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Reactions of *N*-chloramines and *N*-haloamides with unsaturated compounds

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ABSTRACT. The results obtained from studying the reactions of *N*-chloramines, *N*-halocarbamates, and *N*-haloamides of carboxylic, sulphonic, and phosphoric acids with unsaturated compounds have been correlated and classified. It is shown that the direction of addition of *N*-haloamines and *N*-haloamides to alkenes, dienes, alkenynes, and acetylenes, giving saturated adducts, is determined by the conditions of homolytic or heterolytic initiation. The reactions of *N*-chlorodialkylamines with olefins in the presence of sulphur trioxide are discussed. A new method of activating electrophilic reagents by introducing sulphur trioxide on to the N–Cl bond is identified.

An essentially new trend is reported for the reactions of *N,N*-dihaloamides of sulphonic and carboxylic acids and also *N,N*-dihalocarbamates with polyhaloethylenes, giving acylimines of polyhaloaldehydes, which are highly reactive syntones for the synthesis of fine organic chemicals.

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I. Introduction

The chemistry of *N*-haloamines, *N*-halourethanes, and *N*-haloamides of sulphonic and carboxylic acids has undergone considerable development in the last ten years. The interest shown in compounds containing an N–Hal bond is due to their high and varied reactivity, so they have been able to remain for a long time as fertile subjects in theoretical and synthetic organic chemistry. Up to the present time a large amount of experimental material on the study of homolytic and heterolytic addition reactions of *N*-chloramines, *N*-halourethanes, and *N*-halo- and *N,N*-dihaloamides of carboxylic, phosphoric, and sulphonic acids to alkenes, dienes, alkenynes, and acetylenes has been collected.

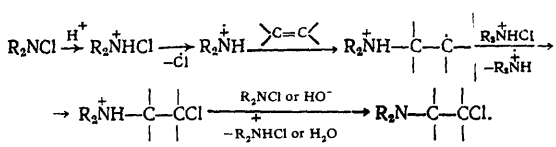
Information on the tendency of compounds with an N–Hal bond to add on to alkenes first appeared in 1930;[1] it was reported that *N*-bromo-*N*-methylbenzenesulphonamide and *N*-monobromoacetamide react with 1-phenylpropylene to give saturated adducts. However, systematic studies of the reactivity of *N*-haloamides in addition reactions to multiple bonds only started 30 years later. The period of rapid development of this branch of chemistry was in the 1960s and 1970s. Progress made up to 1970–1973 in this branch of chemistry was described in reviews.[2–4] Despite the merits of these reviews none of them can be regarded as sufficiently comprehensive. Moreover, in the last 10–12 years the flow of studies devoted to examining the reaction of *N*-haloamides of sulphonic, carboxylic, and carbamic acids with unsaturated compounds has increased steadily. Hence, it is advisable to correlate the literature material on this subject in order to establish the general mechanisms and also the prospects for further development of this branch of chemistry.

We have not examined the problems concerning the methods of forming aminyl and amidyl intermediates since they have been covered in sufficient detail in two reviews[2,5] and three studies.[6–8]

II. Reactions of *N*-chloramines with unsaturated compounds

An extensive series of studies devoted to examining the reactions of *N*-chloramines with unsaturated compounds was carried out in the 1960s by two groups of research workers[3,9–16,17–23] and covered in reviews.[2–4,24] These studies made a decisive contribution to the chemical potentialities of compounds containing an N–Hal bond. In this section the general mechanisms for reactions of this type are summarised.

The reactions of *N*-chloramines with unsaturated compounds mainly take place with homolytic cleavage of the N–Cl bond. Two methods are principally used to initiate them. Thus, the reaction of *N*-chloroalkyl- and *N*-chlorodialkyl-amines with alkenes, dienes, and acetylenes, initiated by UV irradiation or by bivalent iron salts in a mixture of H_2SO_4 and glacial acetic acid, is known to occur.[9–16] The reactions occur rapidly, giving β-chloroalkylamines $(Alk)_2NCH_2CR^1R^2Cl$, β-chloroalkenylamines $(Alk)_2NCH_2CH=CHCH_2Cl$, and α-chloroaldehydes AlkCHClCHO or α-chloroketones AlkCHClCOR. These reactions take place by a free-radical mechanism via the formation of a protonated aminyl radical cation according to the scheme:



The generation of aminyl radicals by redox systems (salts of iron, titanium, and copper) in alcohol solution is also known to occur.[17-24] The addition of these radicals to the multiple carbon–carbon bond of alkenes, dienes, and acetylenes occurs readily:

$$R_2NCl \xrightarrow[-[MCl]^+]{M^+} R_2\dot{N} \xrightarrow{>C=C<} R_2N-\overset{|}{C}-\dot{C}< \xrightarrow[-M^+ \text{ (or } R_2\dot{N})]{[MCl]^+ \text{ (or } R_2NCl)} \rightarrow R_2N\overset{|}{C}-\overset{|}{C}Cl,\ M^+ = Cu^+,\ Fe^{2+},\ Ti^{3+}.$$

The most active redox initiators are bivalent iron salts and methanol is the solvent of choice.[3-4] When other solvents—ethanol [23] or an ethanol–acetone mixture[17]—are used, there is no increase in the yield of adducts.

The yield and structure of the adducts depend on the structure of the unsaturated compound and *N*-chloramine and also on the reaction conditions. Thus, the reactions of *N*-chlorodialkyl-, *N*-chlorocycloalkyl-, and *N*-chloro(hexa- or penta-methylene)-amines with aliphatic,[10,13,16] halogenated [$CH_2=C(Hal)R$ (Hal = Cl, Br, F) and $CH_2=C(X)CH_2Cl$ (X = H, Cl)],[13,16] and functionally substituted alkenes [$CH_2=CHCH_2X$ (X = OH, OC_2H_5, OAc, OPh, CN)] [13,15] in 4 M H_2SO_4 in glacial acetic acid or in methanol in the presence of redox systems give β-chloroalkylamines $R(R^1)NCH_2C(Cl)R^2R^3$. *N*-Chloramines add on to 1,2- and 1,3-dienes at the 1,2- and 1,4-position respectively[10,14] to give β-chloro- and γ-chloro-alkenylamines of the type

$$R(R^1)NCH_2CCl=C(R^2)R^3 \text{ and } R(R^1)NCH_2CH=CHCH_2Cl.$$

The reactions of *N*-chloramines with acetylenes occur in an unique manner; α-chloroaldehydes or, in the case of disubstituted acetylenes, α-chloroketones, have been isolated:[10,14]

$$(Alk)_2NCl + RC\equiv CR^1 \xrightarrow{H_2SO_4-AcOH} (Alk)_2NC(R)=C(R^1)Cl \xrightarrow{H_2O} RCOCHClR^1,$$

$$Alk = C_2H_5,\ n\text{-}C_4H_9,\ n\text{-}C_5H_{11}.$$

Finally, reactions involving chloramination of alkenynes such as vinylacetylene, 1-penten-3-yne, and 2-methyl-1-buten-3-yne,[25] are known; these take place in an acid medium to give mainly 1,4-addition products in 60–85% yield.

In the free radical addition of a protonated *N*-chloramine to alkenes that have allyl hydrogen atoms, a competing reaction occurs—electrophilic chlorination leading to chloroalkenes and β-chloroalkyl acetates by stabilisation of carbocation (A):[13]

$$R_2\overset{+}{N}HCl \rightarrow [R_2NH + Cl^+],$$

$$[Cl^+] + >C=\overset{|}{C}-CH< \rightarrow Cl-\overset{|}{\overset{+}{C}}-CH< \begin{cases} \longrightarrow Cl\overset{|}{C}-\overset{|}{C}=C< + H^+ \\ \xrightarrow[-H^+]{AcOH} Cl\overset{|}{C}-\overset{|}{C}-CH< \\ \qquad\qquad\quad | \\ \qquad\qquad\quad OAc \end{cases}$$

(A)

In a number of cases, namely, in reactions with alkenes that have electron-donating substituents on the double bond (isobutylene, *cis*-2-butene), the yield of products from electrophilic chlorination is considerable (up to 60%). At the same time, electrophilic chlorination occurs to a lesser degree when electron-withdrawing substituents that reduce the stability of the intermediate ion (A) are present in the alkenes, thus assisting the free-radical addition of chloramines to the double bond of unsaturated compounds to give adducts. Thus, in the series $CH_2=CHR$, where R = Cl, F, CH_2Cl, CH_2CF_3, CH_2CN, $CH_2OC_6H_5$, the yield of adducts in the reaction with *N*-chlorodialkylamine increases and it reaches 85%.

It should be noted that chloramination of unsaturated compounds is often accompanied by other side reactions. Thus, *N*-chlorodialkylamines $RCH_2(CH_2)_3N(Cl)R^1$ with long-chain alkyl substituents undergo a Hofmann–Löffler rearrangement to give chlorine-substituted amines, which entails a reduction in yield of 1 : 1 adducts:[3,11,26]

$$RCH_2(CH_2)_3N(Cl)R^1 \xrightarrow[-Cl^\cdot]{H^+} RCH_2(CH_2)_3\overset{\cdot}{\overset{+}{N}}HR^1 \longrightarrow$$

$$\rightarrow R\dot{C}H(CH_2)_3\overset{+}{N}H_2R^1 \xrightarrow{RCH_2(CH_2)_3N(Cl)R^1} RCHCl(CH_2)_3\overset{+}{N}H_2R^1 \rightarrow$$

$$\xrightarrow{OH^-} RCHCl(CH_2)_3NHR^1.$$

Finally, the reaction conditions have a considerable effect on the yield of adducts. Thus, chloramination of aliphatic alkenes takes place with a higher yield of adducts (47–68%) when redox systems are used as initiators and the addition is carried out in methanol[17-24] than when UV irradiation in an acid medium is used for initiation (yield of adducts 16–42%).[10,13-14] At the same time, the use of an acid mixture as solvent and initiation with UV irradiation have proved favourable for the reactions of *N*-chlorodialkylamines with halogenated olefins such as $CH_2=C(Hal)R$ [Hal = Cl, F; R = H, CH_3, $C(CH_3)_3$] and $CH_2=CXCH_2Cl$ (X = H, Cl) (yield of adducts 61–92%) [13,15,16] and also functionally substituted alkenes $CH_2=CHCH_2X$ (X = OC_2H_5, $COCH_3$, CN) (yield of adducts up to 88%).[15] With 1,3-dienes, addition of *N*-chlorodialkylamines takes place both in the presence of redox systems in methanol and with UV irradiation in an acid medium with yields of 44–68%.[10,14]

It should be particularly stressed that the nature of the substituents on the nitrogen atom in *N*-chloramines substantially affects the addition to multiple bonds. In the reactions of substituted *N*-chloroalkylamines of the type $RN(Cl)CH_2Y$ (Y = CH_2OH, CN, $CH(OCH_3)_2$, $CH_2=CH$, $C\equiv CH$, *p*-ClC_6H_4) with 2-chloropropene in a mixture of 4 M H_2SO_4–AcOH at 30 °C in daylight, adducts are not formed,[15] which is probably due to a reduction in the degree of protonation of *N*-chlorodialkylamines by the action of electronegative substituents and also to a decrease in polarity of the N–Cl bond. The only exception to this is *N*-chloromethylbenzylamine (Y = C_6H_5), which gives an adduct in 27% yield.

Introduction of electron-donating substituents into *N*-chloramines, on the other hand, has a favourable effect on their addition to a double bond. An example of this is the reaction of chloramines $CH_3NCl(CH_2)_nN(Cl)CH_3$ with 2-chloropropene, which under similar conditions results in the formation of the bis-adducts $[CH_3CCl_2CH_2N(CH_3)]_2(CH_2)_n$.[15] We should note that their yield depends on the degree of diprotonation of chloraminoalkanes. Thus, as the length of the chain increases to $n = 6$ (a hexamethylenediamine derivative), there is the highest yield of bis-adduct (72%), when $n = 4$ it amounts to 49%, and when $n = 2$ or 3 bis-adducts are not formed. At the same time, steric hindrance, which occurs when a protonated aminyl radical attacks the double bond of the olefin, has a lesser effect, in our opinion. Conformation of this could be the

observation that the reaction of *N*-ethyl-*N*-isopropylchloramine with 2-chloropropene in a mixture of 4 M H_2SO_4–AcOH at 30 °C in daylight does take place (yield of adduct 78%).[15]

Although the method for obtaining *N*,*N*-dichloroamines has been known for a long time,[27] there has been no information in the literature about their addition to a double bond; this is apparently due to the instability and danger of explosion from these compounds. Only after the development of methods for obtaining relatively stable *N*,*N*-dichloroalkylamines that contained functional groups on the α-carbon atom[28–30] was it possible to study their addition to alkenes. Thus, *N*,*N*-dichloro-α-aminonitriles $Alk_2C(CN)NCl_2$ add on to styrene; 1:1 adducts are thereby obtained, but they have low stability and have been isolated as the hydrochloride salts of reduction products:[28]

$$Alk_2C(CN)NCl_2 + C_6H_5CH{=}CH_2 \rightarrow Alk_2C(CN)N(Cl)CH_2CHClC_6H_5 \xrightarrow{HCl} Alk_2C(CN)NHCH_2CHClC_6H_5 \cdot HCl.$$

It transpired in this case that *N*,*N*-dichloramines containing substituents [$OCOCH_3$, $CONH_2$, $P(O)(C_2H_5)_2$] on the α-carbon atom that are less electronegative than a nitrile group do not add on to styrene.[28] *N*,*N*-Dichloro-β-aminopropylnitrile also does not react with styrene (in contrast to *N*,*N*-dichloro-α-aminoalkylnitriles), which suggests that the nitrile group on the β-carbon atom has an insignificant effect on the reactivity of the *N*,*N*-dichloramino group.[28] A similar substituent effect in *N*,*N*-dichloramines occurs in the reaction between *N*,*N*-dichloraminoethyl hypochlorite with hexene, where the *N*,*N*-dichloramino group remains inert and an addition product—$ClCH_2CH(C_4H_9)OCH_2CH_2NCl_2$—is formed with involvement of the O–Cl bond.[28]

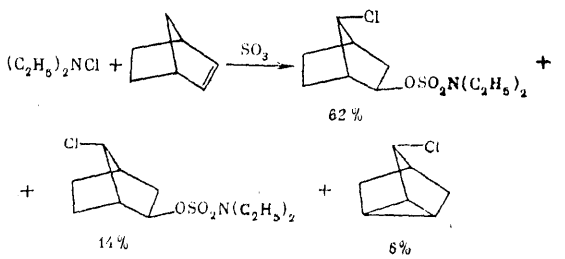
Recently (1984–86), a number of studies have been published,[31–38] in which a new approach to the activation of weak electrophilic reagents in electrophilic addition reactions to olefins is proposed. The authors show that reactions of *N*-chloramines with olefins in the presence of sulphur trioxide initially lead to the formation of highly reactive *O*-chlorosulphamates (R_2NSO_2OCl), which are products derived from introduction of sulphur trioxide into the N–Cl bond of *N*-chloramines, which subsequently add on to the double bond in accordance with Markownikoff's rule to form saturated adducts:

$$R_2NCl + SO_3 \xrightarrow{CH_2Cl_2} R_2NSO_2OCl \xrightarrow{>C=C<} R_2NSO_2OC-CCl$$

The reactions of *O*-chlorosulphamates with ethylene, hexene, styrene, and cyclopentene take place with quite a high yield of adducts (88%).[33,34]

The high regioselectivity of the addition of *N*-chloramines to olefins in the presence of SO_3 was demonstrated in the case of the reaction with 1-hexene [70–88% yield of adducts $C_4H_9CH(CH_2Cl)OSO_2NR_2$, where $R_2 = (C_2H_5)_2$, $(CH_2)_5$, $O(CH_2CH_2)_2$], and there was high stereospecificity—in the reaction with cyclohexene the *trans*-adduct was formed in 85–93% yield.[4] The stereoselectivity and regioselectivity of the addition of *N*-chloramines to olefins are in good agreement with a scheme involving electrophilic addition.

