the synthesis of polyhalogenated imines

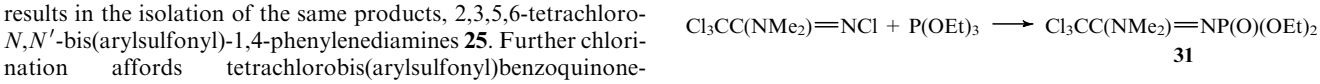
Several methods for the synthesis of *N*-functionally substituted polyhalogenated imines based on organophosphorus compounds and PCl_5 are known.

Dialkyl *N*-(1-amino-2,2-dichloroethylidene) phosphoramidates were prepared by the reaction of trichloroacetylamidines with trialkyl phosphites.[93]

30a–e

R^1 = H, R^2 = Me: R^3 = Me (**a**), Et (**b**), Pr^n (**c**), Pr^i (**d**);
R^1 = H, R^2 = Bu^t, R^3 = Et (**e**).

Diethyl *N*-(1-dimethylamino-2,2,2-trichloroethylidene) phosphoramidate **31** was synthesised from *N*-chloro-*N*′,*N*′-dimethyltrichloroacetylamidines and triethyl phosphite.[93]



31

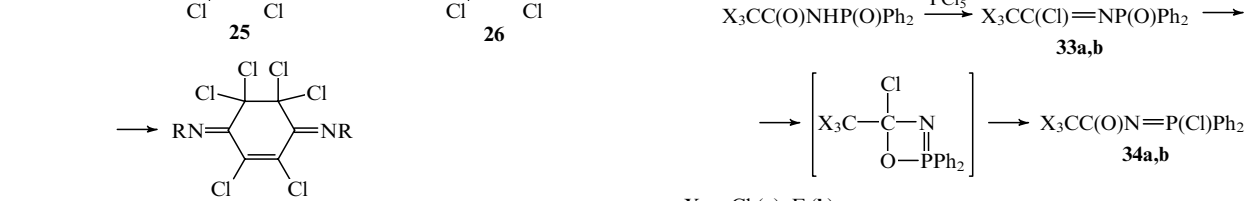
Trialkyl phosphites were shown [94] to react with polychloronitrosoethanes under mild conditions (−20°C) giving rise to the corresponding dialkyl *N*-chloroalkylidene phosphoramidates **32a–h**.



32a–h

R^1 = CH_2Cl: R^2 = Pr^n (**a**), Bu^n (**b**), Bu^i (**c**), C_5H_{11} (**d**), $ClCH_2CH_2$ (**e**);
R^1 = $CHCl_2$: R^2 = Pr^n (**f**), Bu^n (**g**), C_5H_{11} (**h**).

The reaction of *N*-trihaloacetyl diphenylphosphinic amide with PCl_5 affords a mixture of *N*-(tetrachloroethylidene) (**33a**) and *N*-(trifluoro-1-chloroethylidene) (**33b**) diphenylphosphinic amides (70%) and phosphazo compounds **34** (30%).[95] The rearrangement, which occurs presumably *via* a four-centre transition state, is facilitated by the presence of strong electron-withdrawing groups.



33a,b **34a,b**

X = Cl (**a**), F (**b**).

However, trichloroacetamide reacts with excess PCl_5 to give *N*-dichlorophosphoryltetrachloroethanimine **35**.[96] This product reacts with sodium phenoxide giving rise to the products of substitution of phenoxyl residues for the halogen atoms — *N*-diphenoxyphosphoryl-2,2,2-trichloro-1-phenoxyethanimine **36**.[97]

$$Cl_3CCONH_2 \xrightarrow{PCl_5} \underset{\mathbf{35}}{Cl_3CClC{=}NPOCl_2} \xrightarrow{PhONa} \underset{\mathbf{36}}{Cl_3CC(OPh){=}NPO(OPh)_2}$$

Imines of type **35** have also been used to prepare chlorinated and fluorinated imides of phosphorothioic acids **37a**–**d**.[98]

$$RClC{=}NP(O)Cl_2 \xrightarrow{P_2S_5} \underset{\mathbf{37a-d}}{RClC{=}NP(S)Cl_2} + P_2O_5$$

R = CCl_3 (**a**), CH_2ClCCl_2 (**b**), $MeCCl_2$ (**c**), $EtCCl_2$ (**d**).

When the imines **37a**,**c** are made to react with alcohols and amines, the chlorine atoms at phosphorus and carbon are substituted to give compounds **38a**–**e** and **39a**–**f**.[98]

$$\underset{\mathbf{37a,c}}{R^1CCl{=}NP(S)Cl_2} \begin{cases} \xrightarrow{R^2R^3NH} \underset{\mathbf{38a-e}}{R^1C(NR^2R^3){=}NP(S)(NR^2R^3)_2} \\ \xrightarrow[R^4OH,\ Et_3N]{} \underset{\mathbf{39a-f}}{R^1C(OR^4){=}NP(S)(OR^4)_2} \end{cases}$$

R^1 = Cl_3C: NR^2R^3 = PhNH (**38a**), 4-ClC_6H_4NH (**38b**), $N(CH_2CH_2)_2O$ (**38c**);
R^1 = Cl_2CMe: NR^2R^3 = 4-ClC_6H_4NH (**38d**), $N(CH_2CH_2)_2O$ (**38e**);
R^1 = Cl_3C: R^4 = Me (**39a**), Et (**39b**), Pr (**39c**), Bu (**39d**), Ph (**39e**);
R^1 = Cl_2CMe, R^4 = Et (**39f**).

Several *N*-phosphorylimines have been synthesised using trichlorophosphorazoperchloroethane **40**,[99] which reacts with alcohols to yield imides of various structures depending on the reaction temperature and the reactant ratio. When an equimolar amount of an alcohol is employed, one chlorine atom is replaced giving rise to unstable alkyl *N*-(perchloroethyl)dichlorophosphorimidates, which decompose on heating with evolution of an alkyl chloride to give *N*-dichlorophosphoryltetrachloroethanimine **35**.

$$\underset{\mathbf{40}}{Cl_3CCl_2CN{=}PCl_3} + ROH \longrightarrow Cl_3CCl_2CN{=}PCl_2(OR) \xrightarrow[-RCl]{\Delta} \underset{\mathbf{35}}{Cl_3CClC{=}NPOCl_2}$$

R = Me, Et, Pr, Bu, C_8H_{17}.

When a threefold excess of an alcohol is used, this reaction results in the formation of a mixture of dialkyl phosphoramidates **41a**–**h** and the corresponding alkoxy chloro derivatives **42a**–**h** in ~60 : 40 ratio.

$$\mathbf{40} \xrightarrow[-3HCl]{3ROH} \underset{\mathbf{41a-h}}{Cl_3CClC{=}NPO(OR)_2} + \underset{\mathbf{42a-h}}{Cl_3CC(OR){=}NPO(OR)Cl}$$

R = Me (**a**), Et (**b**), Pr^n (**c**), Bu^n (**d**), Bu^i (**e**), C_5H_{11} (**f**), iso-C_5H_{11} (**g**), C_8H_{17} (**h**).

When the alcohol : imine **40** ratio is 4 : 1, dialkyl *N*-(1-alkoxy-2,2,2-trichloroethylidene) phosphoramidates **43** are produced in 65%–85% yields. These compounds can also be obtained by treatment of the compounds **35**, **41** or **42** with an alcohol.

$$\begin{array}{l} \underset{\mathbf{35}}{Cl_3CClCN{=}POCl_2} \xrightarrow{3ROH} \\ \underset{\mathbf{41}}{Cl_3CClC{=}NPO(OR)_2} \xrightarrow{ROH} \underset{\mathbf{43}}{Cl_3CC(OR){=}NPO(OR)_2} \\ \underset{\mathbf{42}}{Cl_3CC(OR){=}NP(O)Cl(OR)} \xrightarrow{ROH} \end{array}$$

The imine **41a** was converted into dimethyl *N*-trichloroacetyl phosphoramidate **44** using a procedure proposed by Kirsanov *et al*.[96] The product **44** can exist in solution as the imine tautomer **45**.[100]

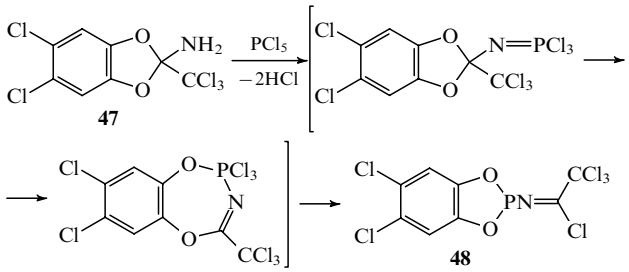
$$\mathbf{41a} \xrightarrow{H_2O} \underset{OH}{Cl_3CC{=}NP(O)(OMe)_2} \rightleftharpoons \underset{O\quad \mathbf{44}}{Cl_3CCNHP(O)(OMe)_2} \rightleftharpoons$$

$$\rightleftharpoons \underset{\mathbf{45}\quad OH}{Cl_3CCN{=}P(OMe)_2}$$

The compound **6a** can be prepared by treatment of *N*-(1,2-dichloro-2-methylpropylidene)aminophosphorus trichloride with sulfur dioxide.[49]

$$\underset{\mathbf{46}}{Me_2CClCHClN{=}PCl_3} \xrightarrow{SO_2} \underset{\mathbf{6a}}{Me_2CClCH{=}NP(O)Cl_2}$$

Tetrachloroethylideneaminodioxaphospholane **48** was prepared by the reaction of 2-amino-2-trichloromethyl-5,6-dichlorobenzo-1,3-dioxolane **47** with PCl_5.[101] Presumably, a phosphazo compound is formed initially and then it rearranges into the dioxaphospholane *via* a seven-membered intermediate.



7. Other methods of synthesis

It is worth noting that chlorovinylamides, structural isomers of chloroethylideneimines, can be used in some cases for the synthesis of imines. Thus bis(dialkoxyphosphoryl)trichlorovinylamines react with two equivalents of a dialkylamine to give dialkyl *N*-(1-dialkylamino-2,2-dichloroethylidene) phosphoramidates **49a**,**b**.[102]

$$Cl_3CClC{=}NPO(OEt)_2 + P(OEt)_3 \longrightarrow$$

$$\longrightarrow Cl_2C{=}CClN[PO(OEt)_2]_2 \xrightarrow{R_2NH} \underset{\mathbf{49a,b}}{Cl_2CHC(NR_2){=}NPO(OEt)_2}$$

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

It has been mentioned above that imines with a similar structure have also been prepared from trichloroacetamidines.[93]

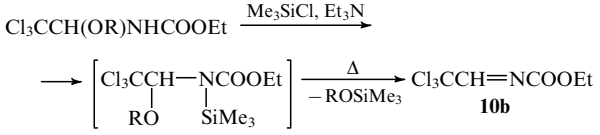
(2,2-Dichloro-1-cyanovinyl)benzenesulfonamide **50** reacts with amines, in the opinion of the researchers cited,[103] in the imine form with replacement of the cyano group by an amino group; *N*-(1-dialkylamino-2,2-dichloroethylidene)arenesulfonamides **51a**–**e** were isolated in good yields.

$$\underset{\mathbf{50}}{Cl_2C{=}C(CN)NHSO_2Ph} \rightleftharpoons [Cl_2CHC(CN){=}NSO_2Ph] \xrightarrow{HNR^1R^2}$$

$$\longrightarrow \underset{\mathbf{51a-e}}{Cl_2CHC(NR^1R^2){=}NSO_2Ph}$$

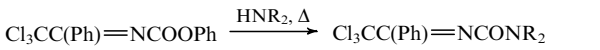
NR^1R^2 = $PhCH_2NH$ (**a**), PhNH (**b**), 4-MeC_6H_4NH (**c**), Me_2N (**d**), $O(CH_2CH_2)_2N$ (**e**).

A quite promising method for the preparation of imines is that based on ethyl *N*-[trichloro-1-alkoxy(aryloxy)ethyl]carbamates and chlorotrimethylsilane. When ethyl *N*-(1-aryloxy-2,2,2-trichloroethyl)carbamates are silylated with chlorotrimethylsilane in the presence of triethylamine, the intermediate product decomposes to give *N*-(ethoxycarbonyl)chloral imine **10b**.[69]

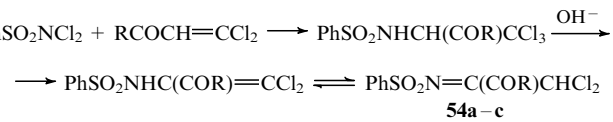


R = Ph, 2,4-$Br_2C_6H_3$.

It has been shown that 1-phenyl-2,2,2-trichloroethylideneureas **52** can be prepared from phenyl *N*-(1-phenyl-2,2,2-trichloroethylidene)carbamate **53**.[62] Under rigorous conditions, the phenoxy group is replaced by the amine residue.[62]



The reaction of *N*,*N*-dichlorobenzenesulfonamide with dichlorovinyl ketones followed by dechlorination of the resulting *N*-(1-acyl-2,2,2-trichloroethyl)benzenesulfonamides on treatment with alkali resulted in the formation of *N*-(1-acyl-2,2-dichloroethylidene)benzenesulfonamides **54a–c**. They can exist as two tautomers.[104]



R = Me (**a**), Pr (**b**), CH_2Cl (**c**).

III. Structure of imines of polyhalogenated aldehydes and ketones: *syn–anti* isomerism; enamide–acylimine tautomerism

1. Structure of *N*-trichloroethylidenearenesulfonamides according to the data of ^{35}Cl NQR and NMR spectroscopy. *syn–anti* Isomerism of polyhaloaldehyde imines

Despite the considerable attention devoted to the chemistry of carboxylic, sulfonic and phosphoric acid *N*-polyhaloalkylideneamides, their structures certainly have not been adequately studied. Most often, these compounds have been characterised by IR and NMR data; the results of NQR studies of trichloroethylidenearenesulfonamides can be found only in two publications.[105, 106]

The ^{35}Cl NQR spectra, as well as ^1H and ^{13}C NMR spectra,[70] indicate that chloral arylsulfonylimines **2a–c** occur as one of the two possible isomers. According to quantum-chemical calculations, *anti*-isomer **A** is more favourable than *syn*-isomer **B**; this is confirmed by experimental and theoretical ^{35}Cl NQR data.[105]



Ar = 4-MeC_6H_4, Ph, 4-ClC_6H_4.



