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Reactions involving the addition of *N*-halogenoamides to unsaturated compounds

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ABSTRACT. The literature data on the reactions involving the addition of *N*-halogeno- and *NN*-dihalogeno-amides of carboxylic sulphonic, sulphuric, and phosphoric acids as well as the esters of *N*-halogeno- and *NN*-dihalogeno-carbamic acids to various types of unsaturated compounds are surveyed. In many cases, the addition takes place with a different regiospecificity than for other compounds with *N*-halogen bonds, which has been explained by differences between the reaction mechanisms. The adducts of halogeno-amides with unsaturated compounds can be used in organic synthesis, especially in the synthesis of amides, aziridines, and other heterocyclic compounds.

The bibliography includes 113 references.

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I. Introduction

Highly reactive and readily available *N*-halogenoamides have long attracted the attention of investigators as effective halogenating agents. The chemistry of *N*-halogen-containing compounds, many representatives of which were already synthesised in the past century, began to develop vigorously during the last 30 years. The chemistry of *N*-chloroamines and *NN*-dichloroamines with various alkyl substituents, of *N*-halogeno- and *NN*-dihalogeno-amides of sulphonic, carboxylic, phosphonic, and sulphuric acids, as well as *N*-halogeno- and *NN*-dihalogeno-carbamic acid esters was investigated during this period. Reactions involving unsaturated compounds, which have now been investigated in relation to many examples, are of special interest because they lead to new possibilities for the introduction of functional groups into unsaturated organic compounds.

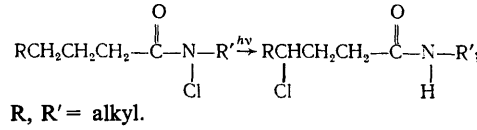
In the present review, which is devoted to the reactions involving the addition of *N*-halogenoamides to unsaturated compounds of different classes, we attempted to survey the available experimental data and to analyse the problems arising in their interpretation.

It is noteworthy that the previously published monographs and reviews by non-Soviet authors, in which this problem was dealt with in one way or another, inadequately reflect the modern advances in this field and hardly take into account the work of Soviet chemists.

II. Aliphatic alkenes

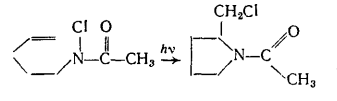
The reactions of alkenes with *N*-halogeno-substituted amides, carbamates, isocyanates, sulphonamides, and phosphoramides have been described in the literature.

The addition of *N*-halogenoamides to alkenes is usually carried out in neutral media under irradiation. Photolysis in the presence of alkenes proceeds via two pathways: with formation of adducts of the products of the substitution of the allyl hydrogen atom by the halogen. The reduction of temperature promotes an increase in the relative yield of the adducts.[1,2] It is noteworthy that, on irradiation, *N*-halogenoamides can rearrange (the Hoffmann–Loeffler reaction). For example, in the case of amides with three and more methylene groups, the following reaction occurs:[3]



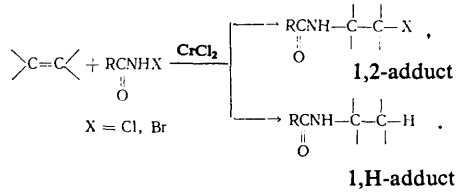
R, R′ = alkyl.

Unsaturated *N*-chloroamides can also react intramolecularly:[4]



A number of studies have been devoted to reactions of this type.[5–8]

The study of the one-electron reduction of *N*-halogenoamides by low-valence transition metal salts led to the conclusion that amidyl radicals can be generated without the accompanying formation of halogen atoms.[9–12] For example, a fairly effective method has been developed for the addition of *N*-halogenoamides to alkenes with participation of chromium(II) chloride. Two types of products are obtained: *N*-(2-halogenoalkyl)amides (1,2-adducts) and *N*-alkylamides (1,H-adducts).