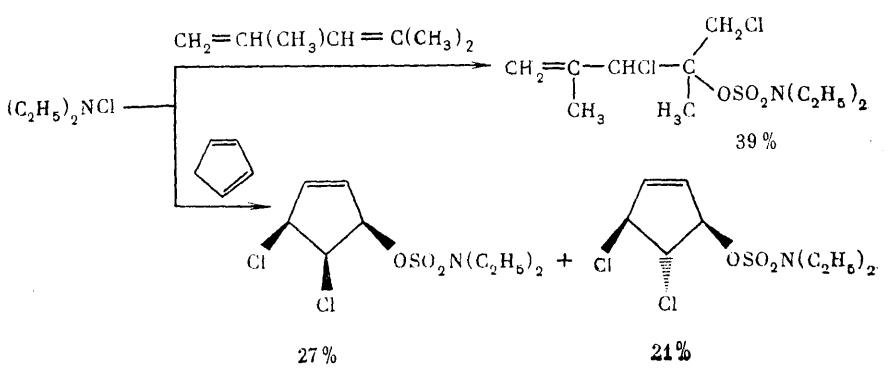
There is an interesting reaction between *O*-chlorosulphamates with norbornene, which results in rearrangement of the adducts, with the adduct in the *syn-exo* configuration for a normal Wagner–Meerwein rearrangement predominating. Formation of the adduct with an *anti-exo* configuration is due to a Wagner–Meerwein rearrangement followed by a 2,6-hydride shift:[33,35]



The skeletal rearrangements that occur in this reaction suggest that *O*-chlorosulphamates have a clearly defined electrophilic nature.

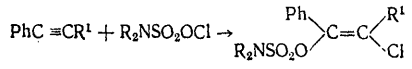
The reactions of *N*-chloramines with dienes (*cis*,*cis*-cyclooctadiene, norbornadiene) in the presence of sulphur trioxide give adducts from 1,2-addition and also isomeric adducts obtained by participation of the second double bond of the diene as well as by-product dichlorides (with a yield of about 34%).[34]

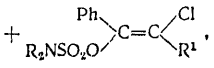
The reactions of *N*-chloramines with cyclopentadiene and 2,4-dimethyl-1,3-pentadiene (with an equimolar ratio of reactants) in the presence of SO_3 take place with the involvement of only one C=C bond of the diene. However, this reaction is complicated by the simultaneous occurrence of electrophilic substitutive chlorination processes:[35]



The reactions of *O*-chlorosulphamates with the dimethyl esters of norbornene and tricyclodecadiene dicarboxylic acids are unusual. Under conditions where the nucleophiles, in particular the ester group and the sulphamate anion, are competing, intramolecular attack by the carbomethoxy group on the double bond of the alkenes is more favourable, giving chlorolactones in 90–95% yield.[34,35]

The possibility of chlorosulphamation of phenyl- and diphenylacetylene has been demonstrated. The reactions take place (at −80 to −60 °C in CH_2Cl_2) in accordance with Markownikoff's law and give the *Z*- (13–36%) and *E*- (5–21%) products:[35,38]





$R_2 = (CH_2)_5$; R = C_2H_5, R^1 = H, Ph.

We should mention in passing the possibility of using *O*-chlorosulphamates as mild chlorinating agents—for ketones or aromatic compounds, for example.[35]

Thus, the reactions of *N*-chloramines with unsaturated compounds are new methods of obtaining β-chloroalkylamines, β-chloroalkenyl- and γ-chloroalkenyl-amines (intermediates in the synthesis of aziridines[3]), and also highly reactive β-chloroaldehydes and β-chloroketones. When these reactions are carried out in the presence of sulphur trioxide there are extensive prospects for the synthesis of β-chloroalkyl- and β-chloroalkenyl-sulphamates, which are biologically active compounds with future potential.

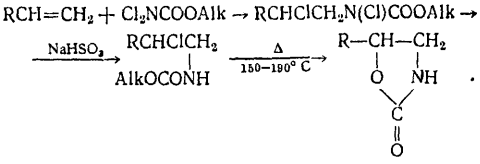
III. The reactions of *N*-haloamides with unsaturated compounds

1. *N*-Halocarbamates

The first successful attempt to obtain *N*-(β-chloro-α-phenylethyl)-*N*-ethoxycarbamate by reactions of *N*, *N*-dichlorourethane with styrene was carried out in 1942.[39] More than 20 years later (in the 1960s) studies by other authors[40–44] on the addition reaction of *N*-halocarbamates to unsaturated compounds started to appear. Three reviews[2–4] cover the reactions of *N*-chloro- and *N*, *N*-dichlorourethanes with styrene, *trans*-stilbene,[43] 2-butene, isobutene,[42] 2-methyl-1-pentene, 1-dodecene, 1-octadecene,[43] cyclic alkenes,[41–43] and alkenes having electron-withdrawing substituents on the double bond (vinyl acetate, methyl vinyl ketone, acrylates).[43,45]

In recent years the number of studies in this area of chemistry has grown considerably, which is due to the perfection of methods for obtaining dihalocarbamates[46] and also because the reactions of *N*, *N*-dihalocarbamates with unsaturated compounds can be used to synthesise highly reactive compounds that are intermediates in the preparation of isocyanates,[47–49] oxazolidinones,[50–51] aziridines,[52] etc.

Investigation of the reactions of *N*, *N*-dichlorourethanes with terminal alkenes was continued in further studies.[47–49] It was established that whatever the method of initiation [UV irradiation (75–80 °C), heating (80–85 °C) in a current of nitrogen or in air] the addition took place with the amidyl fragment being attached to the terminal carbon atom and the formation of saturated adducts—*N*-β-chloroalkyl-*N*-chlorourethanes—with a yield of up to 83%. The N−Cl bond in these products is readily converted to an N−H bond on treatment with sodium bisulphite, and the position of the carbamate group in the adducts obtained has been demonstrated by chemical conversions such as pyrolysis, which gives 5-alkyl-2-oxazolidones:[49]



Products derived from electrophilic chlorination $R^1CHClCH=CH_2$ are formed in side reactions as also are monochlorourethanes, the yield of which increases (from 14 to 42%) in the series of R: $C_4H_9 < C_5H_{11} < C_6H_{13} < C_8H_{17} < C_{10}H_{21} < C_{13}H_{27}$. It should be noted that the occurrence of electrophilic halogenation as a competing reaction is only typical for alkenes that have allylic hydrogen atoms.

The reactions of *N*, *N*-dihalocarbamates with cyclic alkenes in an inert medium with heating (35–40 °C) are interesting; they take place stereospecifically, mainly as a *trans*-addition process, with the formation of adducts and a series of halogenated products, the ratio of which is determined by the nature of the substituents on the nitrogen atom. Thus, methyl *N*, *N*-dibromocarbamate reacts with cyclohexene fairly readily without initiation, giving the *trans*-adduct in high yield (67%).[46] This direction of addition is confirmed by conversion of this adduct to *cis*-perhydrobenzoxazol-2-one, since it is known[53] that only the appropriate compounds having a *trans*-configuration can undergo such a cyclisation .

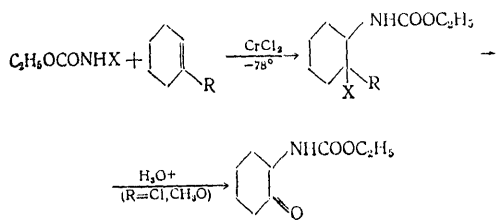
N, *N*-Dichlorocarbamates react with cyclohexene in a more complex manner; in addition to adducts of a similar stereochemistry (44%), a number of chlorinated by-products and monochlorocarbamates are formed.[51]

While heating is required for the reaction of *N*, *N*-dihalocarbamates with aliphatic and cyclic alkenes, the reaction of *N*-monohalocarbamates with cyclic alkenes takes place both with heating (40° to 60 °C) and at low temperatures (0° to −78 °C) in methanol or in a mixture of methanol and chloroform in the presence of Cr(II) halides.[53,54] It was shown[51] that on heating (45 °C) a mixture of *N*-monobromocarbamate and cyclohexene in benzene, the *trans*-adduct was formed in 72% yield. In the presence of Cr(II) at low temperatures (0° to −78 °C), a mixture of *cis*- and *trans*-1,2-adducts was obtained, with their ratio dependent on the reaction conditions (temperature, amount of catalyst, medium) as well as the effect of substituents in the carbamate group and also the nature of the halogen on the nitrogen atom.[53,54] The optimum conditions, ensuring a high yield of adducts, are attained when the reaction is carried out in a mixture of methanol and chloroform cooled to −78 °C in the presence of an equimolar quantity (relative to monochlorocarbamate) of chromium(II) chloride.[53,54] Under these conditions addition of monochlorocarbamate ROCONHCl to cyclohexene takes place with the *cis*-adduct mainly formed in the mixture (by a factor of 4–6). The total yield of isomeric adducts

increases from 65 to 87% in the series of R: $C_2H_5 \leqslant CH_2C_6H_5 < CH_2Cl \leqslant CH_2CCl_3$. A similar dependence of the yield of 1 : 1 adduct (from 61 to 85%) occurs in the analogous series for the reaction with *N*-monobromocarbamates, but the ratio of *cis*- to *trans*-adducts is about 1 : 1. At higher temperatures (0 to −40 °C), carbamates (up to 64%) and halogenated cyclohexene products are mainly formed.[53] When chromium bromide is used as the catalyst, there is a reduction in the yield of adducts and at the same time the yield of carbamates increases up to 53% and that of 1,2-dibromoalkanes rises to 20%.

Similar behaviour occurs in the reaction of *N*-monohalourethanes $C_2H_5OCONHX$ with norbornene (in a mixture of methanol and chloroform at −78 °C in the presence of $CrCl_2$); when X = Cl, the *cis*-adduct is mainly formed, and when X = Br, the *cis*- and *trans*-adducts are formed in equimolar quantities.[53]

The regiospecific and stereospecific nature of the addition of amidyl residues to alkene systems was confirmed when the reactions of *N*-monohalourethanes with 1-chloro-, 1-methyl-, 1-methoxy-, 1-acetyl-, and 1-*N*-(piperidino)-cyclohexene in the presence of Cr(II) in a methanol–chloroform solution at −78 °C were studied. In this case ethyl *N*-(1-halo-1-R-cyclohexyl)carbamates were formed:[5,53,55,56]



X = Cl, Br; R = Cl, CH_3, CH_3O, CH_3CO, $(CH_2)_5N$.

Hydrolysis of the adducts obtained to the corresponding ketones also suggests that these reactions are regiospecific. The addition of benzyl *N*-monochlorocarbamates to trimethylsilyloxynorbornene [56] takes place in a similar manner.

An analysis of the literature data showed that not all *N*-halocarbamates are active in reactions with aliphatic and cyclic alkenes. Thus, *N*-alkyl-substituted *N*-halocarbamates $HalN(R)COOCH_3$ (R = CH_3, $C_6H_5CH_2$) do not add to the double bond of alkenes that contain allylic hydrogen atoms but only form allylic halogenation products in high yield (70–80%).[57-58] Because of this, *N*-alkyl-substituted *N*-bromocarbamates could be recommended as allylic brominating agents.[57] The inertness of *N*-alkyl-*N*-halocarbamates in 1,2-addition reactions to alkenes is apparently due to both steric hindrance and a reduction in electrophilicity of the amidyl radical by the introduction of electron-donating substituents on to the nitrogen atom. On the other hand, for *N*-chlorocarbamates $C_2H_5OCON(R)Cl$ with electronegative substituents on the nitrogen atom (R = CH_3OCO, CH_3CO), an increase in electrophilicity of the amidyl radical is typical. For this reason the reactions of *N*-acyl- and *N*-ethoxycarbonyl-*N*-chloro-urethanes with cyclohexene and 1-octene take place quite readily with UV irradiation (15–20 °C, 3–5 h), and the chlorine atom adds on to the more substituted carbon atom of the C=C bond of 1-octene (yield of adducts 53–67%). Chlorinated alkenes and *N*-substituted urethanes are formed as by-products (39–42%).[58]

The reactions of *N*,*N*-dichlorourethanes with styrene and its derivatives occur readily, with an induction period, most frequently being accompanied by heat liberation, and take place with practically no side reactions to give adducts with an N–Cl bond that readily undergoes reduction with sodium thiosulphate to compounds with an N–H bond. Thus, in the reactions of *N*,*N*-dichloro-substituted methyl, ethyl, and butyl carbamates with styrene, α-chloro-, and α-bromo-styrene, adducts are formed in high yield (59–99%):[51,52,59]

$$AlkOCONCl_2 + C_6H_5CR{=}CH_2 \rightarrow C_6H_5C(R)ClCH_2NClCOOAlk.$$

It is interesting that the nature of the α-substituents has a very marked effect in the reduction of the alkenes. Thus, when ethyl *N*-chloro-*N*-(2-chloro-2-bromo-2-phenylethyl)carbamate, which is obtained by reaction of *N*,*N*-dichlorourethane with α-bromostyrene, is reduced with sodium thiosulphate, hydrogen bromide is eliminated and ethyl *N*-(2-chlorostyryl)carbamate is formed,[59] which is due, in our opinion, to the low strength of the C–Br bond (C–Br bond energy is 68 kcal mol^{-1}, C–Cl bond energy is 81 kcal mol^{-1} [60]):

$$C_6H_5CBr{=}CH_2 + Cl_2NCOOC_2H_5 \rightarrow C_6H_5CClBrCH_2NClCOOC_2H_5 \xrightarrow[-HBr]{Na_2S_2O_3} C_6H_5CCl{=}CHNHCOOC_2H_5.$$