It has been shown by NMR spectroscopy that the dibromochloroacetaldehyde imines **12** and **55** exist as mixtures of *syn*- and *anti*-isomers in 3 : 4 [107] and 1 : 3 [76] ratios, respectively. Indeed, the ^1H NMR spectrum of the imine **55** exhibits, in addition to the multiplet for the phenyl protons, two singlets at 8.30 and 8.40 ppm due to the protons at the double bond, the ratio of their intensities being 3 : 4. The ^{13}C NMR spectrum contains two signals for the carbon atoms of the CH = N group (167.9 and 167.6 ppm) and the $CClBr_2$ group (135.7 and 135.6 ppm).[107] More evidence supporting the existence of *syn*- and *anti*-isomers of imines is provided by the fact that addition of nucleophiles at the C = N bond affords two enantiomers.[107]

It should be noted that *syn*- and *anti*-isomers cannot be detected in the ^1H NMR spectra of chloral sulfonylimines **2a–c** or ethoxycarbonylimines **10b**,[108, 73] dichloroacetaldehyde sulfonylimines **13a–c** or ethoxycarbonylimines **15**,[76, 77] or bromodichloroacetaldehyde sulfonylimines **17a,b** or alkoxycarbonylimines.[23, 78, 109]

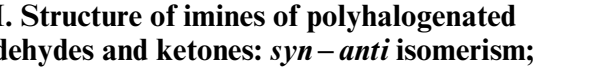
The correlations between the experimental ^{35}Cl NQR frequencies and the C–Cl bond lengths proposed in Ref. 110 were used to calculate the bond lengths in the imines **2a–c**, which were estimated as ranging between 175.8 and 176.3 pm.[105] These values are typical of C–Cl bond lengths in compounds with a trichloromethyl group.

It has been noted that the three chlorine atoms in trichloroethylidene-benzenesulfonamide and -4-toluenesulfonamide **2a**,**b** are nonequivalent in the ^{35}Cl NQR spectra, whereas the ^{35}Cl NQR spectrum of the corresponding 4-chlorophenylsulfonylimine **2c** exhibits a single signal for the trichloromethyl group,[105, 106] which is difficult to explain based on its molecular structure. Apparently, the electron environment of all the chlorine atoms in this imine becomes equivalent due to intermolecular contacts.

Unfortunately, no data of ^{35}Cl NQR spectra for imines that are known to exist as both *syn*- and *anti*-isomers can be found in the literature.

2. Enamide–acylimine tautomerism in dichloroethylideneimines

An interesting problem of theoretical chemistry is the question of the existence of enamide–acylimine tautomerism in haloalkylideneimines *N*-substituted by acid residues.



X = H, Hal.

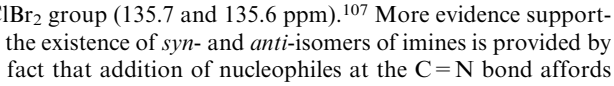
It has been concluded in reviews [20, 21] that, among *N*-acylimines of chloro(bromo)(fluoro)aldehydes and ketones, stable structures with the imine bond can be found for ald- and ketimines containing no β-hydrogen atoms in the haloalkyl groups.

However, now it is known that arylsulfonylimines of dichloroacetaldehyde $ArSO_2N{=}CHCHCl_2$ **13a–c**, Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**c**), which do have a hydrogen atom in the β-position with respect to the imine group, exist in the stable imine form, as indicated by the presence of characteristic absorption bands of the C = N bond in the IR and NMR spectra (the signal for the azomethine proton at δ 8.35–8.44 ppm and for the carbon atom of the CH = N group at δ 166 ppm).[77] Similarly, the dichloroethylidenecarbamate **15** (the signal of the azomethine proton at δ 8.06 ppm [76]) and 1-alkylamino-substituted dialkyl 2,2-dichloroethylidene phosphoramidates also exist as stable imine forms.[93, 102]

According to the data of IR and ^1H NMR spectra, *N*-dichlorovinylamides and *N*-dichlorovinylthioamides exist as stable enamide forms.[111, 112] Nevertheless, they react with nucleophiles to give stable products of addition at the azomethine bond.[112–114]

Some functional substituents, for example CN,[103, 115, 116] $CONH_2$,[117] $POPh_2$,[118] $PO(OEt)_2$ [119, 120] and $P^+Ph_3Cl^-$,[121] present in a dichloroalkyl group stabilise the enamide form $Cl_2C{=}C(R^1)NHCOR^2$, where R^2 = Alk, Ar, OMe, OPh. These amides react with primary and secondary amines in the enamide tautomeric form to give the products of replacement of chlorine atoms.

An exception is provided by *N*-(1-carbamoyl-2,2-dichlorovinyl)benzamide **56**, which reacts with methyl- and ethylamine giving rise to stable addition products **57**.[117]



R = Me, Et.

It has already been mentioned (see Section II.7) that *N*-(2,2-dichloro-1-cyanovinyl)benzenesulfonamide **50** reacts with amines with substitution of the cyano group to afford stable 1-amino-2,2-dichloroethylideneamides **51a**–**e**.[103]

It has also been found that *N*-(1-acyl-2,2-dichloroethylidene)benzenesulfonamides **54a**–**c** can exist as two tautomers;[104] the amide form predominates in the solid state, whereas in solutions the equilibrium shifts towards the imine form. The facts that the equilibrium is established over a relatively long period and that the tautomers can be observed separately indicate that the energy barrier separating these forms is higher than 107 kJ mol^{-1}.[104]

It should be emphasised that bromination of the NH group in *N*-(1-*tert*-butoxycarbonyl-2-methyl- and 2-ethylvinyl)acetamides yields unstable compounds which undergo a 1,3-halotropic rearrangement with migration of the halogen atom giving rise to the imines **20a**,**b** (see Section II.4). Similarly, *N*-chloro-*N*-(2-chloro-2-phenylvinyl)arenesulfonamides and *N*-bromo-*N*-(2-bromo-2-phenylvinyl)benzenesulfonamide, formed in the reaction of *N*,*N*-dichloro(bromo)arenesulfonamides with phenylacetylene (see Section II.4), are converted into the corresponding *N*-(2,2-dihalo-2-phenylethylidene)arenesulfonamides of the type **18** as a result of 1,3-halotropic rearrangement.[79, 80]

Thus, the imine form of dichloroacetaldimines is stable in the case of arylsulfonylimines and alkoxycarbonylimines and for *N*-dichlorovinyl phosphoric amides if the α-position of the vinyl group has electron-donating substituents. *N*-Dichlorovinyl-substituted dialkyl phosphoramidates, carboxamides and thiocarboxamides containing no substituents at the α-position of the vinyl group are stable in the enamide form; however, they react with nucleophiles in the imine form. The presence of electron-withdrawing substituents at the 1-position of the vinyl group of dichlorovinylamides stabilises the enamide tautomer. The introduction of a halogen atom in the NH group facilitates tautomerisation of enamides to give halogen-containing imines.

IV. Reactivity of *N*-acyl-, *N*-sulfonyl- and *N*-phosphorylimines of polyhalogenated aldehydes and ketones

The reactivity of N-functionally substituted polyhalogenated aldimines and ketimines is due to the presence of the highly electrophilic C=N bond. Electron-withdrawing substituents at this bond increase its reactivity towards nucleophiles and electron-rich species such as dienes, alkenes, alkynes or arenes.

1. Reactions of polychlorinated(brominated) aldimines and ketimines with nucleophiles

Acyl-, alkoxy(aryloxy)(amino)carbonyl-, sulfonyl- and phosphoryl-imines of polyhalogenated aldehydes and ketones have been studied in reactions with O-, N-, S- and P-nucleophiles and bifunctional nucleophiles. To elucidate the relationship between the structure of imines and their reactivity towards nucleophiles, the kinetics have been measured for the addition of ethanethiol and 2,4,6-trichloroaniline to chloral imines with various acyl residues, $Cl_3CCH=NCOR$, where R = Ph (**3a**), $PhCH_2O$ (**3b**), Me (**3c**), Et (**3d**), Pr^i (**3e**), Bu^t (**3f**), 4-MeC_6H_4 (**3g**), 4-$MeOC_6H_4$ (**3h**), 4-ClC_6H_4 (**3i**), 4-$O_2NC_6H_4$ (**3j**), 3-MeC_6H_4 (**3k**), 3-ClC_6H_4 (**3l**), and to the imines **10a**,**b**, **2a**,**b** and **7b**.[41, 122] It was found that the reactions obey second-order kinetics, the reactivity of imines sharply decreasing in the series **3** > **10** > **7**.

$Cl_3CCH=NR$	**3a**	**3d**	**10b**	**7b**
R	$PhCH_2CO$	EtCO	EtOCO	$(EtO)_2PO$
k /litre mol^{-1} h^{-1}	226.0	77.0	14.6	4.7

The rate constants for the addition of ethanethiol diminish by factors of 20 to 52 on passing from the acylimines **3** and **10** to the phosphorylimine **7**. Evidently, this is due to the decrease in the electronegativity of the acid residues, resulting in a higher electron density on the carbon atom of the azomethine group. The substantial decrease in the reactivity observed on passing from *N*-ethoxycarbonylchloral imine **10b** to *N*-propionylchloral imine **3d** is due to the decrease in the conjugation of the azomethine group with the carbonyl group involving the alkoxy residue. The considerable influence of conjugation is also supported by the fact that the reactivity of an imino group attached to a phosphonyl residue is even lower because in this case, conjugation is insignificant if at all present.[122]

Study of the reactivity of the chloral aroylimines **3i**–**m** towards 2,4,6-trichloroaniline in benzene, dioxane and acetonitrile demonstrated that the rate of addition of the amine in acetonitrile depends on the substituents in the benzene nucleus.[41] This reaction is accelerated by electron-withdrawing substituents and retarded by electron-donating ones.

Comparison of the reactivity of chloral imines towards 2,4,6-trichloroaniline [41] demonstrated that the influence of the substituent at the nitrogen atom on the capacity of the C=N bond for the addition reactions decreases in the sequence COAr > COAlk > SO_2Ar and also in the sequence COAlk > $PO(OAlk)_2$ > COOAlk.

Although arylsulfonamide groups possess high electronegativity, they have a lesser influence on the reactivity of the C=N bond towards trichloroaniline. The addition of the amine to phosphoryl- and sulfonylimines is characterised by greater negative values of activation entropy than the addition to acylimines. This was interpreted [41] by assuming that the reactions of the amine with the C=N–C=O, C=N–P=O and C=N–SO_2 systems occur *via* different cyclic transition states. In the case of acylimines, a six-membered transition complex is formed, whereas for phosphoryl- and sulfonylimines a four-membered transition state is involved. This assumption is confirmed by the known fact that acylamines enter into 1,4-cycloaddition reactions, whereas arylsulfonylimines tend to undergo 1,2-cycloaddition.

a. Reactions of imines with O-nucleophiles

The reactions of imines with oxygen-containing nucleophiles have been studied most extensively; it was shown that acyl-, alkoxy(aryloxy)carbonyl-, carbamoyl-, sulfonyl- and phosphoryl-imines of polyhaloaldehydes add water and alcohols with heat evolution to give stable hydroxy- **58** and alkoxy-substituted **59** haloalkylamides.

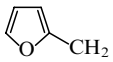
$$RN{=}CHCXHal_2 + H_2O \longrightarrow \underset{\mathbf{58}}{RNHCH(OH)CXHal_2}$$

R	X	Hal	Ref.
MeCO	Cl	Cl	37
PhCO	Cl	Cl	35
$Ph_3P=C(CN)CO$	Cl	Cl	65
MeOCO	Cl	Cl	36
EtOCO	Cl	Cl	36, 72
BuOCO	Cl	Cl	72
PhOCO	Cl	Cl	35
Et_2NCO	Cl	Cl	68
$O(CH_2CH_2)_2N$	Cl	Cl	68
4-$MeC_6H_4SO_2$	Cl	Cl	32, 74, 123, 124
$PhSO_2$	Cl	Cl	74, 123, 124
4-$ClC_6H_4SO_2$	Cl	Cl	74, 123, 124
4-$NO_2C_6H_4SO_2$	Cl	Cl	70
3-$NO_2C_6H_4SO_2$	Cl	Cl	70
$(EtO)_2P(O)$	Cl	Cl	33, 50
$(MeO)_2P(O)$	Cl	Cl	33
$(Pr^nO)_2P(O)$	Cl	Cl	33
$(Pr^iO)_2P(O)$	Cl	Cl	33
$(Bu^iO)_2P(O)$	Cl	Cl	33
$(MeO)_2P(S)$	Cl	Cl	51
MeCO	Br	Cl	43
EtCO	Br	Cl	43

R	X	Hal	Ref.
MeOCO	Br	Cl	43, 44
EtOCO	Br	Cl	109
$PhSO_2$	Br	Cl	78
4-$ClC_6H_4SO_2$	Br	Cl	125, 78
$PhSO_2$	Cl	Br	107
MeOCO	Br	Br	42
EtOCO	Br	Br	36
4-$MeC_6H_4SO_2$	H	Cl	77, 126
$PhSO_2$	H	Cl	77, 126
4-$ClC_6H_4SO_2$	H	Cl	77, 126

$$R^1N{=}CHCXHal_2 + R^2OH \longrightarrow R^1NHCH(OR^2)CXHal_2$$

59

R^1	R^2	X	Hal	Ref.
EtOCO	Me	Cl	Cl	36
Me_2NCO	Me	Cl	Cl	68
4-$MeC_6H_4SO_2$	Me	Cl	Cl	32, 72, 124
$PhSO_2$	Me	Cl	Cl	8, 124
4-$ClC_6H_4SO_2$	Me	Cl	Cl	8, 124
$(MeO)_2P(S)$	Me	Cl	Cl	51
$Ph_3P{=}C(CN)CO$	Me	Cl	Cl	65
MeCO	Me	Br	Cl	43
EtCO	Me	Br	Cl	43
MeOCO	Me	Br	Cl	44
EtOCO	Me	Br	Cl	109
EtOCO	Me	Br	Br	36
MeCO	Me	Pr^n	Cl	34
MeCO	Me	Bu^n	Cl	34
PhCO	Et	Cl	Cl	35
PhOCO	Et	Cl	Cl	35
EtOCO	Et	Cl	Cl	36
Et_2NCO	Et	Cl	Cl	68
4-$MeC_6H_4SO_2$	Et	Cl	Cl	32, 124
$PhSO_2$	Et	Cl	Cl	124
4-$ClC_6H_4SO_2$	Et	Cl	Cl	74
$(EtO)_2P(O)$	Et	Cl	Cl	33
$(MeO)_2P(S)$	Et	Cl	Cl	51
$PhSO_2$	Et	Br	Cl	78, 125
4-$ClC_6H_4SO_2$	Et	Br	Cl	78
$PhSO_2$	Et	H	Cl	8, 77
$PhSO_2$	Et	Br	Cl	107
$(Bu^iO)_2P(O)$	Bu^i	Cl	Cl	33
$PhSO_2$		Cl	Cl	127
$PhSO_2$	Bu^n	Ph	Cl	128
$PhSO_2$	$CH_2{=}CHCH_2$	Cl	Cl	129
4-$MeC_6H_4SO_2$	$CH_2{=}CHCH_2$	Cl	Cl	129
4-$ClC_6H_4SO_2$	$CH_2{=}CHCH_2$	Cl	Cl	129

Allyl alcohol adds to chloral arylsulfonylimines under mild conditions without heating.[129]

The addition of alcohols and ammonia at the C=N bond in trichloromethyl phenyl ketimines is accompanied by simultaneous replacement of the fragment X by an alcoholic residue or an amino group to give 1-[alkoxy(amino)carbonylamino]-2,2,2-trichloroethylbenzenes **60**.[62]

$$Cl_3CC(Ph){=}NCOX \xrightarrow{HY} Cl_3CCY(Ph)NHCOY$$

60

X = OAlk, SAr, $NAlk_2$; Y = MeO, EtO, NH_2.

Reactions of acyl-, sulfonyl- and dialkoxyphosphoryl-trichloroethylideneamines with phenols and 1-naphthol have been studied. It was shown that phenol[33, 36, 37, 50, 123, 124, 130] and *p*-chlorophenol[33, 39, 130] add to almost all types of imines giving rise to aryloxy derivatives **61**.

$$RN{=}CHCXCl_2 + ArOH \longrightarrow RNHCHCXCl_2 \quad (OAr)$$

61

Ar = Ph, 4-ClC_6H_4; X = Cl, CH_2Cl;
R = AlkCO, AlkOCO, $(AlkO)_2PO$, $ArSO_2$.

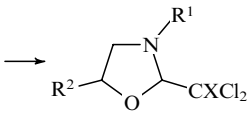
1-Naphthol readily adds to phosphorylimines.[33, 50] However, these imines give no addition products with 2,6-dimethylphenol, 2,6-dinitrophenol or 2,4,6-trinitrophenol even on heating.[33] This is caused not only by steric reasons but also by the low nucleophilicity of nitrophenols.

Chloral arylsulfonylimines, which also react with phenol, do not react with chloro-substituted phenols.[123]

2-Chloroalkanols vigorously react with chloral imines and dichloroacetaldehyde sulfonylimines yielding *N*-[(2,2-dichloro-2-X-1-(2-chloroalkoxy)ethyl]amides **62**, which cyclise on treatment with an alkali giving rise to 1-arylsulfonyl(ethoxycarbonyl)-2-trichloromethyl- and -dichloromethyloxazolidines.[77, 131]

$$R^1N{=}CHCXCl_2 \xrightarrow{ClCH_2CH(R^2)OH} R^1NHCHCXCl_2 \quad (OCH(R^2)CH_2Cl) \xrightarrow{NaOH}$$

62a–g



63a–g

R^1 = $PhSO_2$ (**a**), 4-$ClC_6H_4SO_2$ (**b**), 4-$MeC_6H_4SO_2$ (**c**), EtOCO (**d**), R^2 = H, X = Cl; R^1 = $PhSO_2$, R^2 = CH_2OMe, X = Cl (**e**); R^1 = $PhSO_2$, R^2 = CH_2Cl, X = Cl (**f**); R^1 = $PhSO_2$, R^2 = H, X = H (**g**).

The reactions of imines with carboxylic acids have been studied extensively. Although carboxylic acids are weak nucleophiles, they add at the C=N bond of imines (sometimes on heating) to afford 1-acyloxy-2-polychloroethylalkylamides **64**.

$$R^1N{=}CHCXCl_2 + R^2COOH \longrightarrow R^1NHCHCXCl_2 \quad (OC(O)R^2)$$

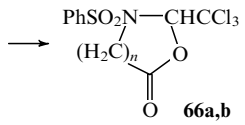
64

R^1	X	R^2	Ref.
MeCO	Cl	Me	37
$PhSO_2$	Cl	Me	124
$(EtO)_2PO$	Cl	Me	33
$(Bu^iO)_2PO$	Cl	Me	33
$PhSO_2$	Ph	CH_2Cl	128
MeCO	Bu^n	Me	34
$PhSO_2$	Cl	Ph	124
$(MeO)_2PO$	Cl	Ph	33
$(Pr^nO)_2PO$	Cl	Ph	33
$(Pr^iO)_2PO$	Cl	Ph	33
$(Bu^iO)_2PO$	Cl	Ph	33
MeCO	Pr^n	Ph	34
MeCO	CH_2Cl	Ph	130
EtCO	CH_2Cl	Ph	130
Pr^nCO	CH_2Cl	Ph	130
MeCO	CH_2Cl	1-naphthyl	130
Pr^nCO	CH_2Cl	1-naphthyl	130
$PhSO_2$	Cl	2-furyl	127

The imine **2b** reacts with halocarboxylic acids to give addition products — sulfonamides **65a**,**b**. An attempt to dehydrohalogenate these products in order to prepare heterocyclic compounds **66a**,**b** failed.[131]

$$PhSO_2N{=}CHCCl_3 \xrightarrow{X(CH_2)_nCOOH} PhSO_2NHCHCCl_3 \quad (OCO(CH_2)_nX) \not\longrightarrow$$

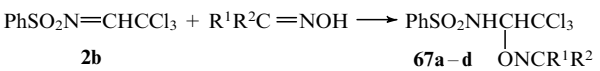
2b **65a,b**



66a,b

X = Cl, n = 1 (**a**); X = Br, n = 2 (**b**).

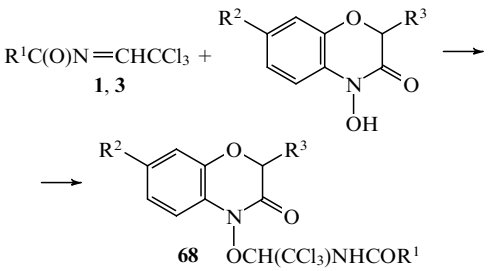
The sulfonylimine **2b** vigorously reacts with oximes of aliphatic, cycloaliphatic and aromatic ketones being thus converted into the addition products **67a–d**.[8,11,124]



2b **67a–d**

R^1 = Me: R^2 = Ph (**a**), Bu^t (**b**), Me (**c**); R^1–R^2 = $(CH_2)_5$ (**d**).

An attempt was made to carry out addition of hydroxylamines to imines. Cyclic hydroxylamines, namely, 4-hydroxy-2*H*-1,4-benzoxazin-3(4*H*)-ones, were found to add to the acylimines **1** and **3**. Compounds **68** were patented as antimicrobial preparations.[132]

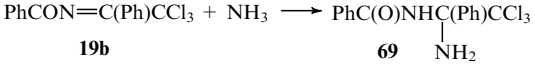


1, **3** **68**

R^1 = Alk, Ar, ArO; R^2, R^3 = H, Hal, AlkO, Alk, Ar, CN, NO_2.

b. Reactions of imines with NH-nucleophiles

Only two examples of addition of ammonia to the imines in question have been reported. The reaction of the benzoylimine **19b** with ammonia has resulted in the isolation of *N*-(1-amino-2,2,2-trichloro-1-phenylethyl)benzamide **69**.[86]



19b **69**

It was shown[65] that biphilic phosphonium ylide **9** reacts with ammonia to give the product of addition to the C=N bond, $Ph_3P{=}C(CN)COCH(NH_2)CCl_3$, in 95% yield, the cyano group and the C=P bond remaining intact. It was also reported that the reaction of ammonia with trichloromethyl phenyl ketimine affords 1-amino-1-phenyl-2,2,2-trichloroethylurea.[62]

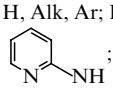
The reactions of N-functionally substituted imines of polyhalogenated aldehydes and ketones with amines, amides and imines have been studied in detail.

Acyl- and alkoxy(aryloxy)carbonyl-imines of polyhaloaldehydes add primary and secondary amines to give addition products **70** in good yields.[34–37,41,43–45,65]

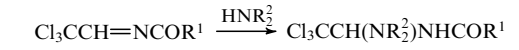


70

R^1 = AlkCO, AlkOCO, ArCO, ArOCO, $Ph_3P{=}C(CN)CO$;
R^2, R^3 = H, Alk, Ar; R^2–R^3 = $(CH_2)_2O(CH_2)_2$, $(CH_2)_4$;

NR^2R^3 =  ; X = Cl, MeCHCl, PhCHCl, Br, Pr, Bu.

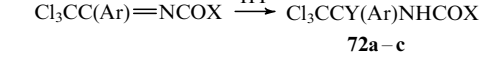
Trichloroethylideneureas show a similar behaviour in the reactions with amines. Thus the amides **11a–c** add diethylamine, morpholine or piperidine at 20 °C to give diethylamide, morpholide and piperidide, respectively, of 1-diethylamino- (**71a**), 1-morpholino- (**71b**) and 1-piperidino-2,2,2-trichloroethylcarbamic acid **71c**.[66,68]



11a–c **71a–c**

R^1 = , , Me_2N; R^2 = Et (**a**), $(CH_2)_2O(CH_2)_2$ (**b**), $(CH_2)_5$ (**c**).

Phenoxy- and methoxycarbonylimines of trichloromethyl aryl ketones also add amines at the C=N bond yielding compounds **72a–c**.[62]

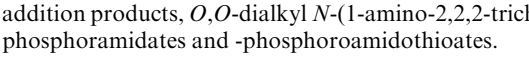


72a–c

X = PhO, Ar = 4-$Cl_3CC_6H_4$, Y = $PhCH_2NH$ (**a**);
X = MeO, Ar = Ph, Y = BuNH (**b**), $PhCH_2NH$ (**c**).

However, it was found that the reaction between phenyl phenyltrichloroethylidenecarbamate **53** and secondary amines, for example, morpholine or diphenylamine, can occur without participation of the C=N bond. Under rigorous conditions, the phenoxy group is replaced by an amine residue to give the imines **52**[62] (see Section II.7).

The reactions of dialkyl *N*-trichloroethylidene phosphoramidates **7** with amines have also been studied in detail. It was shown[41,133] that these imines and their sulfur-containing analogues[51] readily react with primary aromatic amines to give stable addition products, *O*,*O*-dialkyl *N*-(1-amino-2,2,2-trichloeroethyl) phosphoramidates and -phosphoroamidothioates.



7

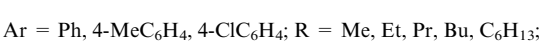
R^1 = $PO(OAlk)_2$ (Alk = Me, Et, Pr^n, Pr^i, Bu^i); $PS(OMe)_2$;
R^2 = H: R^3 = Ph, $PhCH_2$, 4-ClC_6H_4, 4-MeC_6H_4, 2,4,5-$Cl_3C_6H_2$;
R^2 = R^3 = Et; R^2–R^3 = $(CH_2)_5$.

The imines **7** add aniline, 4-chloroaniline and 4-methylaniline at room temperature; the reaction with 2,4,6-trichloroaniline occurs at ~80 °C and that with the least nucleophilic 2,4,6-trinitroaniline does not occur even at 100 °C.[133]

Whereas acyl-, phosphoryl-, alkoxycarbonyl- and carbamoylimines of trichloro- and dichloroacetaldehydes, trichloropropionaldehyde and other aldehydes react to give the products of addition to the azomethine bond, the trichloroethylidenearenesulfonamides **2** can either give the products of addition to the C=N bond or undergo haloform decomposition.

Aniline,[32,124] trichloroaniline,[41] morpholine,[124] *N*-ethylaniline,[136] *N*-methylaniline[136] and primary amines (methylamine, *tert*-butylamine, allylamine[129]) yield products of nucleophilic addition. Diphenylamine does not react with chloral arylsulfonylimine.[73]

Meanwhile, highly basic dialkylamines induce haloform decomposition; this affords the products of substitution of the CCl_3 group, *N*-arylsulfonyl-*N*′,*N*′-dialkylformamidines **73**,[73,134–136] in high yields.

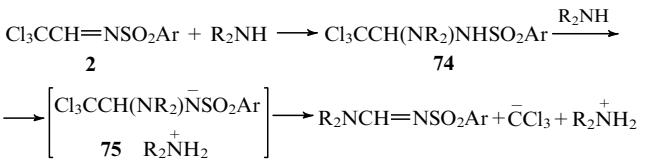


2 **73**

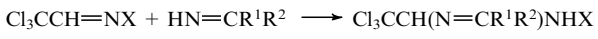
Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4; R = Me, Et, Pr, Bu, C_6H_{13};
R–R = $(CH_2)_2O(CH_2)_2$, $(CH_2)_5$.

In the case of sulfonylimines, this reaction pathway is explained[73] by the fact that the $ArSO_2$ group, unlike acyl or alkoxycarbonyl groups, cannot participate in conjugation and, hence, it cannot ensure stabilisation of the transition state. Therefore, $CHCl_3$ is ejected from the intermediate to give the compound **73**.

The reaction scheme proposed in the literature[136] includes the addition of amine to the double carbon–nitrogen bond and the reaction of the intermediate with a second amine molecule to give ionic species **75**. Fragmentation of this product yields formamide and a trichloromethyl anion.

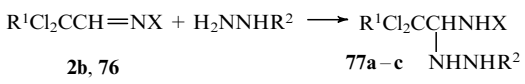


Imines add readily to the azomethine bond of the trichloroethylideneamides **1** and **7** giving rise to azomethines.[37, 136]



X = MeCO, $R^1 = R^2$ = Ph; X = $PO(OEt)_2$: $R^1 = R^2$ = Ph; R^1 = Ph, R^2 = 4-MeC_6H_4; R^1 = Me, R^2 = OEt.

When 2,2-dichloropentanal *N*-acetylimine **76**[34] or the phenylsulfonylimine **2b**[124] are made to react with hydrazines, the addition products, N^1-aryl-N^2-[1-amido-2-(trichloroethyl)- and -(2,2-dichloropentyl)]hydrazines **77a**–**c**, are produced in good yields.[124]

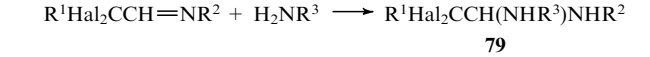


X = $PhSO_2$, R^1 = Cl, R^2 = Ph (**77a**); X = MeCO, R^1 = Pr, R^2 = Ph (**77b**), 2,4-$(NO_2)_2C_6H_3$ (**77c**).