Having analysed the effect of the conditions for initiation, Bal'on and Moskaleva[51,52,59] established that the use of radical initiators—UV irradiation, peroxides, copper powder—accelerated the reaction between *N*,*N*-dichlorocarbamates and substituted styrenes. Thus, the addition of *N*,*N*-dichlorourethane to α-bromostyrene in the absence of radical initiators is complete after 3–5 h and the yield of adduct only reaches 30%, while in the presence of copper powder an almost quantitative yield of adduct is obtained after 40 min. The initiator participates in the reaction both at the initiation and chain transfer stages.[59]

The radical nature of the reaction of *N*,*N*-dichlorourethanes with alkenes is also confirmed by the reaction between *N*,*N*-dichloro-urethane and *trans*-stilbene, which has an induction period, and occurs without stereoselectivity to give a mixture of *erythro* and *threo* isomeric adducts $C_6H_5CHClCH(C_6H_5)NClCOOAlk$.[61] *N*,*N*-Dibromocarbamates and even *N*-alkyl-*N*-bromocarbamates, which are known[57] to be inert to the double bond of aliphatic alkenes, add on to styrene and α-methylstyrene in a similar manner to the corresponding chloro derivatives. However, the yields of the adducts obtained are considerably lower (49–71%) than for the reaction of these alkenes with dichlorocarbamates. A feature of the reaction of *N*-bromo- and *N*,*N*-dibromocarbamates with styrene and its derivatives is that the adducts cannot always be isolated since even on gentle heating they readily cyclise to phenyloxazolidinones with elimination of alkyl bromide.[46,57,62]

In contrast to *N*,*N*-dichlorourethane, *N*-bromo-*N*-alkylcarbamates react with *trans*-β-methylstyene stereoselectively, and in these reactions the stereoselectivity is reduced as the effective size of the substituent on the nitrogen atom decreases. Thus, in the case of *N*-bromo-*N*-benzylcarbamate mainly *trans*-addition products are formed, while *N*-bromo-*N*-methylcarbamate gives an equimolar mixture of *cis*- and *trans*-adducts.[57]

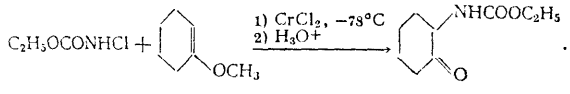
The direction of addition of *N*,*N*-dichlorocarbmates to substituted alkenes containing functional groups—vinyl acetate, methyl vinyl ketone,[45,63] and acrylates[64]—is similar to that for the addition of

amidyl radicals to styrene and its derivatives and is not dependent on the initiation conditions:

$$RCH{=}CH_2 + Cl_2NCOOAlk \rightarrow RCHClCH_2NClCOOAlk \rightarrow \xrightarrow{NaHSO_3} RCHClCH_2NHCOOAlk,$$
$$Alk = CH_3, C_2H_5;\ R = CH_3COO, CN, CONH_2, COOCH_3, COCH_3.$$

An induction period and acceleration by radical initiators are typical for these reactions. Thus, when *N*,*N*-dichlorocarbamates are reacted with acrylonitrile without an initiator the yield of adducts is 25–60% after 4–5 h,[43,51] while in the presence of univalent copper salts the yield is 78–90% after 30–40 min.[64]

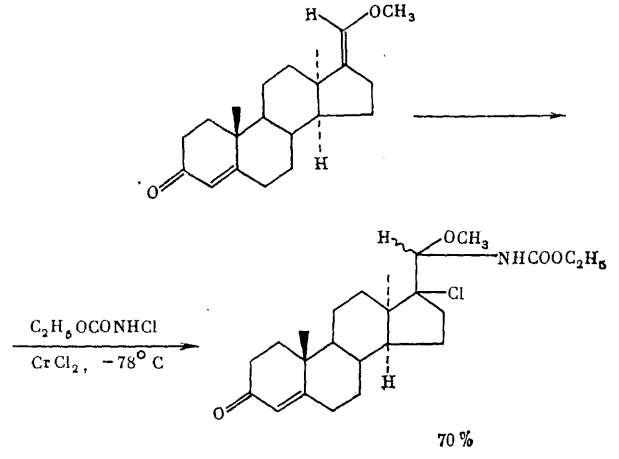
The reactions of *N*-chlorocarbamates with vinyl ethers are interesting; they occur in different directions depending on the initiation conditions. Thus, reaction of ethyl or butyl vinyl ether with *N*,*N*-dichlorocarbamates takes place with the formation of alkyl *N*-chloro-*N*-(2-chloro-1-alkoxyethyl)carbamates if there is no radical initiator present.[65] The direction of addition changes if the same reactions are carried out in the presence of chromium chloride; in this case the amidyl radical becomes attached to the less substituted carbon atom to give adducts $C_2H_5OCHCl-CH_2NHCOOR$, where R = $ClCH_2$, $ClCH_2CH_2$, $C_6H_5CH_2$.[56] The direction of addition of the amidyl radical to the double bond of cyclic vinyl ethers is similar, as is indicated by the structure of the products isolated as a result of hydrolysis or methanolysis of the 1 : 1 adducts:[56]



The products of the 1,2-addition of *N*-monochlorocarbamates to dihydrofuran, triacetyl-*D*-glyoxal, and acetylbenzylidene-*D*-glyoxal have not been isolated, since under the reaction conditions (in the presence of water, methanol) they readily undergo chemical reactions to give acetal derivatives.[56]

The direction of addition of amidyl radicals to the double bond in these reactions, namely, to the 2-position, is determined by electronic effects.

As regards the effect of different factors (electronic and steric) on the direction of addition of the amidyl fragment to the multiple bond of alkenes, the reaction of *N*-monochlorocarbamates with the steroid derivative—17-methoxymethyleneandrost-4-en-3-one—is of interest,[56] attack of the amidyl radical in it being determined to a greater extent by steric rather than electronic effects:

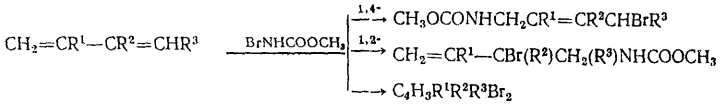


Let us turn to the reaction of *N*,*N*-dichlorourethanes with vinylidene chloride, which enters into the overall scheme of addition of amidyl radicals to unsaturated compounds and takes place independently of the initiation conditions (heating in an atmosphere of argon, in the presence of benzoyl peroxide, or in air) to give alkyl *N*-2,2,2-trichloroethyl-*N*-chlorocarbamates in yields that are almost quantitative:[66]

$$AlkOCONCl_2 + CCl_2{=}CH_2 \rightarrow AlkOCONClCH_2CCl_3.$$

N-Bromo-*N*-alkylcarbamates, in contrast to their dichloro-substituted analogues, undergo reaction with vinylidene chloride with greater difficulty and the yield of adducts amounts to 40–73%,[57] which is due to steric hindrance that occurs during attack by the *N*-alkyl-substituted amidyl radical, which is more bulky than AlkOCONCl.

The reactions of *N*-bromocarbamates with 1,3-alkadienes have been studied in the case of 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-butadiene, and 1,3-pentadiene.[67] They take place at −5° to −10 °C in chloroform and regardless of the structure of the diene mainly give the thermodynamically more stable *trans*-1,4-adducts in high yield (66–70%).[67] 1,2-Adducts are found only in the reactions with butadiene (20%) and piperylene (8%). Diene dibromides are formed as by-products:[67]



$R^1{=}R^2{=}R^3{=}H$; $R^1{=}R^2{=}CH_3$, $R^3{=}H$; $R^1{=}CH_3$, $R^2{=}R^3{=}H$; $R^1{=}R^2{=}H$, $R^3{=}CH_3$.

Addition of *N*-bromocarbamate to piperylene gives a mixture of 1,4- and 4,1-adducts in the ratio 1 : 1, which remains unchanged when the initial quantities of the reactants are varied. In the case of isoprene, a compound (about 10%) that corresponds to an adduct of *N*,*N*-dibromocarbamate and isoprene in the ratio 1 : 2—$[BrCH_2CH=C(CH_3)CH_2]_2NCOOCH_3$—is formed together with the main 1,4-isomer (71%).[67]

The regioselectivity and stereoselectivity of the addition of *N*,*N*-dichlorocarbamates to dienes is virtually no different from that in the analogous reactions of *N*-bromocarbamates. Thus, methyl and isopropyl *N*,*N*-dichlorocarbamates with the same 1,3-alkadienes mainly form *trans*-1,4-adducts with a yield of up to 94%.[44] 1,2-Addition products were only isolated in the case of the reaction with butadiene (14% [44] or 37% [53]), 1,3-cyclohexadiene (78%) [53] and piperylene (26%). With piperylene, 4,1-addition products (30%) are also formed.[67]

The reactions of the *N*,*N*-dichlorocarbamate $[NCl_2COOCH_2]_2$ with chloroprene take place with the exclusive formation of 1,4-adducts (96–98%).[44]

The reaction of 1,5-hexadiene with *N*,*N*-dichlorourethane, in which 1,2-addition products of composition 1 : 1 (27.5%) and 1 : 2 (18%) are formed, has been studied.[68] A distinctive feature of the reactions of *N*,*N*-dichlorocarbamates with dienes is the absence of diene dihalides, which are formed in appreciable yield (10–32%) in the reactions of *N*-bromocarbamates.

Alkenynes, which have two reaction centres, have been of definite interest in recent years. The reactions of *N*,*N*-dichloro- and *N*-bromo-carbamates with conjugated alkenynes such as vinylacetylene,[69] 1-hexen-3-yne, 2-methyl-1-buten-3-yne, and 2-penten-4-yne [67] have been studied. The reactions take place at −10 to −5 °C in an inert atmosphere and proceed exothermically by 1,2- and 1,4-addition pathways to give isomers with acetylene and allene structures

$$R^1C{\equiv}C{-}CR^2{=}CHR^3 + CH_3OCONX^1X^2 \xrightarrow{\text{then } NaHSO_3}$$
$$\xrightarrow{1,2} R^1C{\equiv}CC(R^2)CHNHCOOCH_3 \quad (X^1,\ R^3)$$
$$\xrightarrow{1,4} R^1C{=}C{=}C(R^2)CH(R^3)NHCOOCH_3 \quad (X^1)$$

$R^1{=}R^2{=}H$, $R^3{=}H$, CH_3; $R^1{=}C_2H_5$, $R^3{=}R^3{=}H$;
$R^1{=}R^3{=}H$, $R^2{=}CH_3$; $X^1{=}X^2{=}Cl$; $X^1{=}Br$, $X^2{=}H$.

The ratio of isomers depends on the nature of the enyne system and the nature and number of halogen atoms in the *N*-halocarbamate.[69] Thus, *N*,*N*-dichlorocarbamates react with vinylacetylene to give mainly allene derivatives (70%, only 30% acetylene isomer is formed), while in the reaction with *N*-bromocarbamates the ratio of isomers is the reverse, which is due to steric factors.

Introduction of an alkyl substituent into the 1- or 4-positions of a vinylacetylene molecule mainly assists the formation of an acetylene derivative, while its introduction into the 2-position mainly gives an allene isomer. In fact, the acetylene isomer is the predominant product (95–100%) of the reaction between *N*-halocarbamate and 1-hexen-3-yne,[67] while in the reaction with 2-methyl-1-buten-3-yne (isopropenylacetylene) [67] the allene derivative is formed in 85–100% yield.

It has been suggested by Labeish and co-workers[67] that the addition of *N*,*N*-dichloro- and *N*-bromo-carbamates to conjugated alkenynes is a radical process which starts with attack by an amidyl radical on the terminal ethylene atom of the vinylacetylene molecule rather than attack by chlorine on the terminal carbon atom of the triple bond followed by an allene-acetylene rearrangement.

Reactions between *N*-monochlorocarbamates and acetylenic compounds are known. Reaction with 1-octyne gives the adduct $C_6H_{13}CCl{=}CHNHCOOC_2H_5$ (28%); $C_6H_{13}\underset{\underset{O}{\|}}{C}CH(NHCOOC_2H_5)_2$ is formed as a by-product (13%).[53]

It was recently established that phenylacetylene reacts exothermically under mild conditions with *N*,*N*-dichlorocarbamates, giving alkyl *N*-(2-chlorostyryl)-*N*-chlorocarbamates in 57–59% yield, which rearrange on standing to alkyl *N*-(1,2-dichlorostyryl)-carbamates [70,71]

$$C_6H_5C{\equiv}CH + Cl_2NCOOAlk \rightarrow C_6H_5CCl{=}$$
$$- CHN(Cl)COOAlk \rightarrow C_6H_5CCl{=}CClNHCOOAlk,$$
$$Alk = CH_3,\ C_2H_5.$$

Phenylchloroacetylene (7–9%), *N*-monochlorocarbamate (6–8%), and a compound with a structure that the authors did not establish (24–30%) were isolated as by-products. Unfortunately, Bal'on and Moskaleva[70,71] did not specify any physicochemical constants for this compound in their study. When recent data[72–77] are taken into account, the product of unknown structure is probably a compound with an azomethine bond or a product derived from its subsequent conversion.

Thus, for the reactions of *N*-halo- and *N*,*N*-dihalo-carbamates with unsaturated compounds an induction period is typical; their acceleration in the presence of radical initiators (UV irradiation, peroxides, transition metal salts) and retardation by radical inhibitors as well as the lack of stereospecificity for addition indicate the radical nature of the reaction, which takes place according to the general scheme:

$$AlkOCONX^1X^2 \xrightarrow[-\dot{X}^2]{} AlkOCO\dot{N}X^1 \xrightarrow{>C=C<}$$
$$\rightarrow AlkOCONX^1{-}\overset{|}{\underset{|}{C}}{-}\dot{C}< \xrightarrow[-AlkOCO\dot{N}X^1]{AlkOCONX^1X^2} AlkOCONX^1{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}X^2,$$

$X^1 = H,\ Cl,\ Br,\ Alk;\ X^2 = Cl,\ Br.$

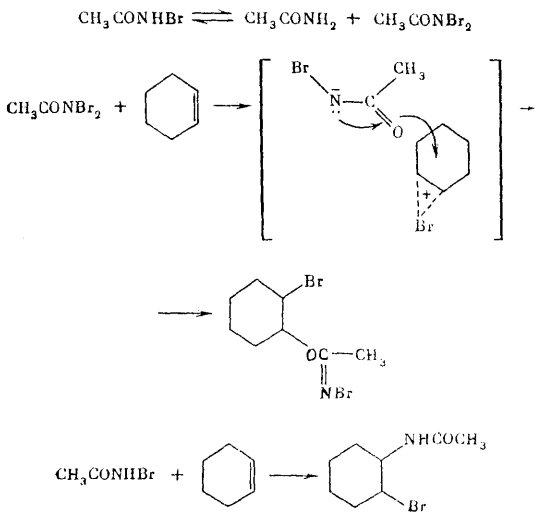
Three studies[53,64,78] describe the mechanism of the reaction between *N*-halocarbamates and olefins in the presence of transition metal salts [CuCl, Cu, Cr(II)] in greater detail.