N-2,2,2-Trichloro-, bromodichloro-, dibromochloro- and 2,2-dichloro-ethylideneamides and 2-R-2,2-dichloroethylideneamides of carboxylic, carbamic and sulfonic acids and of dialkyl phosphates add acid amides and substituted ureas on moderate heating giving rise to polyhaloalkanediylbisamides **78** and **79** in good yields.



R^1	R^2	Ref.
MeCO	MeCO	137
MeCO	PhCO	37
MeCO	$PhSO_2$	37
MeCO	$(EtO)_2PO$	37
MeCO	$(PhO)_2PO$	37
MeCO	$(MeO)_2PS$	138
MeCO	$(Pr^iO)_2PO$	138
MeCO	$(Pr^iO)_2PS$	138
MeCO	(MeO)(MeS)PO	138
MeOCO	MeOCO	39
MeOCO	$(EtO)_2PO$	39
PhCO	PhCO	137
$(EtO)_2PO$	$(EtO)_2PO$	133
$(EtO)_2PO$	MeCO	133
$(EtO)_2PO$	Cl_3CCO	133
$(EtO)_2PO$	Bu^tCO	133
$(EtO)_2PO$	PhCO	133
$(EtO)_2PO$	4-MeC_6H_4CO	133
$(EtO)_2PO$	H_2NCO	133
$(EtO)_2PO$	Me_2NCO	133
$(Pr^nO)_2PO$	MeCO	133
$(Pr^iO)_2PO$	MeCO	133
$(Pr^iO)_2PO$	H_2NCO	133
EtOCO	EtOCO	139
$PhSO_2$	MeCO	140
$PhSO_2$	PhCO	140
$PhSO_2$	H_2NCO	8
$PhSO_2$	—NC(O)$(CH_2)_3$	124
$PhSO_2$	PhNHCO	124
$PhSO_2$	$PhSO_2$	74, 123
$PhSO_2$	4-$MeC_6H_4SO_2$	123
4-$MeC_6H_4SO_2$	4-$MeC_6H_4SO_2$	74
4-$ClC_6H_4SO_2$	4-$ClC_6H_4SO_2$	74

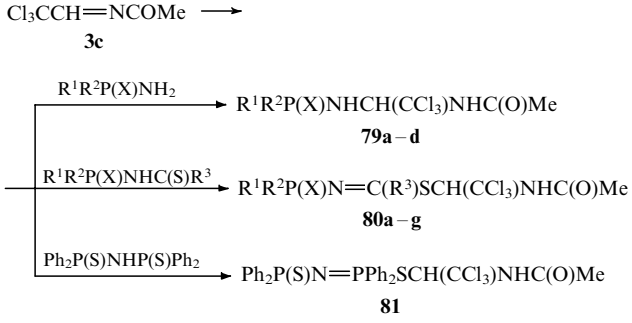


R^1	Hal	R^2	R^3	Ref.
H	Cl	EtOCO	EtOCO	76
Br	Cl	EtOCO	EtOCO	109
Cl	Br	EtOCO	EtOCO	76
MeCHCl	Cl	MeOCO	MeOCO	45
MeCHCl	Cl	PhCO	MeOCO	45
Br	Cl	$PhSO_2$	$PhSO_2$	125, 78
Br	Cl	4-$ClC_6H_4SO_2$	4-$ClC_6H_4SO_2$	78
H	Cl	$PhSO_2$	$PhSO_2$	77, 126
H	Cl	4-$MeC_6H_4SO_2$	4-$MeC_6H_4SO_2$	77, 126
H	Cl	4-$ClC_6H_4SO_2$	4-$ClC_6H_4SO_2$	77, 126
CH_2Cl	Cl	MeCO	MeCO	130
CH_2Cl	Cl	MeCO	EtCO	130
CH_2Cl	Cl	MeCO	Pr^nCO	130
CH_2Cl	Cl	MeCO	Me_2NCO	130
CH_2Cl	Cl	EtCO	EtCO	130
CH_2Cl	Cl	EtCO	Pr^nCO	130
CH_2Cl	Cl	EtCO	Me_2NCO	130
CH_2Cl	Cl	$ClCH_2CO$	$ClCH_2CO$	130
CH_2Cl	Cl	PhCO	PhCO	130

This reaction can be performed for amides of aliphatic and aromatic carboxylic acids unsubstituted at the nitrogen atom as well as phosphoric and phosphorothioic amides and thioamides; *N*-substituted amides do not react with acetylimines even on refluxing for several hours.[34, 138]

Detailed investigation of the reactions of the imines **7** with amides has revealed several characteristic features.[133] The capacity of amides for the addition sharply changes on variation of the electronegativity in the acyl residue. Comparison of the reactivities of acetamide, trichloroacetamide and the amide of pivalic acid demonstrates that the steric factor is insignificant. When the reaction mixture is heated to ~90 °C, pivalamide and acetamide add quantitatively, whereas trichloroacetamide reacts only at 167 °C.[133]

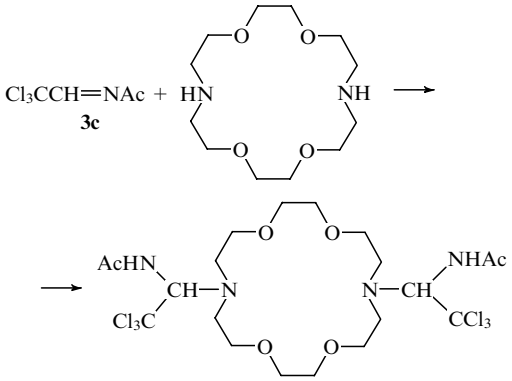
In a study of the addition of amides and thioamides of four-coordinate phosphorus to trichloroethylideneacetamide **3c**, it has been found that amides of phosphorus thioacids add more readily than the oxygen analogues to give the corresponding substituted acetamides **79a**–**d**.[138] *N*-Acylated amides and thioamides of phosphorus-containing acids do not enter into this reaction due to steric shielding and low nucleophilicity of the amide nitrogen atom. *N*-Thioacylamides of phosphorus acids, in which the sulfur atom of the C=S group possesses high nucleophilicity, undergo exothermic addition giving rise to carboximidothioates **80a**–**g**.[138] Addition at a sulfur atom also occurs in the reaction of the aldimine **3c** with bis(diphenylthiophosphinyl)amine; this affords phosphinimidothioate **81**.[138]



Compound	R^1	R^2	R^3	X
79a	Pr^iO	Pr^iO		O
79b	Pr^iO	Pr^iO		S
79c	MeO	MeO		S
79d	MeO	MeS		O
80a	Et	Et	Ph	S
80b	Pr^i	Pr^i	Ph	S
80c	Pr^i	Pr^i	4-$MeOC_6H_4$	S
80d	Pr^i	Pr^i	3-$NO_2C_6H_4$	S
80e	Et	Et	Ph	O
89f	Pr^i	Pr^i	Ph	O
80g	Pr^i	Pr^i	MeO	S

The reactivity of amides and thioamides of phosphorus acids towards chloral acetylimine increases in the sequence $R^1R^2P(X)NHC(O)R^3 < R^1R^2P(O)NH_2 < R^1R^2P(S)NH_2 < R^1R^2P(S)NHP(S)R^3_2 < R^1R^2P(X)NHC(S)R^3$.

Promising complex-forming reagents and biologically active compounds **82** have been prepared by the reaction of diaza-18-crown-6 with two equivalents of the imine **3c**. [141]



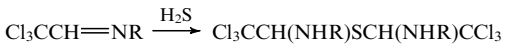
82

These compounds are smectic liquid crystals with fan texture.[141]

c. Reactions with S-nucleophiles

Much attention has been devoted to the reactivity of polyhaloaldehyde imines *N*-substituted by functional groups towards sulfur-containing nucleophiles (hydrogen sulfide, thiols, benzenethiols and thioamides), which add to imines very easily.

The *N*-acetaldimine **3c** and dialkyl phosphoramidates **7d**,**e** react with hydrogen sulfide at 20 °C (ratio 2 : 1) to give bis(1-amido-2,2,2-trichloroethyl) sulfides **83a**–**c**.[33, 37]

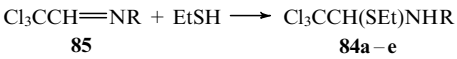


3c, **7d,e** **83a**–**c**

R = MeCO (**3c**, **83a**), $(Pr^iO)_2PO$ (**7d**, **83b**), $(Bu^iO)_2PO$ (**7e**, **83c**).

Unlike the reaction of imines with water, which yields stable hydroxy derivatives, in this case, the corresponding product with a thiol group has not been isolated. Evidently, this difference is related to the higher reactivity of *N*-(2,2,2-trichloro-1-sulfanylethyl)amides, formed in the first stage, towards the addition to the C=N bond of the initial imine compared to that of the hydroxy analogue.

As has already been noted, the rate of the reaction of ethanethiol with chloral imines depends on the nature of the substituent at the nitrogen atom; the reaction gives *N*-(2,2,2-trichloro-1-ethylthioethyl)amides **84**.[122] Later it has been shown that *O*,*O*-dimethyl *N*-(2,2,2-trichloroethylidene) phosphoramidothioate **85** also reacts with ethanethiol being thus converted into the compound **84e**.[51]

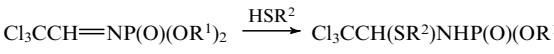


85 **84a**–**e**

R = $PhCH_2CO$ (**a**), EtCO (**b**), EtOCO (**c**), $(EtO)_2PO$ (**d**), $(MeO)_2PS$ (**e**).

Chloral arylsulfonylimines **2** add butanethiol and prop-2-ene-1-thiol.[142, 143]

The reactions of the phosphorus-substituted imines of chloral **7** with thiols and diphenylphosphinothioic acid have been studied extensively.[33, 50] These reactions occur on mixing the reactants without heating, the yields of *N*-(2,2,2-trichloro-1-R-thioethyl)amides **86** being quantitative.

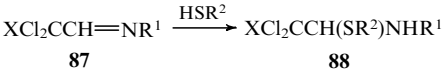


7a–**e** **86**

R^1 = Me, Et, Pr^n, Pr^i, Bu^i; R^2 = 4-ClC_6H_4, 4-$NO_2C_6H_4$, Et, Ph, $Ph_2P(S)$.

The acylimine **3c**,[37] the imine **9**, functionally substituted in the acyl fragment,[65] methoxycarbonylimine **10a** [39] and 2,2-dichloroalkylideneacetamides **76** [34] also react with ethanethiol,[34] 4-nitrobenzenethiol,[39] benzenethiol [34, 39] and 4-chlorobenzenethiol,[65] with heat evolution.

Imines **87** have been introduced *in situ* in the reaction with 4-chlorobenzenethiol; this gave *N*-[polychloroalkyl-1-(4-chlorophenylthio)]amides **88**.[45]

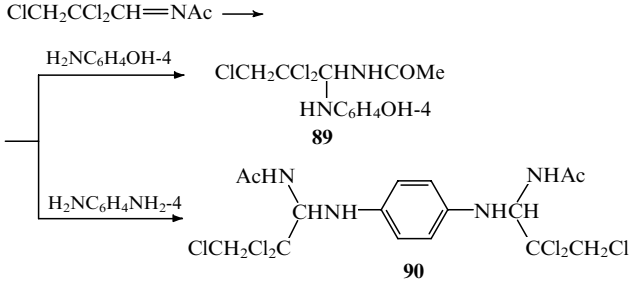


87 **88**

X = MeCHCl, PhCHCl; R^1 = MeOCO, PhCO; R^2 = 4-ClC_6H_4.

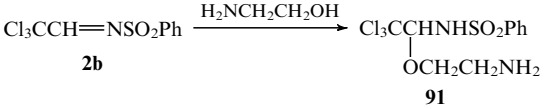
d. Reactions of imines with bifunctional O,O-, O,N-, S,N- and N,N-nucleophiles

The reactions of trichloropropionaldehyde acetylimine with 4-aminophenol and *para*-phenylenediamine have been studied.[130] These reactions were found to involve the amino group of the aminophenol or both amino groups of phenylenediamine and to give 4-(1-acetamido-2,2,3-trichloropropyl)aminophenol **89** or bis(*N*-1-acetamido-2,2,3-trichloropropyl)-1,4-phenylenediamine **90**.



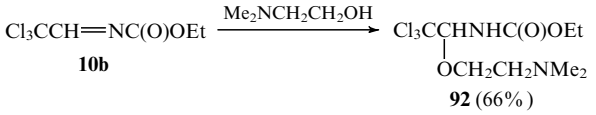
89 **90**

The sulfonylimine **2b** reacts with monoethanolamine at −20 °C giving compound **91** in a quantitative yield.[144]



2b **91**

Treatment of the sulfonylimines **2** with triethanolamine or dimethylethanolamine induces only haloform decomposition of azomethines.[73] However, the ethoxycarbonylimine **10b** reacts with *N*,*N*-dimethylethanolamine giving rise to a stable addition product **92**.[73]

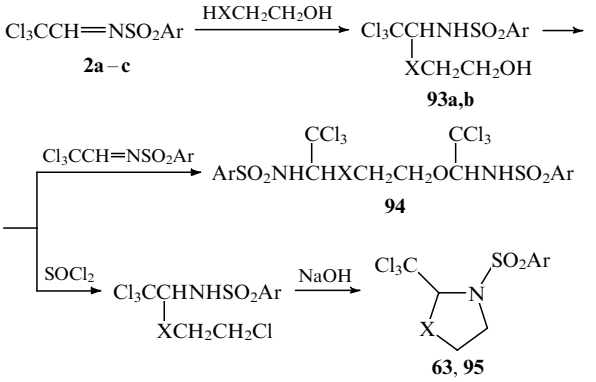


10b **92** (66%)

Only decomposition products — sulfamides, chloroform and aminothiol hydrochloride — have been isolated upon the exothermic reaction of the imines **2** with aminoethanethiol.[144]

The reaction of ethylene glycol with the imines **3** has given both mono- (**93**) and bis-O-amidoalkylation products, [1,2-bis(1-arylsulfonamido-2,2,2-trichloroethoxy]ethanes **94**.[144]

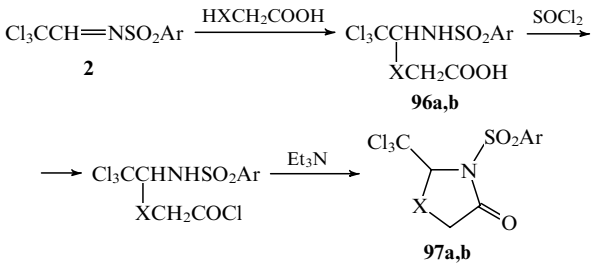
The addition of 2-hydroxyethanethiol to the sulfonylimines **2** at an equimolar ratio of the reactants occurs as an exothermic reaction involving the SH group and affords *N*-[2,2,2-trichloro-1-(2-hydroxyethylthio)ethyl]arenesulfonamides **93b**.[144] Successive treatment of these products with thionyl chloride and alkali results in the formation of the oxazolidines **63** and thiazolidines **95**.[131, 144]



2a–c **93a,b** **94** **63**, **95**

Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4; X = O (**63**, **93a**, **94**), S (**93b**, **95**).

The sulfonylimines **2** react with glycolic and sulfanylacetic acids under mild conditions to give nucleophilic addition products, *O*- or *S*-(2,2,2-trichloro-1-arylsulfonylamino)glycolic **96a** and -thioglycolic **96b** acids, respectively.[124, 145] When these products are treated with thionyl chloride and then with triethylamine, intramolecular cyclisation occurs giving rise to 3-arylsulfonyl-2-trichloromethyl-1,3-oxazolidin-4-ones **97a** and -1,3-thiazolidin-4-ones **97b**.

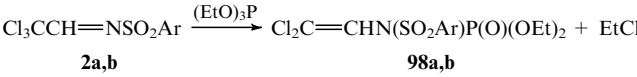


2 **96a,b** **97a,b**

Ar = Ph, 4-ClC_6H_4, 4-MeC_6H_4; X = O (**a**), S (**b**).

2. Reactions of phosphorus compounds with polyhaloaldehyde imines

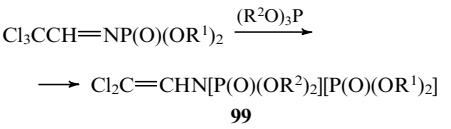
The sulfonylimines **2a**,**b** readily react with triethyl phosphite to give diethyl *N*-(2,2-dichlorovinyl)-*N*-(arylsulfonyl) phosphoramidates **98a**,**b** in high yields.[71, 146]



2a,b **98a,b**

Ar = 4-MeC_6H_4 (**a**), Ph (**b**).

Dialkyl *N*-trichloroethylidene phosphoramidates react with trialkyl phosphites giving rise to bis(phosphorylated) compounds **99**.[147]



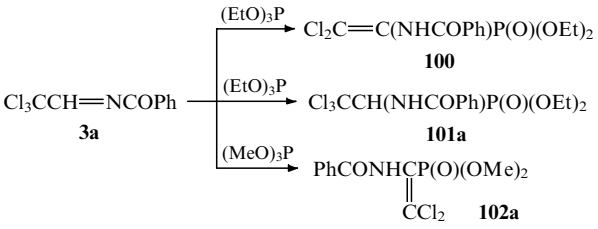
99

R^1 = Et, R^2 = Et, Pr.

The reactions of dialkyl *N*-tetrachloroethylidene phosphoramidates with trimethyl and triethyl phosphites occur in a similar way and result in the formation of trichlorovinylamides $Cl_2C{=}CClN[P(O)(OR^1)_2]$ (R^1 = R^2 = Me, Et; R^1 = Me, R^2 = Et).[102]

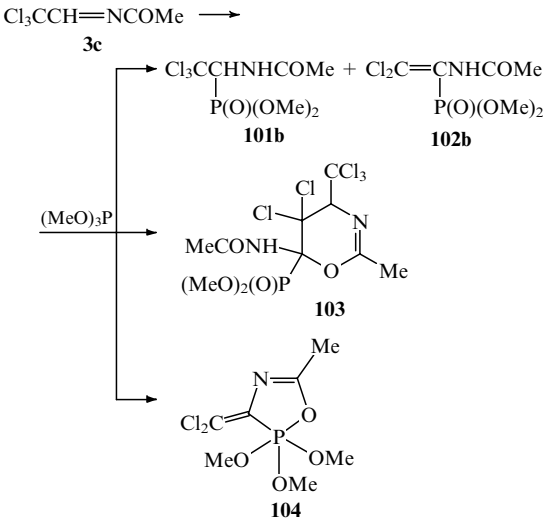
The reaction of benzoylchloral imine **3a** with triethyl phosphite follows a different pathway yielding a complex mixture of products, in which diethyl 1-benzamido-2,2-dichlorovinylphosphonate **100** and diethyl 1-benzamido-2,2,2-trichloroethylphosphonate **101** have been detected.[147]

Trimethyl phosphite reacts with the imine **3a** giving only dimethyl 1-benzamido-2,2-dichlorovinylphosphonate **102**; the yield of this product is not given in the study cited.[148]



3a **100** **101a** **102a**

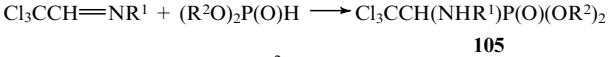
Detailed study of the reaction of the imine **3c** with trimethyl phosphite[148] showed that, depending on the reaction temperature, different products can be obtained.



3c **101b** **102b** **103** **104**

At −13 °C, a mixture of dimethyl α-(*N*-acetyl)amino-2,2,2-trichloroethylphosphonate **101b** and dimethyl α-(*N*-acetyl)amino-2,2-dichlorovinylphosphonate **102b** is formed. The same reaction carried out without cooling (40–45 °C) affords 1,3-oxazine **103**, and at −40 °C, 1,2,4-oxaphosphazole **104** is obtained.[149]

Organophosphorus acids and thioacids react with imines to give addition products.[36, 37, 150, 151] *N*-Acetyl-,[37] *N*-ethoxycarbonyl-[36] and perchloroalkylsulfonyl-trichloroacetaldimines[71] readily add various organophosphorus reagents. In the case of dialkyl phosphites, dialkyl 1-acetyl-, 1-ethoxycarbonyl- and perchloroalkylsulfonyl-amino-2,2,2-trichloroethylphosphonates **105** are formed.



105

R^1 = EtOCO, MeCO, Alk_FSO_2; R^2 = Alk.

The P-substituted imine **7b** also adds diethyl phosphite being thus converted into diethyl *N*-(1-diethoxyphosphoryl-2,2,2-trichloroethyl) phosphoramidate.[50]

The reaction of diphenylphosphinic acid[37] with the acetylimine **3c** results in the formation of the O-addition product, 1-acetylaminotrichloroethyl diphenylphosphinate **106a**; in the case of phosphorothioic and -dithioic acids, S-addition products, namely, 1-acetylamino-2,2,2-trichloroethyl diphenylphosphinodithioates and -thioates **106b**,**c** are produced.[37, 150, 151]

$$Cl_3CCH{=}NCOMe + R_2P(X)YH \longrightarrow \underset{\displaystyle YP(X)R_2}{\overset{\displaystyle |}{Cl_3CCHNHCOMe}}$$

106a–c

R = Ph, X = Y = O (**a**); R = Ph, MeO, EtO, Pr^{n}O, Pr^{i}O, X = Y = S (**b**); R = EtO, Pr^{n}O, Pr^{i}O, X = S, Y = O (**c**).

Phosphorus pentachloride is widely used in the reactions with derivatives of alkyl- and alkoxycarbonylimines of polyhaloaldehydes in order to prepare isocyanates.[62, 63] However, heating of *N*-perchloroethylideneureas **8**[63, 64] with PCl_5 yields highly reactive halo-substituted diazadienes **107a**,**b** in 41% – 76% yields.

$$\underset{\textbf{8}}{Cl_3CClC{=}NC(O)NHR} \xrightarrow{PCl_5} \underset{\textbf{107a,b}}{Cl_3CClC{=}NCCl{=}NR} + POCl_3 + HCl$$

R = Pr^i (**a**), Ph (**b**).

N-Mesityltrichloroethylideneurea reacts with phosphorus pentachloride to give a mixture of two isomers, carbodiimide and diazadiene.[63]

$$Cl_3CClC{=}NC(O)NHMes \xrightarrow[-POCl_3,\ -HCl]{PCl_5} \begin{cases} Cl_3CCl_2CN{=}C{=}NMes \\ Cl_3CClC{=}NCCl{=}NMes \end{cases}$$

An unusual reaction of *N*-*tert*-butyl-*N*′-perchloroethylideneurea with PCl_5 was discovered; in this case, phosphorus pentachloride acts simultaneously as a chlorinating and a phosphorylating agent.[64]

$$Cl_3CClC{=}NC(O)NHBu^t + PCl_5 \longrightarrow Cl_3CCl_2CN{=}CClN{=}PCl_3$$

When *N*-dichlorophosphorylimines of polychloroaldehydes are treated with phosphorus pentachloride, (dichlorophosphorylthio)polyhaloethylideneimines **37a–d** are formed (see Section II.6).[99]

3. Reactions of acylimines with organometallic compounds and metals

Reactions of polyhaloaldehyde imines with organometallic compounds have been less studied. A review has been published[19] dealing mainly with reactions with organomagnesium and -lithium compounds.

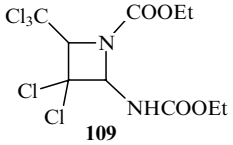
In the general case, alkoxycarbonylimines of chloral **10a**,**b** are converted into nucleophilic addition products **108** upon reactions with non-branched Grignard reagents.[39, 152]

$$\underset{\textbf{10a,b}}{Cl_3CCH{=}NCOR^1} + R^2MgX \longrightarrow \underset{\textbf{108}}{Cl_3CCH(R^2)NHCOR^1}$$

R^1 = MeO, EtO; R^2 = Me, Et, Pr, Bu, Ph, $PhCH_2$, $CH_2{=}CHCH_2$.

Branched organometallic compounds reduce the imine **10b** to the corresponding amine, which adds to the initial compound to give the aminal. This product cyclises giving rise to azetidine **109**.[152]

$$\underset{\textbf{10b}}{Cl_3CCH{=}NCOOEt} \xrightarrow{RMgX} Cl_3CCH_2NHCOOEt \xrightarrow{Cl_3CCH{=}NCOOEt} Cl_3CCH_2\underset{\displaystyle Cl_3CCHNHCOOEt}{\overset{\displaystyle |}{N}}COOEt \longrightarrow$$



109

R = Pr^i, Bu^i.

Acylimines of halogenated aldehydes, like other halogenated imines, react with lithium aluminium hydride yielding substituted aziridines.[19, 153, 154] In particular, *N*-acetyl-R-2,2-dichloroacetaldimines are converted into 1,2-substituted aziridines **110**, in which the acyl group has been reduced to an ethyl group.

$$RCl_2CCH{=}NCOMe \xrightarrow{LiAlH_4} \underset{\displaystyle R}{\overset{\displaystyle |}{N}}\!\!\begin{array}{l}\diagup\ \diagdown\\ \text{COMe}\quad Cl\end{array} \xrightarrow{LiAlH_4} \underset{\displaystyle R}{\overset{\displaystyle |}{N}}\!\!\begin{array}{l}\diagup\ \diagdown\\ \text{Et}\quad\ \ \end{array}$$

110

R = Pr, Bu, C_5H_{11}.

The behaviour of trichloroethylideneacetamide **3c** in reactions with zinc and electrophilic reagents has been studied.[155] The interaction of the imine **3c** with zinc affords a zinc-containing intermediate, which is a polydentate reagent with three nucleophilic centres — the carbon, nitrogen and oxygen atoms. The reaction of this intermediate with α-chlorinated ethers or acyl halides gives *N*-addition products, namely, substituted amides and imides. The reaction with chlorotrimethylsilane affords the O-attack product, *N*-(2,2-dichlorovinyl)-*N*-(1-trimethylsilyloxyethylidene)amine.

$$\underset{\textbf{3c}}{Cl_3CCH{=}NCOMe} \xrightarrow{Zn} [Cl_2C{\cdots}CH{\cdots}N{\cdots}C(Me){=}O]^+Cl^- \longrightarrow \begin{cases} \xrightarrow{ClCH_2OBu} Cl_2C{=}CHN(COMe)CH_2OBu \\ \xrightarrow{ClCOR} Cl_2C{=}CHN(COMe)COR \\ \xrightarrow{ClSiMe_3} Cl_2C{=}CHN{=}CMeOSiMe_3 \end{cases}$$

R = Me, Pr^i, Bu^n, Bu^t, Ph.

4. Reactions of imines with inorganic acids

The reactions of imines with hydrogen chloride have been studied in the greatest detail; it has been shown that polyhaloalkylideneamides of dialkylphosphinic, carboxylic and carbamic acids are converted into chloroalkyl derivatives.[33, 35, 37, 39, 46, 50]

On treatment of the sulfonylimines **2a**,**b** with hydrogen cyanide in the presence of triethylamine, 1-(arylsulfonylamino)-2,2-dichloroacrylonitriles **111a**,**b** are readily formed.[156]

$$\underset{\textbf{2a,b}}{Cl_3CCH{=}NSO_2Ar} + HCN \longrightarrow [Cl_3CCH(CN)\bar{N}SO_2Ar \rightleftharpoons Cl_3C\bar{C}(CN)NHSO_2Ar] \xrightarrow[-HCl]{Et_3N} \underset{\textbf{111a,b}}{Cl_2C{=}C(CN)NHSO_2Ar}$$

Ar = 4-MeC_6H_4 (**a**), Ph (**b**).

Similarly, when the benzoylimine **3a** is treated *in situ* with hydrogen cyanide, *N*-(2,2-dichloro-1-cyanovinyl)benzamide is produced.[38]

On the other hand, the methoxycarbonylimine of trichloromethyl phenyl ketone adds hydrogen cyanide to give the amide $Ph(CCl_3)C(CN)NHCOOMe$.[62]

The reaction of chloral imines with hydrazoic acid has been carried out; this gave 1-amino-2,2,2-trichloroethyl azides **112**.[40]

$$Cl_3CCH{=}NR + HN_3 \longrightarrow Cl_3CCH(N_3)NHR$$
112

R = $PO(OEt)_2$, COEt, COPr, $COCH_2Ph$, COOEt.