2. *N*-Halocarboxamides

The addition of *N*-halocarboxamides to unsaturated compounds has been studied in the reactions of quite a large number of *N*-haloamides with cyclohexene and its derivatives,[24,53,55,56,79–83] 1-hexene, 3,3-dimethyl-1-butene,[82] 1-octene, 1-dodecene,[53,81] and also with cyclohexadiene and norbornadiene.[53,55,78]

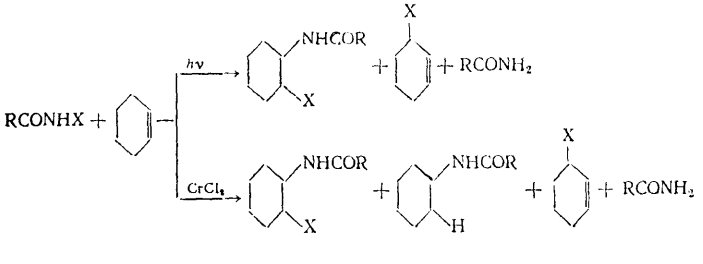
The first known example of a photochemical reaction was the addition of *N*-bromoacetamide to cyclohexene, taking place on refluxing in CCl_4 and giving a low yield of adduct (1%).[79,83] Wolfe and Awang[79,83] maintained that in the main reaction *N*-monobromoacetamide was initially converted to *N*,*N*-dibromo-acetamide, which added on to the double bond of alkene according to

an ionic mechanism, giving *trans*-β-bromoalkyl-*N*-bromoacetimidate in 36% yield:



However, such results were isolated and were not confirmed by subsequent studies.

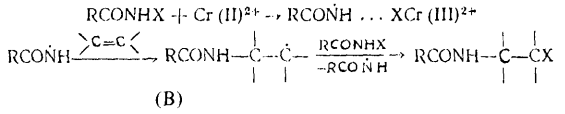
It was possible to carry out the addition of *N*-haloamides to unsaturated compounds both with UV irradiation[55,80,81] and in the presence of $CrCl_2$,[5,53,56,84] substituted adducts being formed in yields of up to 92%. In the case of the reaction of *N*-monohaloamides with cyclohexene a study was made of the dependence of the yield of reaction products on the conditions for carrying out the reaction and on the nature of the halogen atom and substituent R in monohaloamides:



With photochemical initiation the reaction took place in methylene chloride or a chloroform–methanol solution at 20° to −70 °C with a yield of *cis*- and *trans*-adducts of 25 to 99%,[5,55,80,81] in nitromethane the yield was 53%,[55] in benzene it was 42%,[55] while with catalytic initiation the reaction took place in a chloroform–methanol solution at −20 to −78 °C with a yield of isomeric adducts of 34 to 88%.[5,53,56,78]

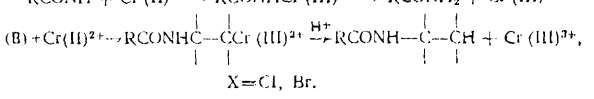
The main competing reaction in the photochemical and catalytic interaction of amidyl radicals with cyclohexene is allylic halogenation, which gives 3-chlorocyclohexene, and *N*-monohaloamide is reduced to amide. One of the main factors that influences the occurrence of electrophilic halogenation is the reaction temperature. At 10–20 °C allylic halogenation is as high as 59%.[81] At lower temperatures (−70° to −78 °C) the formation of adducts is more favourable (64–97%).[55,81]

Driguez and co-workers[53,78] proposed that in allylic halogenation the hydrogen in cyclohexene is removed not by an amidyl radical, as was maintained previously,[85] but by a chlorine free radical. In order to confirm this hypothesis, a study was made of the reactions of *N*-monohaloamides with cyclohexene in the presence of chromium chloride in $CH_3OH-CHCl_3$, in which amidyl radicals were formed but there were no halogen free radicals:[5,24,53,56,78]



(B)

side reaction:



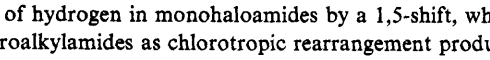
A competing process in these reactions, in addition to halogenation of the olefins, is the formation of 1-*H*-adducts by reduction of the adduct radical (B) with chromium(II) chloride.

The nature of the halogen atom and substituents in *N*-haloamides RCONHX has a considerable effect on the yield of the reaction products. Thus, in photolysis there is an increase in yield of 1,2-adducts in the series of R: $(CH_3)_3C < n\text{-}C_3H_7 < C_2H_5 < CH_3 < CH_2CH_2Cl < CH_2Br < CH_2Cl < CH_2F < CHCl_2 < CCl_3 < CF_3$ ranging from 37 to 99% with the *cis*-adduct predominating (when X = Cl). Although the reaction of *N*-monobromamides occurs more rapidly (4–5.5 h) than with *N*-monochloramides (21–53 h), the yield of 1,2-adducts in the analogous series is considerably lower (from 25 to 84%).[55,80] The increase in the yield of adducts is due to a rise in electrophilicity of the amidyl radical RCONH when electronegative substituents R are introduced.

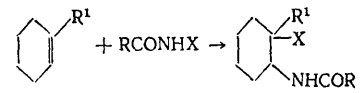
In the presence of chromium chloride when X = Cl, the yield of *cis*- and *trans*-1,2-adducts increases from 34 to 78% in the series of R: $CH_3 \leqslant NH_2 < CCl_3 < CH_2Cl < CF_3$ (there is 1.5–2 times as much *cis*-adduct present compared to *trans*-adduct), while the yield of 1-*H*-adducts, on the other hand, falls (from 36 to 2%).[53]

The effect of the structure of R on the yield of addition products when the reaction is catalysed by $CrCl_2$ is not significant in the case of *N*-monobromamides. Thus, in the reaction of cyclohexene with *N*-bromamides RCONHBr, the yield of 1,2-adducts varies from 66% to 74% with a change of substituents in the series: $CH_3(CH_2)_3 \leqslant CH_3 \leqslant CCl_3 < CH_2Cl$, and the ratio of *cis*- to *trans*-adducts is almost equimolar; the yield of 1-*H*-adducts is insignificant (~2%). In the reaction of bromamides RCONHBr (R = Alk), in contrast to chloramides, there is a side-reaction—electrophilic bromination.[53]

The effect of the length of the alkyl chain in *N*-monohaloamides RCONHX is shown principally with alkyl substituents containing more than four carbon atoms, since in this case addition of amidyl radicals to the double bond of alkene competes with intramolecular detachment of hydrogen in monohaloamides by a 1,5-shift, which gives γ-chloroalkylamides as chlorotropic rearrangement products:[85]

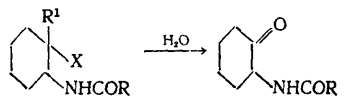


Photochemical and catalytic ($CrCl_2$) addition of amidyl radicals to the double bond occurs regiospecifically, as is suggested by the results of the reactions of 1-chloro-, 1-methyl-, 1-methoxy-, and 1-acetyl-cyclohexene with *N*-monohaloamides, which give a mixture of the *cis*- and *trans*-adducts with yields of 35 to 85%:[5,53,56,80]



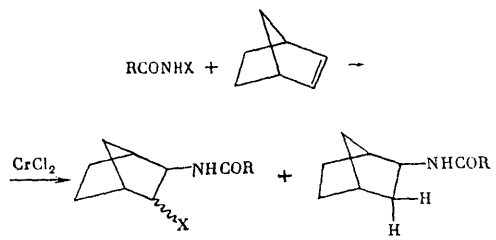
$R=CH_3$, CH_2Cl, CF_3; $R^1=CH_3$, OCH_3, Cl, $COCH_3$.

Confirmation of this orientation of substituents in the adducts is also provided by the conversion of the latter on treatment with water to the corresponding ketones:[55]



$R=CH_2Cl$, CH_3; $R^1=Cl$, OCH_3; X=Cl, Br.

There is high regiospecificity in the reaction of *N*-monohaloamides RCONHX with 1-octene [53,81] and 1,1-diethoxyethylene [55] to form adducts $RCONHCR^1(R^2)CH_2X$ ($R^1 = C_6H_{13}$, $R^2 = H$, $R^1 = R^2 = OC_2H_5$) in 80–92% yield. An adduct with norbornene is also formed in high yield (88–91%), but in a number of cases, namely, in the reaction of the *N*-monochloramide of acetic and monochloroacetic acids with this alkene the yield of 1-*H*-adducts (55 and 93%) is greater than the yield of 1,2-adducts (2 and 33%):[53]



cis, trans

R = CH_3, CH_2Cl; X=Cl, Br.

By studying the reaction of *N*-halocarboxamides with alkenes, the effect of the alkyl substituents on the nitrogen atom has been established. Like *N*-alkyl-*N*-halocarbamates, *N*-alkyl-*N*-halocarboxamides are inert towards reaction with olefins. Thus, attempts to add on the *N*-methyl-*N*-chloramides of acetic and monochloroacetic acids to cyclohexene have proved unsuccessful even with UV irradiation and at a temperature of 20 to −70 °C; in this case only chlorination of cyclohexene and conversion of the *N*-methyl-*N*-chloramides $RCON(CH_3)Cl$ to the corresponding amides occurred (yield 96–98%).[58,81] Exceptions to this were the reactions of *N*-methyl-, *N*-ethyl-, and *N*-chloroacetyl-*N*-chloroacetamides with 1-octene, norbornene, and 1-dodecene, which were initiated by UV irradiation at 20 to −70 °C. Although the main products were the corresponding amides (up to 87%), the 1,2-adducts were however formed in low yield.[55,81] It was only possible to achieve a higher yield of adducts (70–71%) in the reaction of *N*-methyl-*N*-chlorotrifluoroacetylamide with 1-dodecene.[55] It transpired that introduction of electronegative substituents on to the nitrogen atom helped to increase the reactivity of the amidyl radicals. Thus, it was possible to carry out the addition of *N*-acyl-*N*-chloroacetamide to cyclohexene with UV irradiation in CH_2Cl_2 (15–20 °C), although with an insufficiently high yield of adduct (24%).[58]

Cyclic *N*-haloamides are characterised by a fairly high reactivity. In the photochemical initiation of the reaction between *N*-halosuccinimides and ethylene, 3,3-dimethyl-1-butene,[86,87] styrene,[86] 1-octene,[58] and cyclohexene and 1-methylcyclohexene [58] in CH_2Cl_2 or CCl_4 (15–20 °C), adducts are formed with yields ranging from low (16–22%) to high (80%), and the yield for *N*-bromo derivatives is 1.5–2 times lower than with the corresponding chloro derivatives. High yields of adducts (60–85%) were obtained in the photochemical reaction of *N*-bromosuccinimide with 3,3-dimethyl-1-butene and 1-hexene in a mixture of acetonitrile and ethylene oxide at −10 °C.

Finally, there are some individual examples in the study of the reactivity of *N*,*N*-dihalocarboxamides in reactions with unsaturated compounds.

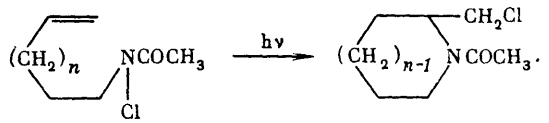
In contrast to monohaloamides, *N*,*N*-dichlorobenzamides are known to react with styrene without secondary processes, forming *N*-(2-chloro-2-phenylethyl)arenamides in high yield (75–92%).[88]

It was possible to react *N*,*N*-dichlorobenzamide with phenylacetylene, resulting in the formation of a mixture of products: *N*-(1,2-dichlorostyryl)benzamide (I) (68.5%) and 1,1-dichloro-1-phenyl-2,2-di(benzoylamino)ethane (II) (12.7%):[89]

$$C_6H_5C{\equiv}CH + Cl_2NCOC_6H_5 \rightarrow$$
$$\rightarrow \underset{\text{(I)}}{C_6H_5CCl{=}CClNHCOC_6H_5} + \underset{\text{(II)}}{C_6H_5CCl_2CH(NHCOC_6H_5)_2}.$$

Unfortunately, the authors did not suggest possible routes for the formation of these compounds.

It is also interesting to note reactions involving intramolecular addition to the double bond in olefinic *N*-haloamides of the type:



These reactions take place with UV irradiation and give various cyclic compounds.[5] A number of studies[90–93] have been devoted to reactions of this type and so they are not examined in detail in the present review. We should also note the tendency of *N*-haloamides RCONHHal with three or more methylene groups to undergo a Hofmann–Löffler rearrangement,[85,94] while *N*-alkyl-*N*-chloramides $RCONR^1Cl$ with alkyl substituents on the nitrogen atom (t-butyl, 1,1-dimethyl-2-phenylethyl, 1,1-dimethylpentyl) tend to undergo intramolecular rearrangements with UV irradiation (20 °C) with migration of the chlorine atom to the alkyl substituent R^1 and formation of *N*-(chloroalkyl)amides, which are readily cyclised on heating to oxazoline and pyrrolidine derivatives.[95,96]

3. *N*-Halosulphonamides

In *N*-halosulphonamides the nitrogen-halogen bond is susceptible to both homolytic and heterolytic cleavage, so that it is possible under different reaction conditions to obtain from *N*,*N*-dihalosulphonamides and alkenes various structural forms of β-haloalkylsulphonamides, which are intermediates in the synthesis of aziridines.[97-99]

The first study in which it was found to be possible to add on *N*-halosulphonamides to the double bond of unsaturated compounds was published in 1930.[1] Several years later, in 1937–38, a series of studies appeared,[100-103] in which in the course of seeking new methods for the chloroalkoxylation of olefins in order to obtain β-chloroethers it was found that when *N*,*N*-dichlorosulphonamides react with alkenes in the presence of phenols,[100] alcohols,[101,102] or carboxylic acids,[103] *N*-(β-chloroalkyl)arenesulphonamides are formed together with β-chloroethers.

At the present time it is established that addition of *N*,*N*-dichloro- and *N*-chloro-*N*-methyl-ethanesulphonamide to terminal alkenes such as 1-hexene, 1-butene, 1-octene, and 1-dodecene takes place with the formation of saturated adducts, the structure of which depends on the initiation conditions.[104,105]

Under conditions where radicals are formed (UV irradiation) the sulphonamide residue adds on to the terminal carbon atom according to the scheme:

$$C_2H_5SO_2NClR \xrightarrow[-Cl^\cdot]{} C_2H_5SO_2\dot{N}R \xrightarrow{R^1CH=CH_2}$$

$$\rightarrow C_2H_5SO_2N(R)CH_2\dot{C}HR^1 \xrightarrow[-C_2H_5SO_2\dot{N}R]{C_2H_5SO_2NClR} C_2H_5SO_2N(R)CH_2CH(Cl)R^1,$$

$R=Cl,\ CH_3;\ R^1=C_2H_5,\ C_4H_9,\ CH_3(CH_2)_3,\ CH_3(CH_2)_5,\ CH_3(CH_2)_{10}.$

These reactions are inhibited by oxygen, which also confirms their radical character.