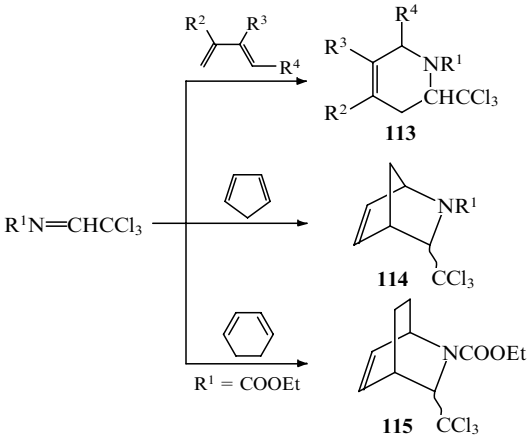
5. Cycloaddition reactions involving alkoxycarbonyl-, acyl- and sulfonyl-imines of polyhaloaldehydes

The capability of acylimines, including halogenated ones, of exhibiting the properties of both dienophiles and dienes has been discussed in reviews.[157,158] Sulfonylimines can act as dienophiles.[158] It should be noted that these reviews[157,158] are far from embracing all publications devoted to this topic.

The high reactivity of chloral sulfonylimine **2a** towards dienes (2,3-dimethylbutadiene and cyclopentadiene) was first reported in 1964.[159] Reactions of chloral sulfonylimines with a large number of dienes (piperylene,[160] butadiene,[161] cyclopentadiene,[57,158–164] dimethylbutadiene[161,162,165] and isoprene[160,161]) have been studied much later. The cycloaddition products, 1-arylsulfonyl- and 1-alkoxycarbonyl-2-trichloromethyl-1,2,3,6-tetrahydropyridines **113** and *N*-arylsulfonyl- and *N*-alkoxycarbonyl-2-azabicyclo[2.2.1]hept-5-enes **114** are formed in 50%–94% yields.

N-Ethoxycarbonyl-2-azanorbornenes have been synthesised and some of their reactions, for example, dehydrochlorination and bromination, have been studied.[161,162]

N-Ethoxycarbonyl-2-azabicyclo[2.2.2]oct-5-ene **115** has been prepared[163] by the reaction of the imine **10b** with cyclohexadiene. Chloral 4-tolylsulfonylimine **2a** does not enter into the cycloaddition reaction with cyclohexadiene either on heating or under acid catalysis.[163]

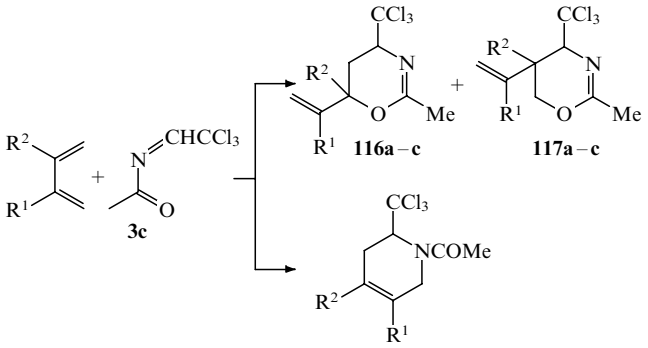


R^1 = MeOCO, EtOCO, MeCO, 4-$XC_6H_4SO_2$ (X = H, Me, Cl, MeO); R^2, R^3, R^4 = H, Me.

Cycloaddition of halogenated azomethines to non-symmetrical dienes occurs regiospecifically giving only one of the two possible isomeric heterocycles.[160]

Study of the ^{1}H NMR spectra of 4-tolylsulfonyl-, alkoxycarbonyl-, and acetyl-substituted 2-azanorbornenes and bicyclooctenes, prepared by the reactions of chloral imines **2a**, **3c**, and **10a**,**b** with cyclopentadiene and cyclohexadiene, showed that these bicyclic systems are mixtures of two isomers with *exo*- and *endo*-arrangement of the trichloromethyl group, the isomer ratio being dependent on the reaction temperature and on whether or not a Lewis acid is present in the system.[161–164]

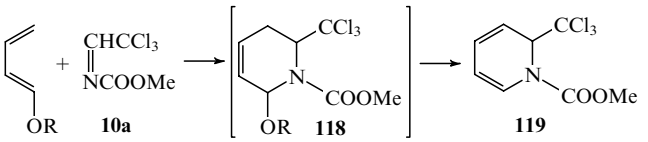
Acylimines of polyhaloaldehydes are able to participate in reactions with dienes not only as dienophiles but as heterodienes.[162]



R^1 = R^2 = Me (**a**); R^1 = Me, R^2 = H (**b**); R^1 = OMe, R^2 = H (**c**).

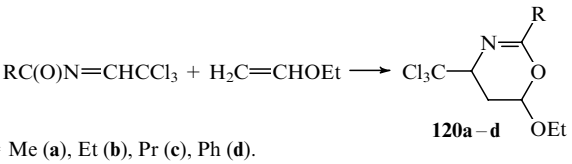
Thus the acetylimine **3c** reacts with 2,3-dimethyl-, 2-methyl- and 2-methoxybuta-1,3-dienes mainly as a diene to give mixtures of 5,6-dihydro-4*H*-1,3-oxazine derivatives **116a**–**c** and **117a**–**c**. When the acetylimine reacts with 2,3-dimethylbuta-1,3-diene, it acts as a dienophile; a compound of the type **113** was isolated.[165]

The methoxycarbonylimine **10a** reacts with 1-alkoxydienes as a dienophile, the final reaction product, 1-methoxycarbonyl-2-trichloromethyl-1,2-dihydropyridine **119**, being formed in 84% yield upon elimination of an alcohol molecule with simultaneous migration of the double bond in the intermediate **118**.[166]



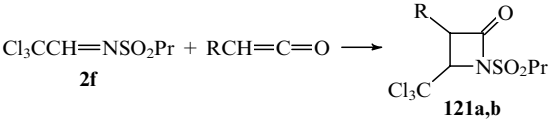
R = Me, Et.

Chloral acylimines introduced in reactions with vinyl ethyl ether act as heterodienes, which leads to 2-alkyl-6-ethoxy-4-trichloromethyl-5,6-dihydro-4*H*-1,3-oxazines **120a**–**d**.[167]



R = Me (**a**), Et (**b**), Pr (**c**), Ph (**d**).

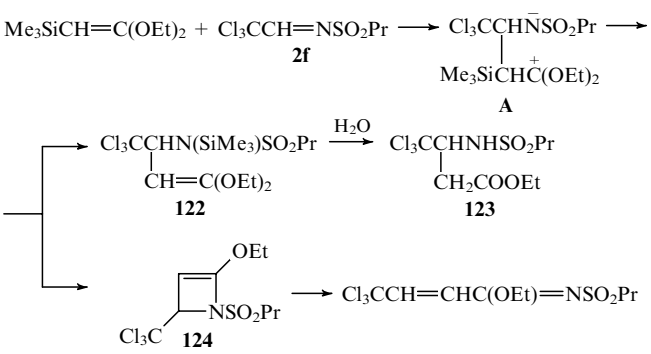
Sulfonylimines are capable of forming [2 + 2]-cycloadducts. Thus the imine **2f** reacts with trimethylsilyl ketene or ketene at room temperature to afford 1-propylsulfonyl-4-trichloromethylazetidin-2-ones **121a**,**b**.[168,169]



R = H (**a**), $SiMe_3$ (**b**).

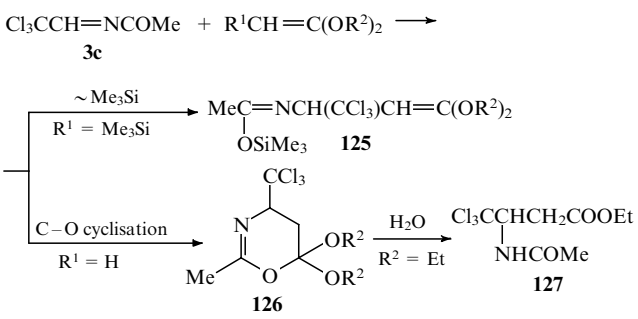
The reaction of the sulfonylimine **2f** with trimethylsilyl ketene diethylacetal gives 3-(*N*-trimethylsilylpropylsulfonylamino)-1,1-diethoxy-4,4,4-trichlorobut-1-ene **122** instead of a cyclic product. The compound **122** undergoes desilylation and hydrolysis yielding ethyl 3-(propylsulfonylamino)-4,4,4-trichlorobutanoate **123**.[53]

The researchers[53] suggested that the reactions with trimethylsilyl ketene acetals occur *via* bipolar intermediate **A**, which is stabilised upon migration of the trimethylsilyl group. An alternative pathway in which the silyl group migrates in [2 + 2]-cycloadduct **124** formed from the intermediate **A** is also possible.



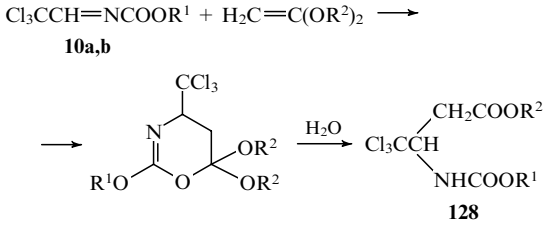
O-Silylated analogues of the compound **122**, 1 : 1 adducts **125**, have been isolated upon reactions of trimethylsilyl ketene dialkylacetal with the acetylimine **3c**. No desilylation was observed in this case.[169, 170]

It is noteworthy that the reaction of the imine **3c** with ketene acetals occurs without heating and gives [2 + 4]-cycloadducts, 6,6-dialkoxy-2-methyl-4-trichloromethyl-5,6-dihydro-4*H*-1,3-oxazines **126**. Under hydrolysis conditions, they are converted into alkyl 3-(methylcarbonylamino)-4,4,4-trichlorobutanoates, for example, compound **127**.[170]



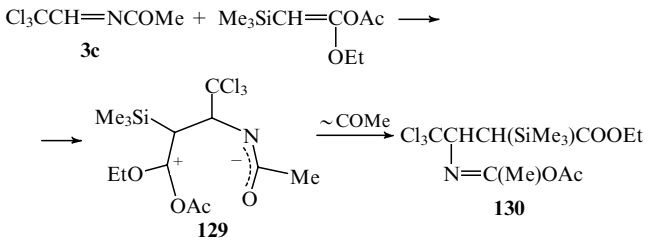
R^1 = H, Me_3Si; R^2 = Me, Et, Pr^i.

No cyclic products have been isolated after the reactions of the imines **10a**,**b** with ketene diethyl- and dimethylacetals. However, the formation of these products was proved by spectroscopy and by isolation of esters **128**, resulting from their transformations, in quantitative yields.[171]

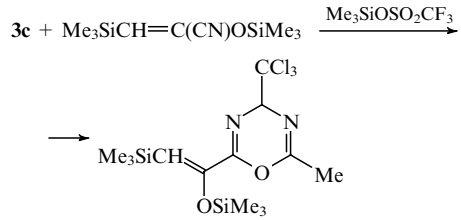


R^1, R^2 = Me, Et.

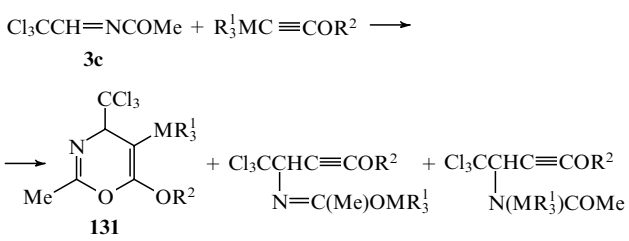
The reaction of chloral acetylimine **3c** with *O*-acetyl-*O*-ethyltrimethylsilyl ketene acetal gives a 1 : 1 product **130**, which is an ester of substituted butyric acid containing a trimethylsilyl group at the α-position. Presumably, this product results from migration of the acetyl group in the intermediate **129**.[172]



Meanwhile, 2-trimethylsilyloxy-3-trimethylsilylacrylonitrile reacts with the imine **3c** only in the presence of a catalyst, trimethylsilyl trifluoromethanesulfonate. The reaction involves the activated cyano group and results in [4 + 2]-cycloadduct, 4*H*-1,3,5-oxadiazine.[173]



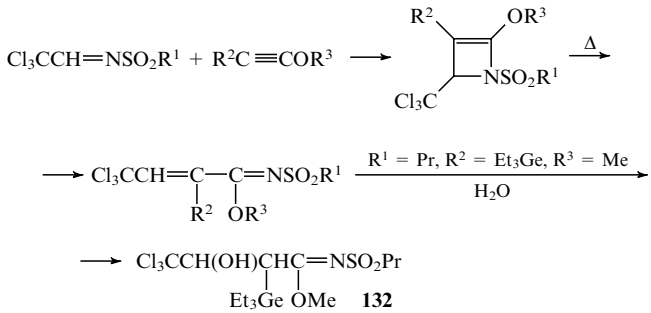
The reactions of imines with several acetylene derivatives have been studied. The chloral imine **3c** reacts with silicon- and germanium-substituted alkoxyacetylenes at room temperature without a catalyst to give a mixture of [4 + 2]-cycloadducts — 6-alkoxy-2-methyl-4-trichloromethyl-5-trialkylsilyl(trialkylgermyl)-4*H*-1,3-oxazines **131** — and *N*- and *O*-element-substituted acyclic compounds isomeric to them.[172]



R^1, R^2 = Me, Et; M = Si, Ge.

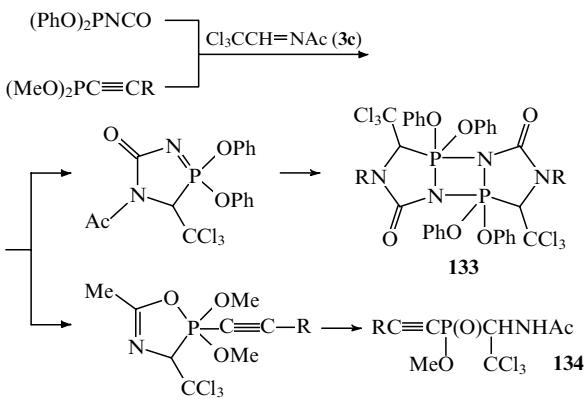
It is noteworthy that the reactions of ethoxyacetylene and methoxymethylacetylene with the imine **3c** occur over a period of 20 h at room temperature and give [4 + 2]-cycloadducts of type **131**, 6-alkoxy-2-methyl-4-trichloromethyl-1,3-4*H*-oxazines.[52]

The reactions of trialkylsilyl(germyl)ethoxyacetylenes with sulfonylimines follow the [2 + 2]-cycloaddition route. The resulting cycloadducts, 1-alkylsulfonyl-2-alkoxy-3-trialkylsilyl(germyl)-4-trichloromethyl-2-azetines, undergo ring opening under thermolysis conditions. The addition of water to the product of recyclisation of the triethylgermyl derivative of azetidine involves the C=C bond and gives compound **132**, the azomethine group remaining intact.[52]



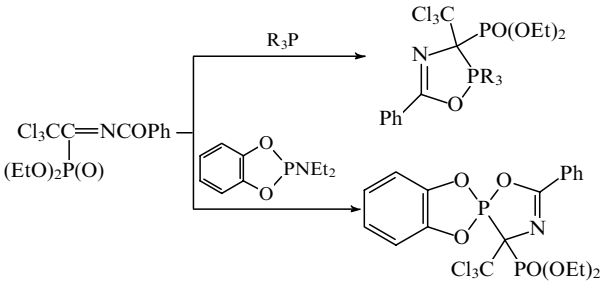
R^1 = Me, Pr; R^2 = Me_3Si, Et_3Si, Me_3Ge, Et_3Ge; R^3 = Me, Et.