It is interesting to note that with more prolonged UV irradiation the adduct of *N*,*N*-dichloroethanesulphonamide with 1-hexene undergoes a free-radical rearrangement with 1,5-migration of hydrogen to give *N*-(2,4-dichlorohexyl)ethanesulphonamide.[104,105]

Under ionic conditions for initiating the reactions of *N*,*N*-dichloro-substituted arene- and ethane-sulphonamides with 1-hexene, the direction of addition changes, and the reactions lead to the adducts $RCH(NHSO_2C_2H_5)CH_2Cl$.[104,106] A similar direction of addition occurs in the reactions of *N*,*N*-dibromoarenesulphonamides with acyclic alkenes of known stereochemistry—*cis*- and *trans*-3-hexene, *cis*-2-heptene, *cis*-5-decene, and *cis*- and *trans*-9-octadecene; in this case *N*-bromo-*N*-(2-bromo-1,2-dialkylethyl)arenesulphonamides are formed as adducts in 42–70% yield.[107]

The mechanism of this reaction involves the formation of a bromonium ion:

$$ArSO_2NBr_2 + \rangle C{=}C\langle \rightarrow \rangle \overset{Br^+}{C{-}C}\langle + ArSO_2\bar{N}Br \rightarrow$$

$$\rightarrow ArSO_2NBrC{-}CBr$$

This type of mechanism dictates the high stereoselectivity of the process. In fact, as a result of the addition of *N*,*N*-dibromoarenesulphonamides to a *cis*-alkene, an adduct with a *threo*-configuration is obtained, while for reaction with a *trans*-alkene, the adduct has an *erythro*-configuration.[107] It was shown that the yield of adducts in heterolytic reactions of *N*,*N*-dibromoarenesulphonamides with aliphatic alkenes depends on the structure of alkene. Thus, with long-chain alkenes (*cis*- and *trans*-octadecene) the yield of adducts is considerably lower (38–42%) than with C_6 and C_7 alkenes (75 to 80%).[107] With a tertiary alkene (2,3-dimethyl-1-butene) the yield of adduct is only 16%, with a secondary alkene (isobutene) it is 22%,[108] and with 2-butene it increases to 61%,[109] which is due to the effect of steric factors on attack by the amidyl anion on the bromonium ion.

The effect of the substituents on the nitrogen atom in sulphonamides on the yield of adducts during heterolytic reaction should also be noted. The reactions of *N*,*N*-dibromo- and *N*-bromo-*N*-alkyl-substituted arenesulphonamides with alkenes (2-butene and isobutene) take place with a higher yield of adducts.[109,110] In the reactions of the *N*-chloro derivatives, chlorination of the alkenes is preferred, and adducts are only isolated in low yield (10%).[111]

A number of studies by Japanese research workers are devoted to the reactions of *N*,*N*-dihaloarenesulphonamides with cyclohexene [112-116] and cyclopentene.[117] These reactions, as for the addition of *N*,*N*-dihalocarbamates to cyclic alkenes, are stereoselective and take place mainly as a *trans*-addition with the formation of 1 : 1 adducts (yield 50–96%). *cis*-Adducts are also formed, but in low yield. Moreover, reactions with cyclic alkenes are accompanied by side-reactions—halogenation of the double bond of alkene, allylic halogenation, oxidation of cyclohexene to 1-cyclohexen-3-one, and also dehydrogenation of the cycloalkene to a 1,3-cycloalkadiene (with a substantial yield—49%).[112-117]

It is interesting that *N*-bromo-*N*-alkylsulphonamides, by analogy with *N*-bromo-*N*-alkylcarbamates, do not add on to the double bond of cyclohexene but behave as brominating agents.[114] The inertness of *N*-bromo-*N*-alkyl-substituted amides in addition reactions to the double bond of alkenes is probably due to a decrease in electrophilicity of *N*-alkyl-substituted amidyl radicals.

The possibility of heterolytic bromosulphonamidation of cyclic alkenes has been shown for the reactions of *N*-bromosulphonamides with bicyclic alkenes such as bicyclo[2.2.1]heptene, bicyclo[2.2.2]-octene, and *endo*-bicyclo[2.2.1]-5-hepten-2,3-dicarboxyanhydride. The reactions are exothermic and stereoselective and involve the formation of a bromonium ion or a bridgehead carbocation.[118] The yields of 1 : 1 adducts in these reactions, however, are low, the main products being brominated bicycloalkenes.

In contrast to the reactions of aliphatic alkenes, reactions of styrene and its derivatives with *N*,*N*-dichloroalkane-, *N*,*N*-dichloroarene-, and *N*,*N*-dichloro-N^1-dimethyl-sulphonamides take place with virtually no side reactions and they give the saturated adducts $4\text{-X-}C_6H_4CCl(R^1)CH(R^2)NClSO_2R$ [R = Ar, Alk, $R^1 = R^2 = H$, X = H; R = $(CH_3)_2N$, R^1 = H, C_6H_5, R^2 = H, X = H, *p*-CH_3O] in high yield.[99,106,111,119] The reactions occur readily under mild conditions in chloroform or methyl chloride on cooling[111,119] or in benzene at 20–22 °C in an atmosphere of nitrogen,[106] most frequently exothermically. It was shown that these reactions are considerably accelerated by UV irradiation, with the yields of adducts being almost quantitative. Subsituents at the α- and β-positions of styrene do not have any substantial effect on the yield of adducts. The reactions with both styrene (yield 85–96%) [106] and α-phenylstyrene (85%) or 1-*p*-methoxyphenyl-propene [119] occur with equal ease. Meanwhile, the direction of addition of *N*,*N*-chloroarenesulphonamides to styrene changes

if the reaction is carried out in air in the presence of Lewis acids:[106,111,120,121]

$$C_6H_5CH{=}CH_2 + ArSO_2NCl_2 \longrightarrow$$
$$\xrightarrow[N_2,\ then\ NaHSO_3]{} C_6H_5CHClCH_2NHSO_2Ar$$
$$\xrightarrow[SnCl_4,\ AlCl_3\ in\ air,\ then\ NaHSO_3]{} C_6H_5CH(NHSO_2Ar)CH_2Cl$$

It is interesting that not only the initiation conditions but also the nature of the halogen atom in the sulphonamide affect the direction of addition of *N,N*-dihalosulphonamides to styrene and its analogues. Thus, in contrast to *N,N*-dichlorosulphonamides, *N,N*-dibromosulphonamides add on to styrene,[107,110,116] α-methylstyrene,[98] and propenylbenzenes 3-R-4-$R^1C_6H_3CH{=}CHCH_3$ (R = H, OMe; R^1 = H, OMe, OBz; RR^1 = OCH_2O [122-123]) with attachment of the amidyl fragment to the more substituted carbon atom of the double bond in these alkenes. *N*-Bromo-*N*-alkyl-substituted sulphonamides add on to styrene in the same direction.

Chlorosulphonamidation of alkanes which contain electron-withdrawing groups on the double bond has been studied in the case of reactions with allyl chloride,[99,120,124] 1,1,1-trichloropropene,[125] and acrylates;[98,108,124,126] they take place with the formation of adducts $ArSO_2NClCH_2CHClR$ (R = CH_2Cl, CCl_3, CN, $CONH_2$, $COOCH_3$).

It has been established that the use of radical initiators considerably accelerates these reactions. Thus, the reaction of allyl chloride with *N,N*-dichloro-*p*-chlorobenzenesulphonamide takes place on heating in CCl_4 (75–80 °C) for 5 h, while in the presence of $(C_6H_{11}OCO_2)_2$ or $(C_6H_5OCO)_2$ only 1.5 h is needed and the yield of the adduct p-$ClC_6H_4SO_2NHCH_2CHClCH_2Cl$ increases from 75% to 93%.[120,124] Another example is the addition of *N,N*-dichloroarenesulphonamides to acrylonitrile, which is complete after 30 h without a catalyst to give a 51% yield of the adduct $C_6H_5SO_2NHCH_2CHClCN$,[98] while with initiation by $(C_6H_{11}OCO)_2$ only 1.5 h is needed and the yield is 84%.[124]

An initiation system such as a mixture of a univalent copper salt and tetraethylammonium bromide has proved effective.[126] When using it, the time of reaction of *N,N*-dichloroarenesulphonamides with acrylates $XCH{=}CH_2$ could be reduced to 40 min and the yield of adducts $ArSO_2NHCH_2CHClX$ could be increased to 95% (X = CN), 86% (X = $COOCH_3$), or 88% (X = $CONH_2$). The low redox potential of the system $Cu^0 \rightleftarrows Cu^+ \rightleftarrows Cu^{2+}$ favours these reactions involving copper or its univalent salt both at the initiation stage and in chain propagation, thereby increasing the yield of adducts.

N,N-Dibromoarenesulphonamides add on to acrylates in a similar manner to give 1:1 or 1:2 adducts, depending on the ratio of reactants.[108]

An alkene with a trichloromethyl group on the double bond (1,1,1-trichloropropene) during homolytic initiation forms adducts $ArSO_2NHCH_2CHClCCl_3$ in 60–63% yield.[125] Under initiation conditions for formation of ions (in the presence of $SnCl_4$, in air), adducts of the same structure are formed (yield 18–70%), which is in line with the usual principles for electrophilic addition to unsaturated compounds that contain electron-withdrawing substituents on the double bond.[125]

Finally, the reactions of *N,N*-dichloroarenesulphonamides with polyhaloethylenes (vinylidene chloride[120] and 1,1,3-chloropropene[97]) deserve special consideration. A characteristic feature of these reactions is that the direction of addition does not depend on the initiation conditions as was the case for other alkenes.[104,106] The reaction takes place with the same ease both in an inert medium in the presence of peroxides and in air in the presence of $AlCl_3$, with adducts formed in high yield (up to 97%):

$$ArSO_2NCl_2 + CCl_2{=}CHR \rightarrow ArSO_2NClCHRCCl_3,$$
$$R{=}H,\ CH_2Cl;\ Ar{=}C_6H_5,\ p\text{-}ClC_6H_4.$$

In continuing our investigation of the free-radical reactions of halogenated derivatives of ethylene, we have studied for the first time the reactions of 2,2-dichlorovinyl acylates, 2,2-dichlorovinylketones, *N*-(2,2-dichlorovinyl)carboxamides, and 2,2-dichlorovinyl ethers with *N,N*-dichlorosulphonamides.[127-132] Free-radical additions to the double bond were not known for these compounds. Moreover, the reactions of *N,N*-dichloroarenesulphonamides with functional derivatives of 2,2-dichloroethylene attracted our interest as a method for obtaining the previously unknown trichloroethyl derivatives of arenesulphonamides of the type $ArSO_2NHCH(R)CCl_3$, which are biologically active compounds with future potential:

$$ArSO_2NCl_2 + CCl_2{=}CHR \rightarrow ArSO_2NClCH(R)CCl_3 \rightarrow ArSO_2NHCH(R)CCl_3,$$
$$Ar = C_6H_5,\ p\text{-}CH_3C_6H_4,\ p\text{-}ClC_6H_4;\ R = OCOCH_3,\ NHCOAr^1,\ COR^1,\ OAlk.$$

The reaction of *N,N*-dichloroarenesulphonamides with 2,2-dichlorovinyl acetate is the first example of a free-radical addition to the double bond of this compound. The reaction occurs readily when there is a twofold excess of dichlorovinyl acetate, which also serves as the solvent, and leads to adducts in 90–97% yield.[127,128]

A high regiospecificity for addition was recorded in the reaction of 2,2-dichlorovinylamides with *N,N*-dichloroarenesulphonamides; the adducts were isolated with yields up to 95%.[128,129] It was of particular significance that this reaction showed for the first time the possibility of the enamide tautomeric form of 2,2-dichlorovinylamides participating in free-radical addition reactions to the double bond.

The reaction of 2,2-dichlorovinyl ketones and 2,2-dichlorovinyl ethers with *N,N*-dichlorobenzenesulphonamide is complicated by a side-reaction—reduction of the dichlorosulphonamide to a benzenesulphonamide in about 30–40% yield.[130,131] The high activity of the N–Cl bond in the adducts should be noted; it is very readily converted to an N–H bond even in air and *N*-(2,2,2-trichloro-1-R-ethyl)benzenesulphonamides are formed in about 75% yield.[130,131]

The reactions of functional derivatives of vinylidene chloride with *N,N*-dichloroarenesulphonamides have an induction period, and they are inhibited in the presence of hydroquinone, which is confirmation of their free-radical nature:

$$ArSO_2NCl_2 \xrightarrow[-Cl]{} ArSO_2\dot{N}Cl \xrightarrow{CCl_2=CHR} \rightarrow \dot{C}Cl_2CH(R)NClSO_2Ar \xrightarrow{ArSO_2NCl_2} \rightarrow$$
$$(C)$$
$$\rightarrow CCl_3CH(R)NClSO_2Ar \rightarrow CCl_3CH(R)NHSO_2Ar,$$
$$R{=}OCOCH_3,\ NHCOAr,\ COR^1,\ OAlk.$$

A characteristic feature of these reactions is that the addition is highly regiospecific. This is due to polar effects of the substituents in the amidyl radical $ArSO_2\dot{N}Cl$ and the vinylidene chloride

derivative and to steric hindrance which would occur if the amidyl radical attacked the β-carbon atom in molecules of the substituted vinylidene chloride derivatives $CCl_2=CHR$ to form the radical $ArSO_2NClCCl_2\dot{C}HR$ (D). The driving force of the reaction would appear to be the formation of the more stable radical (C).

A study has been made of the addition of *N,N*-dichloroarenesulphonamides to dienes that takes place exothermically under mild conditions (−10 °C) at the 1,4-position with a high yield of adducts (77–88%):[111]

$$CH_2=C(R)CH=CH_2 + R^1SO_2NCl_2 \xrightarrow{NaHSO_3} R^1SO_2NHCH_2C(R)=CHCH_2Cl,$$
$$R=H,\ Cl;\ R^1=C_6H_5,\ p\text{-}ClC_6H_4,\ CH_3,\ (CH_3)_2N.$$

Yamasaki and co-workers[68] have shown that the reactions of *N,N*-dihalosulphonamides with 1,5-hexadiene, 1,4-pentadiene, 1,4-diphenyl-1,3-butadiene, and 1,4-cyclohexadiene are not regiospecific and 1 : 1 and 1 : 2 adducts of 1,2- and 1,4-addition are formed. The yields of these compounds, however, are low—only 2–21.3%.