Arylsulfonyl-, acetyl- and alkoxycarbonyl-imines of chloral enter into cycloaddition reactions with azomethines and azadienes. Thus cycloaddition of diphenyl isocyanatophosphite to the imine **3c** yields cycloadducts, the dimerisation of which during the reaction leads to tricyclodecanes **133**.[174] When the imine **3c** reacts with dimethyl alkynylphosphonites, unstable cycloadducts are formed, which are hydrolysed to give linear derivatives **134**.

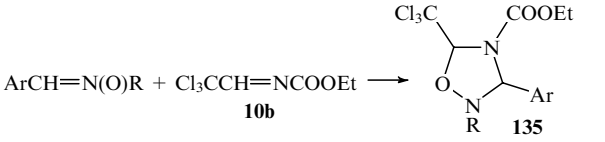


R = Me, Ph.

The imine **19c** containing a $P(O)(OEt)_2$ group reacts with acyclic phosphines in a similar way, giving rise to unstable [4 + 1]-cycloaddition products. The reaction of this imine with *P*-diethylaminobenzo-1,3-dioxaphospholane gives a stable spirophosphorane.[87]

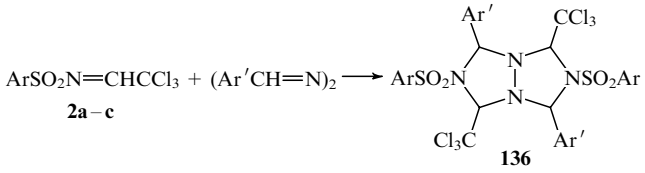


Ethyl 2-R-3-aryl-5-trichloromethyl-1,2,4-oxadiazolidine-4-carboxylates **135** have been prepared by the reaction of azomethine *N*-oxides with the imine **10b**.[175]



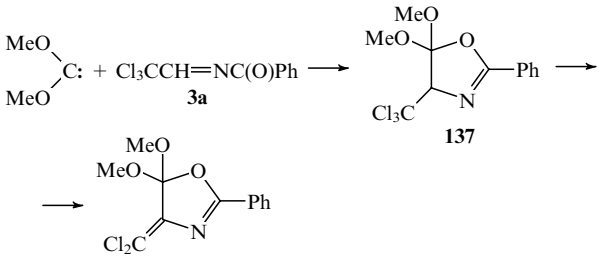
R = Ph; Ar = Ph, 4-$NO_2C_6H_4$, 4-$MeOC_6H_4$.

It was shown that the arylsulfonylimines **2a–c** react with benzal- and 4-methoxybenzal-azines by a two-stage cross-[2 + 3]-cycloaddition mechanism giving bicyclic triazole derivatives **136** but do not react with azines derived from other aromatic aldehydes.[176, 177] Arylsulfonylimines give no cycloaddition products when react with aliphatic ald- and ketazines; only the products of C-arenesulfonamidoethylation of azines were isolated.[177]



Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4; Ar′ = Ph, 4-$MeOC_6H_4$.

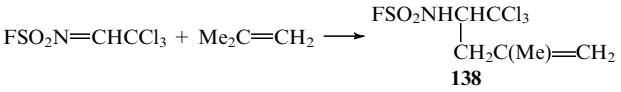
Dimethoxycarbene acts as the dienophile in the reactions with the heterodiene system of the benzoylimine of chloral **3a**; 5,5-dimethoxy-2-phenyl-4-trichloromethyl-4,5-dihydro-1,3-oxazolidine **137** thus formed is dehydrochlorinated under the reaction conditions.[178]



6. C-Amidoalkylation with polyhaloaldehyde imines

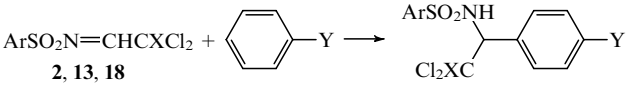
C-Amidoalkylation reactions had been unknown before 1970; it had only been reported[179] that chloral acylimines do not react with anisole.

The first example of involvement of imines of polyhaloaldehydes in C-amidoalkylation is represented by the reaction of chloral *N*-fluorosulfonylimine with isobutene, which gives the product of alkylation of the methyl group — 4-fluorosulfonylamino-5,5,5-trichloro-2-methylpent-1-ene **138**.[59]



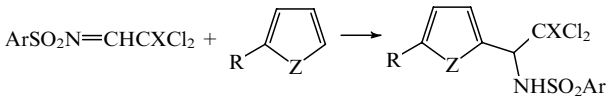
Later it has been shown that it is a general type of reaction. Arylsulfonylimines of chloral, dichloroacetaldehyde and dichlorophenylacetaldehyde can also amidoalkylate aromatic and heteroatromatic compounds.

Trichloro- **2**,[180] dichloro- **13**[77] and phenyldichloro-ethylidenearenesulfonamides **18**[181] react with electron-enriched arenes, namely, with anisole and thioanisole in the presence of boron trifluoride etherate and with dimethylaniline without a catalyst; the substituent enters the *para*-position with respect to the electron-donating group. The sulfonylimines **2** C-amidoalkylate benzene, toluene, chlorobenzene, naphthalene and chlorothiophene only in the presence of oleum.[182]



Ar = Ph, 4-ClC_6H_4, 4-MeC_6H_4; X = H, Cl, Ph;
Y = H, Me, OMe, SMe, NMe_2, Cl.

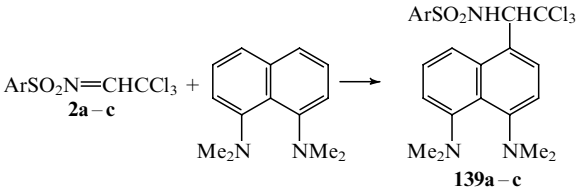
Pyrrole,[183] 1-methylpyrrole,[183] thiophene,[77, 182, 184] furan and sylvan [α-methylfuran, Ed.][77,127] have been C-arylsulfamidoalkylated by the imines **2** and **13**, the substituent entering the 2-position. 4,5-Tetramethylene-, 3*H*- and 3-methyl-4,5-pentamethylene-pyrroles react in a similar way.[183, 185] 2-Chlorothiophene reacts only in the presence of oleum.[182]



Ar = Ph, 4-ClC_6H_4, 4-MeC_6H_4; X = H, Cl; R = H, Cl, Me;
Z = S, O, NH, NMe.

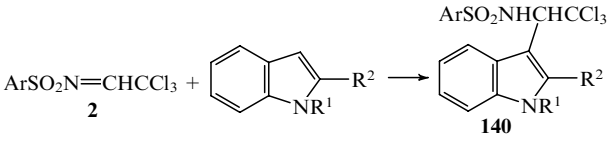
2-Acetyl- and 2-ethoxyfuran do not react with the imines **2**, and the reactions of 2-hydroxymethylfuran- and 2-furan-carboxylic acids involve the hydroxy or the carboxy group and afford addition products of types **59** and **64**, respectively, (see Section IV.1.a).[127]

The sulfonylimines **2a–c** react with 1,8-bis(dimethylamino)naphthalene without heating or catalysts giving rise to 4-[1-(arylsulfonylamino)-2,2,2-trichloroethyl]-1,8-bis(dimethylamino)naphthalenes **139**.[186]



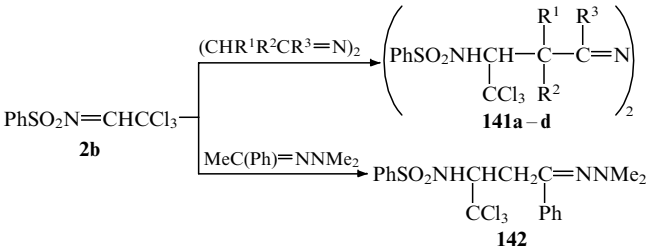
Ar = 4-MeC_6H_4 (**a**), Ph (**b**), 4-ClC_6H_4 (**c**).

The sulfonylimines **2** react equally easily with indole and its substituted derivatives being thus converted in good yields into compounds **140**, resulting from C-amidoalkylation at the 3-position.[187]



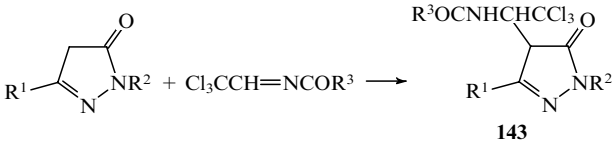
Ar = Ph, 4-ClC_6H_4; R^1, R^2 = H, Me.

The sulfonylimine **2b** C-amidoalkylates azines and hydrazones of aldehydes and ketones containing α-methylene and α-methine groups; this leads to 3-arylsulfonylamino-4,4,4-trichlorobutyl ketazines **141a**,**b**, aldazines **141c**,**d** and hydrazone **142**.[177]



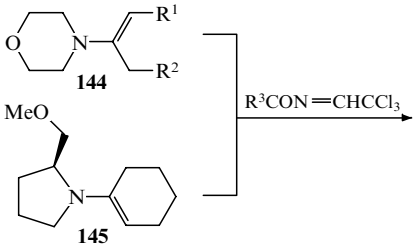
R^1 = R^2 = H: R^3 = Me (**a**), Ph (**b**); R^1 = R^2 = Me, R^3 = H (**c**);
R^1 = R^3 = H, R^2 = Et (**d**).

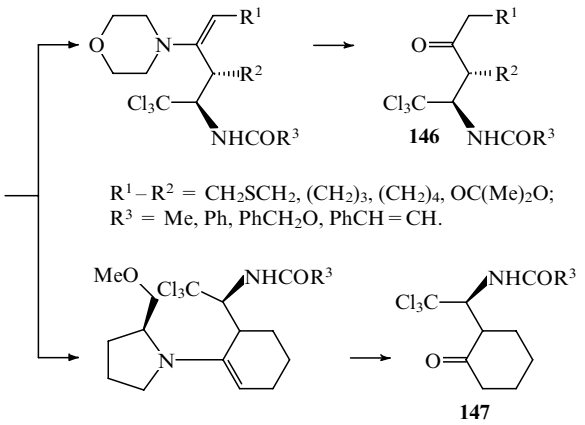
The use of polyhaloaldehyde imines for C-amidoalkylation of heterocyclic compounds extends the capacity for the preparation of new derivatives. Thus chloral imines of carboxylic and carbamic acids have been used in C-amidoalkylation of pyrazolones. This resulted in the synthesis of 2-aryl(alkyl)-4-[1-acetyl(benzoyl)aminoethyl-2,2,2-trichloro]-3-alkyl(phenyl)-2-pyr-azolones **143** in high yields.[188]



R^1 = Me, Et, Bu^i, Ph; R^2 = Ph, 2,4,6-$Cl_3C_6H_2$, Me; R^3 = Me, Ph, OEt.

The reactions of *N*-acyl-*N*-(2,2,2-trichloroethylidene)amines (which were prepared *in situ* from the corresponding 1,2,2,2-tetrachloroethylamides) with enamines **144** and **145** occur with high diastereo- and enantioselectivity yielding amidoalkylation products, which are hydrolysed to give chiral 2,2,2-trichloroethylamides **146**, **147**.[189]

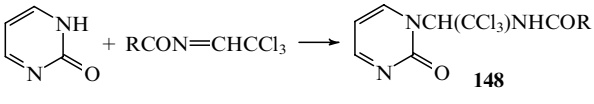




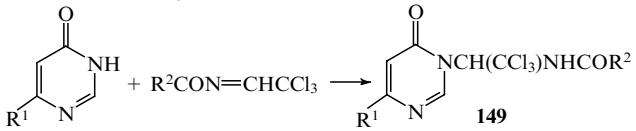
R^1–R^2 = CH_2SCH_2, $(CH_2)_3$, $(CH_2)_4$, $OC(Me)_2O$;
R^3 = Me, Ph, $PhCH_2O$, PhCH=CH.

R^3 = Ph, $PhCH_2O$.

Reactions of various types of monohydroxypyrimidines with *N*-(benzoyl)trichloroacetaldimine **3a** and other acylimines **3**, generated *in situ* from the corresponding tetrachloroethylamides have been studied.[190, 191] It was found that 2-hydroxypyrimidines and 4-hydroxypyrimidines containing no substituents at the 2-position form the products of amidoalkylation of the NH group — 1-(1-acylamino-2,2,2-trichloroethyl)-2- (**148**) and -4-hydroxypyrimidines **149**, respectively.[190]



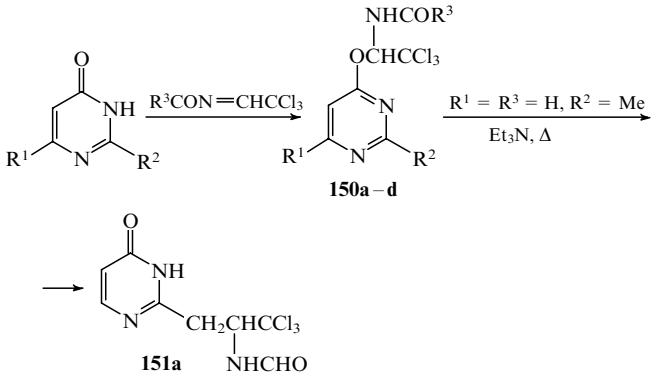
R = Ph, H, Bu^t, .



R^1 = H: R^2 = Ph, H, Bu^t, , 4-ClC_6H_4;

R^1 = Me: R^2 = Ph, H, Bu^t, .

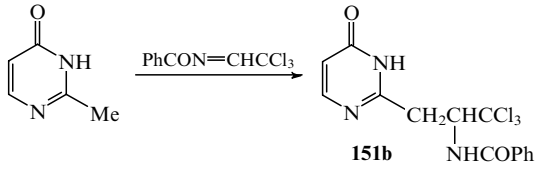
In the case of 2-alkyl-4-hydroxypyrimidines, the reaction involves the oxygen atom and gives *O*-(1-acylamino-2,2,2-trichloroethyl)-4-hydroxypyrimidines **150a**–**d**; in the opinion of the authors cited,[190] this is due to the steric shielding of both nucleophilic centres at the nitrogen atoms.