The reactivity of *N,N*-dihaloarenesulphonamides in reactions with alkenynes, resulting in the formation of allene and acetylene isomers, was studied in the case of reactions with vinylacetylene, isopropenylacetylene, and vinylethylacetylene:[133]

$$R^1C\equiv C-CR^2=CH_2 + n\text{-}ClC_6H_4SO_2NCl_2 \xrightarrow{\text{then } NaHSO_3}$$
$$\xrightarrow{1,2-} R^1C\equiv C-C(R^2)ClCH_2NHSO_2C_6H_4Cl\text{-}p$$
$$\xrightarrow{1,4-} R^1CCl=C=CR^2CH_2NHSO_2C_6H_4Cl\text{-}p$$
$$R^1=R^2=H;\ R^1=C_2H_5,\ R^2=H;\ R^1=H,\ R^2=CH_3.$$

It has been established that the direction of addition of *N,N*-dichloro-*p*-chlorobenzenesulphonamide to conjugated vinylacetylenes is similar to that which occurs in the reactions of *N,N*-dihalocarbamates with alkenynes [67] and is determined by the structure of the alkenyne, in other words, when an alkyl substituent is introduced into the 2-position of a vinylacetylene molecule (isopropenylacetylene) the 1,4-adduct is mainly formed (allene isomer), while introduction into the 4-position gives an acetylene isomer. A distinctive feature of the reaction of *N,N*-dichloro-*p*-chlorobenzenesulphonamide with 5,5-dimethyl-1-hexen-3-yne is the absence of a 1,4-adduct—only the acetylene derivative $CH_3C(CH_3)_2C\equiv CCHClCH_2NClSO_2C_6H_4Cl\text{-}p$ is isolated—while in the reaction with an unsubstituted alkenyne (vinylacetylene) the allene isomer predominates (ratio of 1,4- to 1,2-adducts is 2 : 1).[133] In the case of *N,N*-dibromo-*p*-chlorobenzenesulphonamide only the reaction with hexen-3-yne was studied and, in contrast to the analogous reaction of *N,N*-dichloroarenesulphonamides and *N,N*-dihalocarbamates, the main product in this reaction is the dibromide of the 1,2-adduct; the 1,2-adduct is also formed, but in low yield:[133]

$$C_2H_5C\equiv C-CH=CH_2 + p\text{-}ClC_6H_4SO_2NBr_2 \xrightarrow{\text{then } NaHSO_3}$$
$$\longrightarrow C_2H_5CBr=CBr-CHBrCH_2NHSO_2C_6H_4Cl\text{-}p$$
$$\longrightarrow C_2H_5C\equiv C-CHBrCH_2NHSO_2C_6H_4Cl\text{-}p$$

N,N-Dichloroarenesulphonamides also add on to organosilicon derivatives of vinylacetylene such as 1-trimethylsilyl-3-buten-1-yne, 1-trimethylsilyl-3-penten-1-yne, 1-trimethylsilyl-3-methyl-3-buten-1-yne [134–138] both at the 1,2- and 1,4-positions to give allene and acetylene isomers, the ratio of which is determined by the structure of the alkenyne. Thus, in the reaction with 1-trimethylsilyl-3-buten-1-yne the 1,2-adduct is mainly formed, while with an alkenyne containing alkyl substituents on the double bond (1-trimethylsilyl-3-penten-1-yne) the 1,4 adduct is mainly formed:

$$(CH_3)_3SiC\equiv CCR^1=CHR^2 + ArSO_2NCl_2 \rightarrow$$
$$\xrightarrow{1,2-} (CH_3)_3SiC\equiv CCClR^1CHR^2NClSO_2Ar$$
$$\xrightarrow{1,4-} (CH_3)_3SiCCl=C=CR^1CHR^2NClSO_2Ar$$
$$R^1=R^2=H;\ R^1=H,\ R^2=CH_3;\ R^1=CH_3,\ R^2=H.$$

1,2-Adducts and 1,4-adducts tend to undergo allene-acetylene isomerisation. Their reduction with $NaHSO_3$ is also accompanied by allene-acetylene isomerisation. The triple bond of organosilicon vinylacetylene remains inert towards the addition of *N,N*-dichlorosulphonamides.

A characteristic feature of the reactions of *N,N*-dihalosulphonamides with carbon and organosilicon alkenynes is the induction period, which is an indication of the free-radical nature of the course of these reactions. In all cases attack by the amidyl radical is directed at a carbon atom on the double bond with formation of the most stable adduct radicals.[133,134]

In a single study,[139] where the reaction of *N,N*-dichloro-*p*-chlorobenzenesulphonamide with phenylacetylene was investigated, the formation of an azomethine in 66.7% yield was recorded; in this case a saturated adduct was isolated in low yield (5%):

$$C_6H_5C\equiv CH + Cl_2NSO_2C_6H_4Cl\text{-}p \rightarrow C_6H_5CCl=CHNClSO_2C_6H_4Cl\text{-}p \rightarrow$$
$$\text{(E)}$$
$$\xrightarrow{NaHSO_3} C_6H_5CCl=CHNHSO_2C_6H_4Cl\text{-}p$$
$$\longrightarrow C_6H_5CCl_2CH=NSO_2C_6H_4Cl\text{-}p$$

The authors attribute the formation of an azomethine to an intramolecular 1,3-migration of chlorine in the initial adduct (E).

(a) Dichloroarenesulphonamides in telomerisation reactions

Finally, it was established that *N,N*-dichloroarenesulphonamides are initiators for the telomerisation of alkenes. Thus, Freidlina and co-workers[124] carried out the radical telomerisation of allyl chloride and acrylonitrile with *N,N*-dichloroarenesulphonamide to form the telomers $p\text{-}ClC_6H_4SO_2N(X)(-CH_2-\underset{\displaystyle R}{\underset{|}{CH}}-)_nCl$ (X = H, Cl; R = CN, CH_2Cl; *n* = 1, 2).

The radical nature of these reactions is borne out by their significant acceleration on exposure to UV radiation and in the presence of peroxides. It was shown that with an increase in the ratio of acrylonitrile to *N,N*-dichloro-*p*-chlorobenzenesulphonamide the yield of lower telomers decreases and the yield of higher telomers ($n > 3$) increases.[140]

The ionic telomerisation of styrene with *N,N*-dichloro-*p*-chlorobenzenesulphonamide occurs in the presence of $SnCl_4$ in methylene

chloride in air,[141] telomers with the following composition being formed:

$$p\text{-}ClC_6H_4SO_2NH\left(-CH(C_6H_5)-CH_2-\right)_nCl,\quad n=1,\ 3,\ 6.$$

$$p\text{-}ClC_6H_4SO_2N\left[\left(-CH(C_6H_5)CH_2-\right)_nCl\right]_2,\quad n=2,\ 5,\ 6,\ 14.$$

(b) Nucleophilic addition of *N*-chloro-*N*-sodium arenesulphonamides to alkenes

There are several known examples of the nucleophilic addition of *N*-chloro-*N*-sodium arenesulphonamides to alkenes such as 1,1,3-trichloropropene,[142] 3,3,3-trichloropropene,[143], allyl chloride,[144] and acrylonitrile.[144]

Thus, the reaction with 1,1,3-trichloropropene in an aqueous medium mainly gave 1,3,3,3-tetrachloro-2-(arenesulphonamido)-propane (28–49%); this indicates the greater readiness of *N*-chloro-*N*-sodium arenesulphonamides to add on to the dichlorovinyl group of 1,1,3-trichloropropene than to replace the allylic chlorine in this compound:

$$ArSO_2\bar{N}Cl + ClCH_2CH{=}CCl_2 \longrightarrow$$

$$\rightarrow ArSO_2NClCH(CH_2Cl)\bar{C}Cl_2 \xrightarrow{H_2O,\ ArSO_2NClNa} ArSO_2NHCH(CH_2Cl)CCl_3$$

$$\rightarrow ArSO_2NClCH_2CH{=}CCl_2 \rightarrow \underset{NSO_2Ar}{CH_2{-}CHCCl_3} \rightarrow HOCH_2CH(NHSO_2Ar)CCl_3$$

(F)

Ar=C_6H_5, *p*-ClC_6H_4.

The dichlorovinyl derivative (F) was not isolated pure, since its intramolecular cyclisation to an aziridine took place. Hydrolysis of the latter gave 1-hydroxo-2-(arenesulphonamido)-3,3,3-trichloropropane in low yield (3–5%).

In the reaction of *N*-chloro-*N*-sodium arenesulphonamides with 3,3,3-trichloropropene the product of addition to the double bond $ArSO_2NHCH_2CHClCCl_3$ is only formed in 2–8% yield. The main product of this reaction is 1-hydroxy-2-(arenesulphonamido)-3,3,3-trichloropropane (37–51%), which, as Rybakova and co-workers[143,144] suggest, is formed by migration of the reaction centre when the amidyl anion attacks the terminal carbon atom of the alkene to form the unstable compound (F) and its subsequent conversion during reaction in a similar manner to the scheme suggested above.

In contrast to the reactions mentioned above, chlorosulphonamidation of allyl chloride mainly occurs via substitution of the allylic chlorine to form *N*-chloro-*N*-allyl-*p*-chlorobenzenesulphonamide (about 50%). The competing nucleophilic addition to the double bond does not occur to any significant extent.[144]

The reaction of *N*-chloro-*N*-sodium-*p*-chlorobenzenesulphonamide with a two- or three-fold excess of acrylonitrile in an aqueous medium takes place as a cyanoethylation reaction and *N*,*N*-di(2-cyanoethyl)-*p*-chlorobenzenesulphonamide is formed with a yield of about 61%.[144]

The reaction studied in the greatest detail has been that between the sodium salt of *N*-chloro-*p*-toluenesulphonamide and alkenes (cyclohexene, methylcyclohexene, cyclooctene, norbornene, 1-dodecene, 5-dodecene, 2-methyl-2-hexene, styrene and its derivatives, acrylates, cyclohexadiene, etc.),[145–148] which occurs in an alcoholic medium (60 °C) in the presence of OsO_4 and results in the formation of hydroxyalkyl derivatives of sulphonamides with fairly high yields:

$$p\text{-}CH_3C_6H_4SO_2NClNa\cdot 3H_2O + RCH{=}CHR^1 \rightarrow$$

$$\xrightarrow[t\text{-}C_4H_9OH,\ 60\ ^\circ C]{1\%\ OsO_4} p\text{-}CH_3C_6H_4SO_2NHCH(R){-}CH(OH)R^1 + NaCl.$$

Unfortunately, the number of studies on the reaction of *N*-halo-*N*-sodium arenesulphonamides are not sufficient to make any conclusions about the general mechanisms for these reactions.

Thus, analysis of the literature data on the reactions of *N*-halo- and *N*,*N*-dihalosulphonamides with unsaturated compounds has shown that these reactions take place, depending on the initiation conditions, by homolytic and heterolytic cleavage of the N–Hal bond to form *N*-haloalkyl-substituted sulphonamides, which are important intermediates for the synthesis of aziridines.[97–99,149] *N*-Halosulphonamides add on to functional derivatives of vinylidene chloride $CCl_2{=}CHR$ (R = H, $COOCH_3$, NHCOAr, COAlk, COAr, OR^1), dienes, and vinylacetylenes only according to a radical mechanism, as is suggested by the acceleration of these reactions in the presence of radical initiators and their inhibition in the presence of hydroquinone or atmospheric oxygen.

4. *N*,*N*-Dihalophosphoramidates

The addition of *N*,*N*-dihalophosphoramidates to alkenes has been studied in the case of reactions with ethylene,[150] hexene,[150] 2-ethyl-1-hexene,[150,151] 2-ethyl-1-butene, isobutene, 1-octene,[150,152,153] and styrene.[154–158] In the majority of cases the reactions have an induction period when exposed to UV radiation and on heating in benzene or carbon tetrachloride, and they are regiospecific, with the adducts formed in high yield (70–97%):

$$(RO)_2P(O)NX_2 + CH_2{=}CHR^1 \rightarrow (RO)_2P(O)NXCH_2CHR^1X \xrightarrow{NaHSO_3}$$

$$\rightarrow (RO)_2P(O)NHCH_2CHR^1X \xrightarrow[0\text{–}10\ ^\circ C]{HHal} NH_2CH_2CHR^1X,$$

X=Cl, Ar; R=C_2H_5, C_3H_7, iso-C_3H_7, C_4H_9, C_6H_5, R^1=C_6H_5;
R=C_2H_5, R^1=H, C_3H_7, C_4H_9, C_5H_{11}, n-C_6H_{13}, t-C_4H_9.

Confirmation of the orientation of the substituents in the adducts, namely, attachment of the amidyl fragment to the less substituted carbon atom of the alkene double bond is the conversion of dialkyl *N*-[2-halo-2-alkyl(phenyl)ethyl]phosphoramidate to the hydrochloride or hydrobromide salts of 2-halo-2-alkyl(phenyl)ethylamine by treatment with hydrogen chloride or bromide.

Addition of *N*,*N*-dibromophosphoramidates to long-chain terminal alkenes $RCH{=}CH_2$ (R = t-C_3H_7, t-C_4H_9, C_4H_9, C_6H_{13}), in contrast to the reactions of the chloro analogues, is complicated by side-reactions involving bromination of alkenes, which reduces the yield of the adducts.[159]

Formation of adducts $PhCCl(R)CH(R^1)NHP(O)(OC_2H_5)_2$ occurs in the reaction of diethyl *N*,*N*-dichlorophosphoramidate with phenylethylenes $Ph(R)C{=}CHR^1$, where R and R^1 = CH_3, Ph.[160]

In order to carry out the reactions of diethyl dihalophosphoramidates with alkyl esters of α,β-unsaturated carboxylic acids,[150,157,158] more prolonged UV irradiation (3–4 h) is required. The addition is

regiospecific, and adducts are formed in high yield:

$$R^1CH{=}C(R^2)COOR^3 + (C_2H_5O)_2P(O)NX_2 \xrightarrow{h\nu} \rightarrow (C_2H_5O)_2P(O)NXCH(R^1)CX(R^2)COOR^3 \xrightarrow{NaHSO_3,\ 0-5^\circ C} (C_2H_5O)_2P(O)NHCH(R^1)CX(R^2)COOR^3,$$

$X{=}Cl,\ Br;\ R^1{=}R^2{=}H,\ R^3{=}C_2H_5;\ R^1{=}H,\ R^2{=}R^3{=}CH_3;$
$R^1{=}R^3{=}CH_3,\ R^2{=}H.$

In contrast to the chloro analogues, diethyl *N,N*-dibromophosphoramidate [157] adds on to these olefins more readily (at 20–45 °C) and with a quantitative yield of adducts.

The occurrence of an induction period, acceleration of the reactions by UV irradiation, and also the regiospecificity in addition of *N,N*-dihalophosphoramidates to terminal $RCH{=}CH_2$ and α,β-substituted alkenes $R^1CH{=}C(R^2)COOR^3$ are indications of the radical nature of the addition taking place according to the scheme:

$$(RO)_2P(O)NX_2 \xrightarrow[-\dot{X}]{h\nu,\Delta} (RO)_2P(O)\dot{N}X \xrightarrow{-\dot{C}{=}\dot{C}-Y} \rightarrow (RO)_2P(O)N(X)\dot{C}-\dot{C}(Y) \xrightarrow[(RO)_2P(O)\dot{N}X]{(RO)_2P(O)NX_2}$$

(G)

$$\longrightarrow (RO)_2P(O)NXC(Y)-C(Y),$$

$X{=}Cl,\ Br;\ Y{=}Alk,\ COOR,\ CONH_2.$

The regiospecificity of addition is determined by the formation of the adduct radical (G), which is more stable than the adduct radical $\dot{C}-C(Y)NXP(O)(RO)_2$.

N,N-Dihalophosphoramidates are most active in reactions with terminal 1,3-alkadienes. These reactions occur under mild conditions (at 0–15 °C in CH_2Cl_2 for 30 min) and give (*E*)-1,4-adducts in 87–93% yield:[161]

$$(C_2H_5O)_2P(O)NCl_2 + CH_2{=}CR^1{-}CR^2{=}CH_2 \xrightarrow[0-15^\circ C]{CH_2Cl_2} \rightarrow (C_2H_5O)_2P(O)NClCH_2CR^1{=}CR^2CH_2Cl \xrightarrow[0-10^\circ C]{\text{then } 10\%\ Na_2SO_3} \rightarrow (C_2H_5O)_2P(O)NHCH_2CR^1{=}CR^2CH_2Cl,$$

$R^1{=}R^2{=}H;\ R^1{=}CH_3,\ R^2{=}H,\ CH_3.$

The reactions have high regiospecificity. They are inhibited in the presence of hydroquinone. The mechanism proposed by Gajda and Zwierzak[162] involves formation of an allylic type of adduct radical (H):

$$(RO)_2P(O)NCl_2 + \text{C=C-C=C} \xrightarrow{-\dot{C}l} (RO)_2P(O)NCl-\text{C-C-C=C} \longrightarrow$$

(H)

$$\xrightarrow[-(RO)_2P(O)N\dot{C}l]{(RO)_2P(O)NCl_2} (RO)_2P(O)NCl-\text{C-C=C-CCl}$$

$$(RO)_2P(O)N\dot{C}l + \text{C=C-C=C} \longrightarrow (H)$$

Radical (H) is stabilised by removal of a chlorine atom from the *N,N*-dichlorophosphoramidate, and so the thermodynamically more favourable 1,4-addition product is formed, which dictates the high regiospecificity of the reaction.

N,N-Dichlorophosphoramidates add on to 1,3-alkadienes such as *trans*-piperylene, 2,5-dimethyl-2,4-hexadiene, and 4-methyl-1,3-pentadiene only when initiated with UV irradiation.[162] These reactions are not regiospecific—1,2- and 4,1-addition products are formed together with 1,4-adducts.

It is interesting to note that the reaction of 1,4-diphenyl-1,3-butadiene with diethyl *N,N*-dichlorophosphoramidate has high regiospecificity—only the 1,2-addition product is formed:

$$(C_2H_5O)_2P(O)NCl_2 + PhCH{=}CH{-}CH{=}CHPh \xrightarrow{\text{then } 10\%\ Na_2SO_3} \rightarrow (C_2H_5O)_2P(O)NHCH(Ph)CHClCH{=}CHPh.$$

81%

This orientation of substituents in the adduct is consistent with the proposal[162] about stabilisation of the radical

$$(C_2H_5O)_2P(O)NClCH(Ph)\dot{C}H{-}CH{-}CHPh \qquad (I)$$

by addition of a chlorine atom to the 2-position with formation of the more stable compound.

There is an interesting study[163] in which the spontaneous addition of *N,N*-dichlorophosphoramidates to α-pinene is investigated; the products isolated are not those from addition of amidyl radicals to the double bond but products in the *trans* configuration formed from them by an intramolecular Wagner–Meerwein rearrangement (33%).

One study[164] was recently published, in which the addition of diethyl *N,N*-dibromophosphoramidate to olefins was examined using conditions for a heterolytic reaction—in the presence of boron trifluoride ethereate. It was shown that the reaction is regiospecific and gives saturated adducts:

$$PhCR{=}CHR^1 + Br_2NP(O)(C_2H_5O)_2 \xrightarrow[-20^\circ C]{BF_3\cdot(C_2H_5)_2O} \rightarrow PhC(R)CH(Br)R^1 \xrightarrow{NaHSO_3} PhC(R)CH(Br)R^1,$$

$NBrP(O)(OC_2H_5)_2$ $NHP(O)(OC_2H_5)_2$

$R{=}R^1{=}H;\ R{=}H,\ R^1{=}CH_3$ (*E*- and *Z*-isomers)
$R{=}H,\ R^1{=}Ph;\ R{=}Ph,\ R^1{=}H;\ R{=}R^1{=}CH_3.$

The high regiospecificity of addition is consistent with the principles of electrophilic addition to a double bond. The role of boron trifluoride ethereate, in the opinion of Osowska-Pacewicka and Zwierzak,[164] is to increase the electrophilicity of the dibromophosphoramidate, which is achieved by the formation of a complex which assists the heterolytic cleavage of the N–Br bond and an ionic process takes place. The structure of the complex can be represented by the following resonance forms:

$$\begin{matrix}C_2H_5O\\C_2H_5O\end{matrix}\!\!>\!P(O)\!-\!NBr_2 \leftrightarrow \begin{matrix}C_2H_5O\\C_2H_5O\end{matrix}\!\!>\!\overset{+}{P}\!-\!NBr_2 \leftrightarrow \begin{matrix}C_2H_5O\\C_2H_5O\end{matrix}\!\!>\!\overset{+}{P}{=}\overset{+}{N}Br_2$$

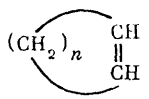
$^+O-\bar{B}F_3$ $O-\bar{B}F_3$ $O-\bar{B}F_3$

The addition of *N,N*-dibromophosphoramidates to 1,2-dialkyl-substituted ethylenes is not regiospecific:

$$R^1CH{=}CHR^2 + Br_2NP(O)(OC_2H_5)_2 \xrightarrow[2)\ NaHSO_3]{1)\ BF_3\cdot(C_2H_5)_2O} \rightarrow \underset{(C_2H_5O)_2P(O)NH\ \ Br}{R^1CH{-}CHR^2} + \underset{Br\ \ NHP(O)(OC_2H_5)_2}{R^1CH{-}CHR^2}$$

(I) (II)

With terminal alkenes ($R^1 = C_4H_9$, $R^2 = H$ and $R^1 = C_3H_7$, $R^2 = H$), mainly products (I) are formed, while the 2-pentene and 2-hexene products (I) and (II) are formed in equimolar quantities. The reactions with 3-hexene and 2-butene are highly stereoselective (only products with the *erythro*-configuration are formed, in 84–92% yield).[164] The addition of diethyl *N,N*-dibromophosphoramidates to cyclic



alkenes is highly stereospecific, only the *trans*-isomers are formed (79–80%). A similar reaction with indene has high regiospecificity and stereospecificity and gives *trans*-2-bromo-3-(diethoxyphosphoramido)indane (yield 96%).[164]

It is interesting that, in contrast to *N*-alkyl-*N*-halocarbamates, N–R-substituted *N*-halophosphoramidates $(C_2H_5O)_2P(O)N(R)Br$ undergo a reaction with styrene on heating to form saturated adducts in appreciable yield: 40% (R = C_2H_5); 76% (R = CH_3).[165] The introduction of stronger electron-donating substituents on to the nitrogen atom (R = OAlk, OCH_2Ph) hinders the addition to styrene, since stabilisation of the amidyl radicals $(C_2H_5O)_2P(O)\dot{N}OR^1$ occurs with elimination of nitrogen and formation of alkyl diethyl phosphates.[166] In this case chlorination of styrene is the preferred process (about 66%). It was also possible to identify products from the non-regiospecific addition of amidyl radicals to styrene, with the adduct $(C_2H_5O)_2P(O)N(OR)CH_2CHClPh$ present in threefold excess. It was not possible to isolate adducts in the reaction between *N*-methyl- or *N*-ethyl-*N*-bromophosphoramidate with 2-methyl-1-butene. However, when the reaction mixtures were treated with hydrogen chloride in tetrahydrofuran, the formation of *N*-alkyl-*N*-(2-bromoalkyl)amine hydrochlorides occurred in 10–28% yield.[165]

The introduction of bulkier alkyl substituents on to the nitrogen atom in the phosphoramidates $(AlkO)_2P(O)N(R)Br$ (R = n-C_4H_9, t-C_4H_9) hinders the addition of amidyl radicals to the double bond of an alkene or prevents it completely.[165]

In the presence of boron trifluoride etherate the addition of similar *N*-alkyl-*N*-halophosphoramidates to styrene or cyclohexene gives saturated adducts or products derived from their subsequent conversion.[165,167,168]

Thus, the direction of addition of dialkyl *N*-halophosphoramidates to the C=C bond is mainly determined by the conditions of homolytic and heterolytic initiation.

IV. Reactions of *N,N*-dihaloamides with polyhaloethylenes—a new method for the synthesis of compounds with an azomethine bond

In the large number of studies discussed in the preceding sections of this review it was shown that the *N,N*-dihaloamides of different acids add on to unsaturated compounds, including halogenated products (vinylidene chloride,[120] 1,1,3-trichloropropene,[97] chloroprene [44]), to form saturated adducts.

It was of interest to study the reaction of polyhaloethylenes with amidyl radicals in order to extend the range of homolytic reactions of haloolefins as well as amidyl radicals centred on nitrogen.

The results obtained from studying the reactions of homolytic thiylation of trichloroethylene and 1,2-dichloroethylene[169–173] and chlorovinylation of triethylsilane with trichloroethylene[174] suggest that the adduct radical $RCHCl\dot{C}Cl_2$ formed is stabilised not by formation of a saturated adduct but by elimination of a halogen atom from the α-position relative to the radical site, and an unsaturated compound $RCH{=}CCl_2$ is isolated. In the reaction of amidyl radicals with trichloroethylene, formation of an unsaturated compound could also be expected.

In fact, when *N,N*-dichloroarenesulphonamides react with trichloroethylene, chloral *N*-arylsulphonylimines are formed in quantitative yield. The saturated adducts $CCl_3CHClNClSO_2Ar$ were not detected in this reaction even though the ratio of reactants, the reaction conditions, and the structure of the aromatic group were varied:[72,74]

$$ArSO_2NCl_2 + CHCl{=}CCl_2 \rightarrow CCl_3CH{=}NSO_2Ar + Cl_2 + CHCl_2CCl_3,$$
$$Ar = C_6H_5,\ p\text{-}ClC_6H_4,\ p\text{-}CH_3C_6H_4.$$

The reactions were carried out in a stream of inert gas (nitrogen or argon) with UV irradiation (30 °C) in the presence of azobisisobutyronitrile or benzoyl peroxide (50–60 °C) and also without an initiator (85 °C). The maximum yield of imines (98–99%) was achieved when a four- to six-fold excess of trichloroethylene was used and the reactants were heated at 85 °C for 12–14 h. The chlorination of trichloroethylene to pentachloroethane by the chlorine generated occurred as a parallel process.

The acceleration of the reaction by radical initiators and its retardation in the presence of radical inhibitors (hydroquinone, atmospheric oxygen, etc.) suggests that the reaction of *N,N*-dichloroarenesulphonamides with trichloroethylene has a radical nature. The following reaction scheme has been proposed:[74]

N-Arylsulphonylimines are obtained via the formation of adduct radical (J). It can be stabilised in several ways: by 1,2- or 1,3-migration of a chlorine atom followed by elimination of a chlorine atom from the α-position of the isomerised radicals or by formation of an enamide derivative (K) followed by its chlorotropic rearrangement (the possibility of stabilising the adduct radicals by elimination of a chlorine atom from the α-position relative to the radical site to give enamides has been reported[169–174]).

The possibility that *N*-arylsulphonylimines are synthesised by dehalogenation of the saturated adducts (L) cannot be ruled out, but this reaction route is not the main one, as is indicated by the ^1H NMR spectroscopic data.[74]

The routes involving 1,2-migration of a chlorine atom in radical adduct (J) and also formation of enamide (K) from it seem less probable because of the greater tendency of the N–Cl bond towards homolytic cleavage (37 kcal mol^{-1}) than the C–Cl bond (81 kcal mol^{-1}).[60] When the reaction mixtures were studied by IR and ^1H NMR spectroscopy there was no indication that compounds with the $CCl_2=CH-NCl$ group were present in them. 1,1,1,2-Tetrachloroethylsulphonamides $ArSO_2NHCHClCCl_3$ were also not detected.

The previously known methods for obtaining chloral sulphonylimines [175–179] are characterised by multiple-stage reactions, the use of catalysts, and the toxicity and instability of the reactants. The new method for obtaining chloral sulphonylimines that has been developed is based on a large-tonnage organochlorine feedstock. As a result of the high yield of the products, the single-stage reaction, and technological effectiveness of the method it can be recommended as a new convenient method for the synthesis of highly reactive azomethines.

In order to extend the limits of the reaction that had been found for the synthesis of compounds with an azomethine bond and also to verify its mechanism, a study was made of the reaction between *N*,*N*-dichlorobenzenesulphonamide and tribromoethylene.[75] The reaction took place in an inert solvent by heating (85–90 °C) the dichloramide with a four- to six-fold excess of tribromoethylene for 9–14 h. The previously unknown dibromochloroacetaldehyde *N*-benzenesulphonylimine was formed (yield 80%) as a mixture of *syn*- and *anti*-isomers.[75] The reaction was accompanied by the evolution of chlorine and bromine and the formation of 1,2-dichloro-1,2,2-tribromoethane. Dibromochloroacetaldehyde *N*-benzenesulphonylimine is formed in a similar manner to that given in Scheme 1.

The structure of this imine can be used to verify the reaction mechanism, namely to exclude the reaction pathway via a 1,2-halotropic rearrangement in the adduct radical $C_6H_5SO_2NClCHBr\dot{C}Br_2$ since this would lead to the formation of the corresponding bromal derivative $C_6H_5SO_2N=CHCBr_3$. Exclusion of the reaction pathway via a 1,2-halotropic rearrangement in the adduct radical (see Scheme 1) is also confirmed by the reaction between *N*,*N*-dibromobenzenesulphonamide and trichloroethylene, which gives dichlorobromoacetaldehyde *N*-benzenesulphonylimine:[180]

$$C_6H_5SO_2NBr_2 + CHCl=CCl_2 \rightarrow C_6H_5SO_2N=CHCCl_2Br.$$

In order to obtain highly reactive sulphonylimines of polyhaloaldehydes, the reaction of *N*,*N*-dichloroarenesulphonamides with 1,2-dichloroethylene [73,181,182] has been studied.