R^1 = H, R^2 = Me: R^3 = H (**a**), Ph (**b**);
R^1 = Me, R^2 = Pr^i: R^3 = Ph (**c**), 4-ClC_6H_4 (**d**).

Long refluxing of the imine **3a** with 4-hydroxy-2-methylpyrimidine induces C-amidoalkylation involving the methyl group of the pyrimidine, which affords 2-(2-benzamido-3,3,3-trichloropropyl)-4-hydroxypyrimidine **151b**.[190] The product **151a** with a

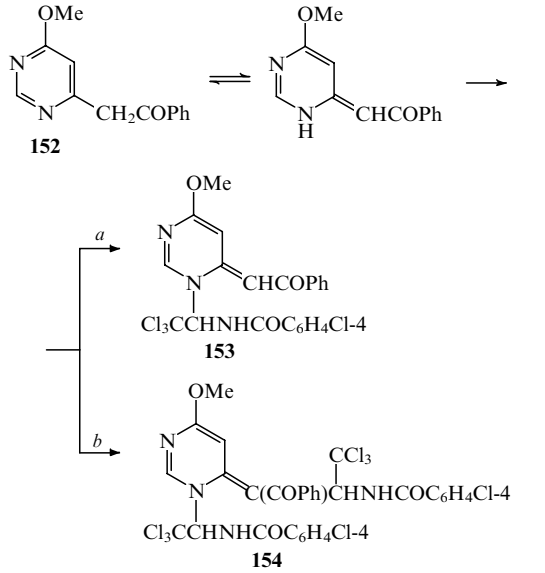
similar structure was also isolated when the pyrimidine **150a** was heated in the presence of triethylamine.[190]



151b

C-Amidoalkylation of 4-hydroxy-6-methylpyrimidine does not proceed even under rigorous conditions.[190]

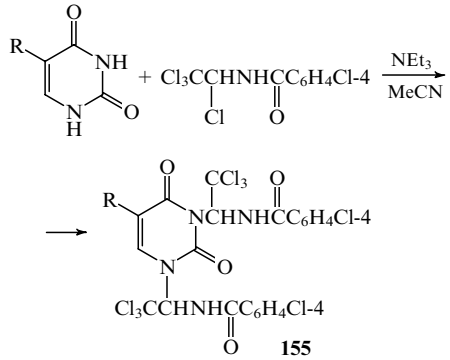
When 4-methoxy-6-phenacylpyrimidine **152** reacts with *N*-(1,2,2,2-tetrachloroethyl)amide of 4-chlorobenzoic acid in the presence of Et_3N, monoamidoalkylation product **153** is formed. When **152** reacts with the imine **3j**, the activated methylene group in the side chain and the ring nitrogen atom may be amidoalkylated simultaneously giving rise to compound **154**.[191]



(*a*) $Cl_3CCHClNHCOC_6H_4Cl$-4, Et_3N, Δ; (*b*) $Cl_3CCH{=}NCOC_6H_4Cl$-4 (**3g**).

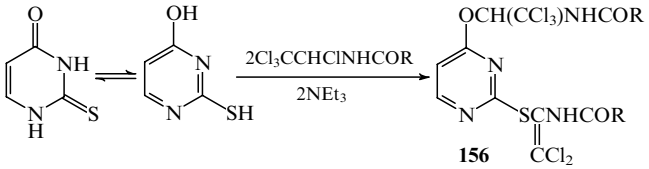
C-Amidoalkylation of the closest analogues of pyrimidine **152** — 4-dimethylamino-, 4-methyl-, 4-benzoylmethyl-6-(benzoyl)methyl-pyrimidines — has been accomplished by introducing these compounds into reactions with *N*-(1,2,2,2-tetrachloroethyl)amide of 4-chlorobenzoic acid in acetonitrile in the presence of triethylamine.[191] The alkylation involves the benzoylmethylene group and affords compounds of the type **153** — 4-dimethylamino-, 4-methyl-, 4-benzoylmethyl-6-[3,3,3-trichloro-2-(4-chlorobenzoylamino)-1-benzoylpropyl]pyrimidines.[191]

Under similar conditions, amidoalkylation of some 5-R-uracils by tetrachloroethylamides of benzoic acids involves both nitrogen atoms and affords 1,3-bis[2,2,2-trichloro-1-(4-chlorobenzoylamino)ethyl]-5-R-pyrimidine-2,4-diones **155**.[192]



R = H, Ph, OMe.

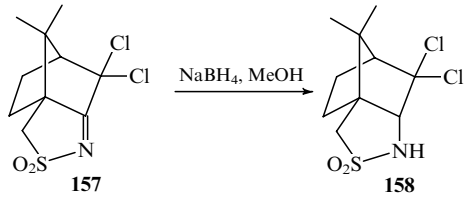
The reaction of 2-thiouracil with tetrachloroethylamides in the presence of triethylamine follows a more complex pathway, which includes not only amidoalkylation at the nitrogen and sulfur atoms but also dehydrochlorination; this gives 2-[(1-amido-2,2-dichlorovinyl)thio]-4-(1-amido-2,2,2-trichloroethoxy)pyrimidines **156**.[193]



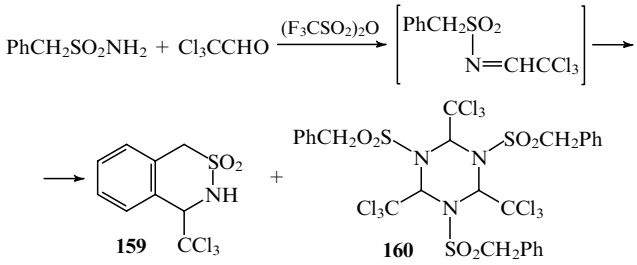
R = Bu^t, Ph, C_6H_4Cl-4, OMe.

7. Other reactions of polyhaloaldehyde imines

Reduction of imines presents interest as a method for the synthesis of amines. Only a single example of diastereoselective reduction of an azomethine group in cyclic dichlorocamphorsulfonylimine **157** to camphorsultam **158** (yield 93% – 97%) was reported.[194] In the case of the corresponding bromo-derivative, debromination is the predominant reaction route.



It was found[195] that when benzylsulfonamide reacts with chloral in the presence of trifluoromethanesulfonic anhydride or another similar reagent, the chloral benzylsulfonylimine formed at the first stage undergoes intra- and intermolecular heterocyclisation under the reaction conditions to afford 3,4-dihydro-1*H*-1,3-benzothiazine 2,2-dioxide **159** (yield 3% – 58%) and 1,3,5-tribenzylsulfonylhexahydrotriazine **160** (yield 17%).



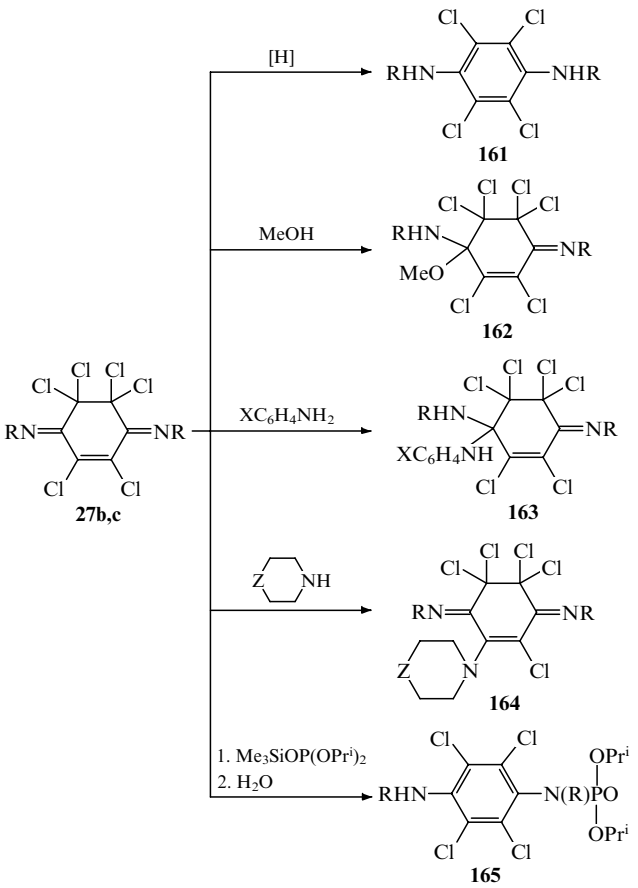
8. Reactivity of arylsulfonyliminopolychlorocyclohexenes

The reactions of bis(arylsulfonylimino)-2,3,5,5,6,6-hexachlorocyclohex-2-enes **27b**,**c** with reducing agents, organophosphorus and organosilicon compounds, alcohols, primary aromatic amines, secondary cyclic amines[196,197] and with hydrazoic acid[198] have been studied.

When the compounds **27b**,**c** react with $Na_2S_2O_4$, zinc in acetic acid or with dialkyl phosphites, elimination of two chlorine atoms from the 5- and 6-positions occurs to give the benzoid structure **161**.[196]

The reactions with methanol give products **162** resulting from addition to one azomethine bond. It was shown that 1,4-bis(arylsulfonylimino)hexachlorocyclohex-2-enes **27b**,**c** do not react with any other alcohols.[196]

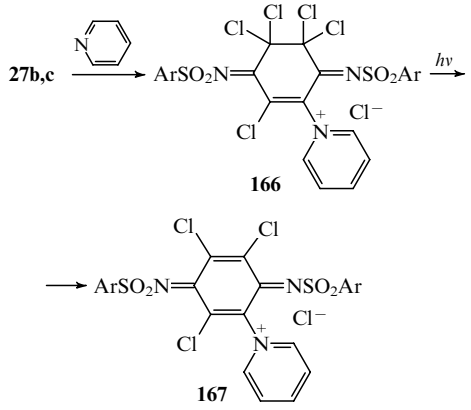
The reactions of the bis(sulfonylimines) **27b**,**c** with aromatic amines containing no electron-withdrawing groups in the aromatic ring also involve the addition to the C=N bond and give rise to compounds **163**.[196]



R = 4-$MeC_6H_4SO_2$ (**b**), 4-$ClC_6H_4SO_2$ (**c**); X = H, 4-Me, 3-Me; Z = O, CH_2.

The reactions with morpholine and piperidine occur as nucleophilic substitution of the chlorine atom at the sp^2-hybridised carbon atom of the bisimine and give products **164**.[196] Two processes — elimination of two chlorine atoms and 1,6-addition to the system of conjugated double bonds — occur simultaneously in the reactions of **27b**,**c** with trimethylsilyl diisopropyl phosphite. The addition products are subsequently hydrolysed with elimination of the trimethylsilyl group, which leads to compounds **165**.[196]

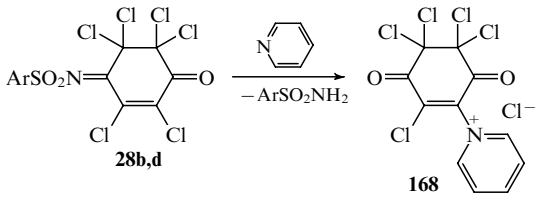
When the bis(sulfonylimines) **27b**,**c** react with pyridine, this gives the products of substitution of the vinylic halogen atom, *N*-[3,6-di(arylsulfonylimino)-2,4,4,5,5-pentachlorocyclohex-1-enyl]pyridinium chloride **166**; on exposure to UV radiation or under electron impact, these compounds eliminate two chlorine atoms to give quinone structures, *N*-[3,6-di(arylsulfonylimino)-2,4,5-trichlorocyclohex-1,4-dienyl]pyridinium chlorides **167**.[196]



Ar = 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**c**).

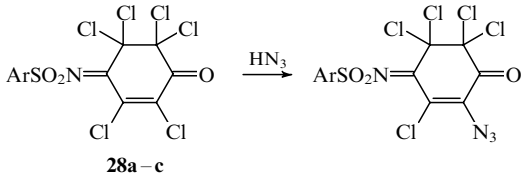
The reaction of 4-arylsulfonyliminohexachlorocyclohex-2-en-1-ones **28b**,**d** with pyridine results in the isolation of arenesulfamides and compounds **168**, formed upon the substitution of a pyridinium ion for the chlorine atom in the resulting 1,4-dioxo-2,3,5,5,6,6-hexachlorocyclohex-2-ene.[197]

It is of interest that 4-arylsulfonylimino-2,2,3,3-tetrachloro-1-oxo-1,2,4,4-tetrahydronaphthalenes **29** do not react with pyridine.



Ar = 4-ClC_6H_4 (**b**), 4-MeC_6H_4 (**d**).

The reaction of the imines **28a**–**c** with hydrazoic acid occurs as nucleophilic replacement of the chlorine atom at the sp^2-hybridised carbon atom located at the 2-position, accompanied by competing elimination of chlorine with restoration of the benzoid structure.[198]



Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**c**).

V. Conclusion

Analysis of the published data indicates that *N*-functionally substituted halogenated imines are highly stable and can be prepared by reactions of *N*,*N*-dihaloamides with 1,2-polyhaloethenes, transformation of an isocyanate bond and by other non-trivial methods, which require further development.

Electronegative substituents at the C=N bond account for the high reactivity of *N*-functionally substituted halogenated imines towards nucleophiles. A specific feature of these reactions is that nucleophiles attack the sp^2-hybridised carbon atom of the C=N bond. The enhanced electrophilicity of the C=N bond in polyhaloaldimines permits the use of acyl- and sulfonyl-imines for C-amidoalkylation of aromatic and heterocyclic compounds. Search for conditions under which acyl- and phosphonyl-imines of polyhalogenated aldehydes and ketones could be involved in similar reactions appears to be topical task.

Chloral acyl- and alkoxycarbonyl-imines can enter into cycloaddition reactions as heterodienes but can also act as dienophiles. Unfortunately, imines of the largest class, polyhaloalkylphosphonylimines, have not been studied in cycloaddition reactions.

Halogen-containing imines are of interest regarding investigation of the enamide–imine tautomerism and *syn*–*anti* isomerism of azomethines and determination of the energy parameters of tautomerisation and isomerisation.

The synthetic potential of imines is now far from being completely utilised. The data on the reactivity of halogenated imines can serve as the basis for targeted design of required structures with important biogenic groups: acyl-, phosphonyl- and sulfonyl-amide groups and polyhalomethyl groups. It can be expected that more extensive studies along this line would permit the researchers to perform intra- and intermolecular heterocyclisation of imines, reactions involving haloalkyl groups, *etc*.

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