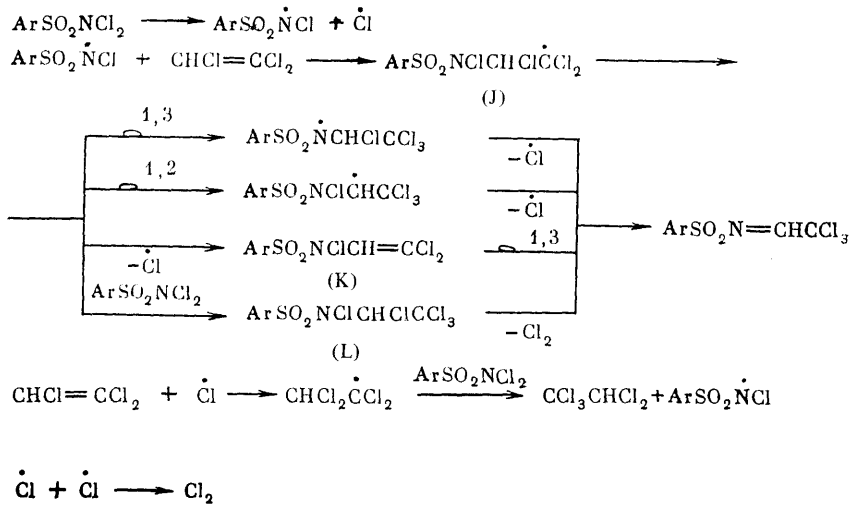
It should be noted that an attempt to react 1,2-dichloroethylene with compounds containing an N–Cl bond was made in an earlier study,[3] where the inertness of this olefin towards amidyl radicals was noted. However, it was later established that the reaction of 1,2-dichloroethylene with *N*,*N*-dichloroarenesulphonamides, occurring on exposure to UV radiation (47–55 °C) for 4 h and a ratio of reactants of 10 : 1, takes place in a similar manner to the reactions of *N*,*N*-dichloroarenesulphonamides with trichloro- and tribromo-ethylene and gives the corresponding azomethines in 50–60% yield. When the reaction time is increased to 9–26 h and the initiation conditions are also changed, the result is that the reaction is complicated by a number of subsidiary processes, which give 2,2-dichloro-1,1-di(*N*-arenesulphonamido)ethanes, chloral *N*-arylsulphonylimines, sulphonamides, and also products derived from chlorination of 1,2-dichloroethylene:[73]

$ArSO_2NCl_2 + CHCl=CHCl$ →
- $ArSO_2N=CHCHCl_2$
- $(ArSO_2NH)_2CHCHCl_2$
- $ArSO_2N=CHCCl_3$
- $ArSO_2NH_2$
- $CHCl_2CHCl_2 + CHCl=CCl_2 + CCl_2=CCl_2$

Ar = C_6H_5, *p*-ClC_6H_4, *p*-$CH_3C_6H_4$.

The yield of the reaction products depends on the conditions. When mixtures of 1,2-dichloroethylene and *N*,*N*-dichloroarenesulphonamides (in the ratio 1 : 8–10) are exposed to UV radiation at

Scheme 1



47–55 °C for 8–9 h the main reaction products are dichloroacetaldehyde sulphonylimines and 2,2-dichloro-1,1-di(*N*-arenesulphonamido)-ethanes. On heating without UV irradiation there is a considerable increase in the proportion of 1,2-dichloroethylene chlorination products and chloral sulphonylimines formed as a result of a side reaction between trichloroethylene and *N*,*N*-dichloroarene-sulphonamides.[74]

The reaction of *N*,*N*-dichlorourethane with trichloroethylene occurred under conditions similar to those for the reaction between *N*,*N*-dichloroarenesulphonamides and trichloroethylene[74] and led to the formation of chloral *N*-ethoxycarbonylimine in 75% yield.[76–77] When the reactants were heated for a longer period and water was introduced into the reaction mixture, the main reaction products isolated were 2,2,2-trichloro-1,1-di(*N*-ethoxycarbonylamino)ethane (50%) and 2,2,2-trichloro-1-hydroxy(1-*N*-ethoxycarbonylamino)ethane (20%) as a result of the reaction between chloral *N*-ethoxycarbonyl-imine and urethane which is formed in a side reaction and by reaction with water:[76]

$$C_2H_5OCONCl_2 + CHCl{=}CCl_2 \rightarrow C_2H_5OCON{=}CHCCl_3 \rightarrow$$
$$\rightarrow \begin{cases} \xrightarrow{C_2H_5OCONH_2} (C_2H_5OCONH)_2CHCCl_3 \\ \xrightarrow{H_2O} C_2H_5OCONHCH(OH)CCl_3 \end{cases}$$

The reaction of *N*,*N*-dibromourethane with trichloroethylene takes place in a similar manner, the main product being dichloro-bromoacetaldehyde *N*-ethoxycarbonylimine $C_2H_5OCON{=}CHCCl_2Br$, which is isolated in 67% yield. 2-Bromo-2,2-dichloro-1,1-di(*N*-ethoxy-carbonylamino)ethane—derived from the addition of a urethane molecule to the double bond of the dichlorobromoacetaldehyde imine—is formed as a by-product (10%):[183]

$$C_2H_5OCON{=}CHCBrCl_2 \xrightarrow{C_2H_5OCONH_2} \rightarrow (C_2H_5OCONH)_2CHCBrCl_2$$

The reaction occurs in a similar manner to that given in Scheme 1. Since the dichlorobromacetaldehyde acylimine is formed, the possible route involving a 1,2-chlorotropic rearrangement of the adduct radical (M) followed by elimination of bromine can be excluded, as in this case the reaction product would be chloral acylimine:

$$C_2H_5OCONBrCHCl\dot{C}Cl_2 \xrightarrow{1,2}$$
(M)
$$\rightarrow C_2H_5OCONBr\dot{C}HCCl_3 \xrightarrow[-Br^{\cdot}]{} C_2H_5OCON{=}CHCl_3$$

It was possible to carry out the reaction of *N*,*N*-dichlorobenzamide and *N*,*N*-dichloroacetamide with trichloroethylene under similar conditions, with products from further reaction of azomethines $RCON{=}CHCCl_3$ being formed, namely, *N*-(2,2,2-trichloro-1-hydroxy-ethyl)-substituted benzamide or acetamide and 1,1-di(*N*-benzamido)- or 1,1,-di(*N*-acetamido)-2,2,2-trichloroethanes.[184]

In the presence of atmospheric oxygen these reactions are complicated by the concurrent oxidation of trichloroethylene to dichloroacetyl chloride and the reaction of by-products to give the mixed amide $C_6H_5CONHCOCHCl_2$.

The reaction of diethyl *N*,*N*-dichlorophosphoramidate with trichloroethylene also takes place in accordance with Scheme 1 as proposed and gives 1,1,1-trichloro-2,2-bis(diethylphosphamido)-ethane.[185]

A study of the reactions of *N*,*N*-dihaloamides of sulphonic and carboxylic acids as well as *N*,*N*-dihalourethanes and dialkyl *N*,*N*-dichlorophosphoramidates with trichloro-, tribromo-, and 1,2-dichloro-ethylene showed that the reactions were accelerated by photochemical and thermal initiation as well as in the presence of peroxides and were inhibited in the presence of air or hydroquinone, which was an indication of their free-radical nature. The free-radical nature of the process was confirmed by chemically induced polarisation of ^1H nuclei and EPR spectroscopy.[186]

A study of the photochemically induced reaction of *N*,*N*-dichlorobenzenesulphonamide with trichloroethylene and 1,2-dichloroethylene by EPR in the presence of a 2-methyl-2-nitroso-propane trap (in benzene) demonstrated the formation during reaction of adduct radicals $C_6H_5SO_2NClCHClCXCl$ (J) (see Scheme 1), for which the EPR spectrum showed a characteristic splitting on the nitrogen atom with hyperfine coupling constant = 12.2 G, on the two non-equivalent chlorine nuclei $a_{Cl(1)}$ = 4.1 G, $a_{Cl(2)}$ = 1.0 G (X = Cl) and the chlorine atoms: $a_{^{35}Cl}$ = 6.2 G, $a_{^{37}Cl}$ = 4.7 G (X = H). Thus, the reactions of amidyl radicals $R\dot{N}Hal$ (R = SO_2Ar, COOAlk, COAlk, COAr) with polyhaloethylenes are of a common type and constitute an essentially new method for the synthesis of compounds with an azomethine bond. By selecting suitable partners the synthesis of azomethines $CHal_3CH{=}NR$ can likewise be carried out with different combinations of halogen atoms.

At the same time mention should be made of the high reactivity of synthesised polyhaloaldehyde acylimines in nucleophilic addition reactions of alcohols,[74–76] phenols, carboxylic acids,[127,184] sulphonamides and carboxamides,[129,176,184,187] thiols,[176] oximes, hydrazines,[187,188] bifunctional compounds,[176,187] chloroalkanols, α-halocarboxylic acids,[189] and benzalazine.[190]

Diene condensation reactions of chloral sulphonylimines with butadiene, isoprene, piperylene, and cyclopentadiene [178,191] have been carried out. For the first time the possibility of using chloral sulphonylimines as *C*-amidoalkylation agents of aromatic compounds (anisole, thioanisole, *N*,*N*-dimethylaniline),[192] heterocycles (thiophene, furan and its derivatives),[193] etc. has been demonstrated.

V. Conclusion

Thus, a common property of the reactions of *N*-haloamines, *N*-halocarbamates, and *N*-haloamides of carboxylic, sulphonic, and phosphoric acids with unsaturated compounds is the formation of saturated adducts. An analysis of the literature data showed that the majority of these reactions have a radical nature. The abundance of experimental and theoretical material which has been collected makes it possible to propose a general scheme for these reactions, involving the formation of a radical adduct $RN(X)\overset{|}{C}-\dot{C}\overset{|}{<}$ [R = Alk, R^1COO, R^1CO, $ArSO_2$, $AlkSO_2$, $(AlkO)_2P(O)$; X = H, Alk, Cl, Br] obtained by attack of an amidyl radical on the less substituted carbon atom at the double bond of alkene derivatives. Thus, the driving force of the process is formation of the most stable radical.

It follows from the material presented in this review that in recent years a new trend has developed in the sphere of radical reactions between *N*-haloamides and olefins—the reaction of acid

N,N-dihaloamides with polyhaloethylenes to form polyhaloaldehyde acylimines, which are highly reactive syntones in organic synthesis.

From among the known ionic reactions of *N*-haloamides and *N*-haloamines with unsaturated compounds, in recent years there has been active study of the reaction of *N*-chloramines with olefins in the presence of SO_3, which can give a new type of highly reactive electrophilic reagent at the first stage—*O*-chlorosulphamates—which then readily add on to the double bond of different alkenes.

Nevertheless, there are still a number of unresolved problems relating to the study of the mechanism of reactions between acid *N*-haloamides with alkenes under ionic initiation conditions. The reactions of acid *N*-haloamides with acetylene and polyhaloethylenes have not been studied in sufficient detail. There are no quantitative data on these reactions.

The various reactions described in this review illustrate the extensive reaction possibilities which are opened up by the chemistry of aminyl and amidyl intermediates.

Various types of compounds which have extensive application both in fine organic synthesis and in practical work can be obtained from these reactions (Scheme 2).

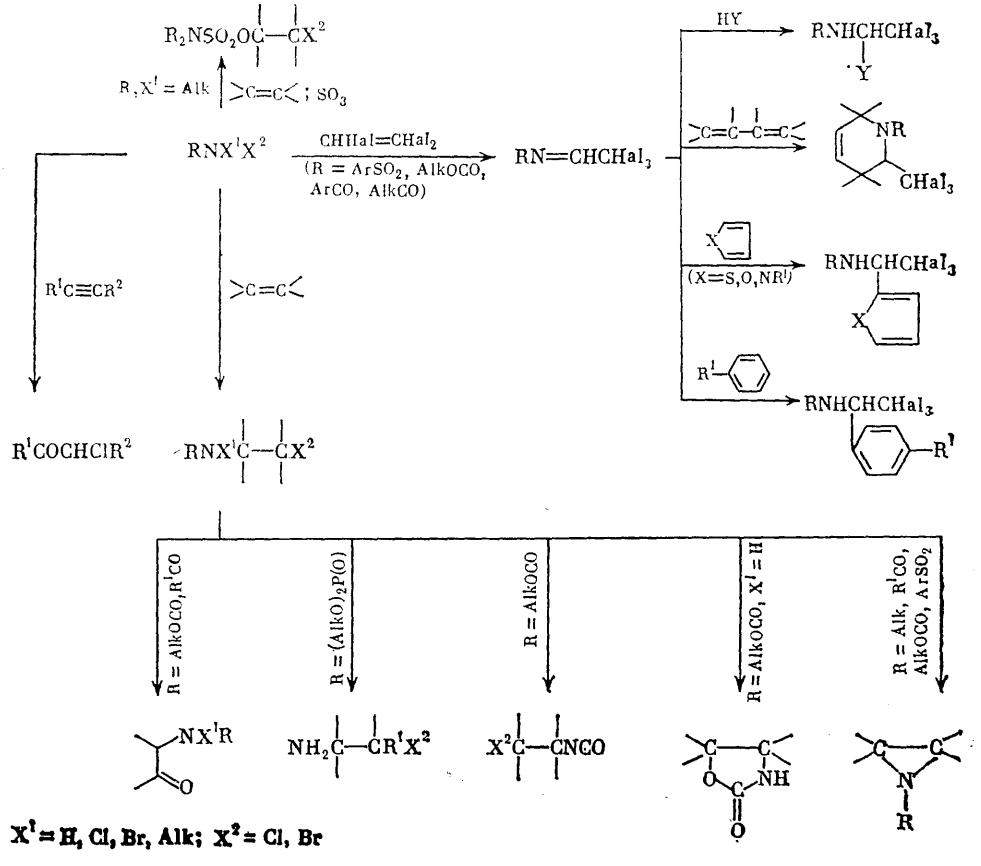
Among these products there are biologically active compounds with neurotropic and antibactericidal activity,[188] and insecticides,[194-198] herbicides,[199,200] and plant growth regulators[201] have been identified.

Aziridine derivatives—compounds with anticancer activity—have attracted considerable attention in recent years.[149] Various derivatives of isocyanates and oxazolidines have been widely used in the production of foamed plastics,[202] lacquers,[203] electrical insulating materials,[203] components of rubber mixtures,[204,205] etc.

The recent results should act as a stimulus for carrying out new studies aimed at investigating the reactions of *N*-haloamines and *N*-haloamides with different unsaturated compounds.

We can draw the attention of research workers to this field of chemistry by indicating the studies in which are reported the methods for synthesising *N*-chloramines,[23,27-30,206-208] *N*-monohalo- and *N,N*-dihalo-carbamates,[43,46,50,209] *N*-alkyl-*N*-halo- and *N,N*-dihalo-carboxamides,[95,210,211] *N,N*-dihaloarenesulphonamides,[112,212] and dialkyl *N,N*-dihalo- and *N*-alkyl-*N*-halophosphoramidates.[152,153,165,166,213-216]

Scheme 2



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