X = Cl, Br

1,2-adduct

1,H-adduct

The overall yield of the adducts, the ratios of the yields of the 1,2- and 1,H-adducts, as well as the ratio of the *cis*- and *trans*-isomers depend on the nature of the alkene, the halogen, and the structure of the group R.

In the case of trisubstituted alkenes, 1,H-adducts have not been detected, whereas conjugated dienes afford exclusively 1,H-adducts. The following features have been observed for *N*-chloroamides:

(1) an increase in the overall capacity for 1,2-addition when R is varied in the sequence $CCl_3 < CH_3 < CF_3 < CH_2Cl < OAlk$;

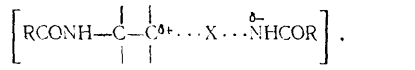
(2) an increase in the ratio of the 1,2- and 1,H-adducts in the sequence $CH_3 < CH_2Cl < OAlk < CCl_3 \leqslant CF_2$;

(3) an increase in the ratio of the *cis*- and *trans*-products in the sequence $CF_3 \simeq CCl_3 \leqslant CH_3 \simeq CH_2Cl < OAlk$.

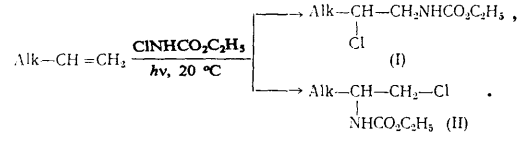
Thus both the best yields of the adducts and high selectivity of the reaction are obtained when *N*-chlorocarbamates are used.[11]

The influence of the structure of R on the yield of the adducts, on the ratio of the 1,2- and 1,H-adducts, and on the ratio of the *cis*- and *trans*-isomers is less significant when *N*-bromoamides are used. It is noteworthy that the competing electrophilic bromination (20–35%) in experiments with *N*-bromocarbamates lowers the yield of the adducts and thereby reduces the synthetic value of these reagents.

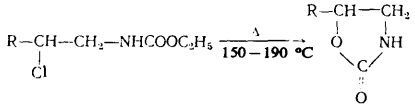
A radical mechanism has been proposed for the reactions described above.[12,13] The best chain transfer agent gives rise to the highest ratio of the 1,2- and 1,H-adducts for the given alkenes. Indeed, the *N*-bromoamide (the bromine atom is the actual chain transfer agent) is a better chain transfer agent than the *N*-chloroamide (where the chlorine atom is the actual chain transfer agent). On the other hand, the activity of the *N*-halogenoamide as a chain transfer agent increases as the electron-accepting capacity of the acyl residue (RCO) is enhanced as a result of the stabilisation of the polar transition state:



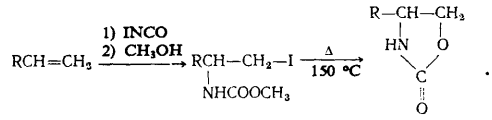
In the first studies on the addition of *NN*-dichlorocarbamate to a double bond,[14] it was already shown that the reaction proceeds with formation mainly of the adduct (contrary to the Markovnikov rule), i.e. with fixation of the nitrogen atom at the terminal carbon atom of the terminal double bond.[15,16] The UV-induced addition of *N*-chlorourethane proceeds with formation of a mixture of products (I) and (II) in proportions of 33 : 1:[17]



The position of the carbamate group was demonstrated both spectroscopically by ^1H NMR and chemically by pyrolysing the adduct with formation of 5-alkyl-2-oxazolidones:



The alternative formation of 4-alkyl-2-oxazolidinones has been observed in the pyrolysis of α-iodocarbamates obtained from iodine isocyanate and alkenes of a type similar to that described above:[18,19]

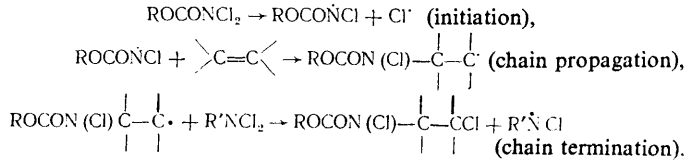


It is noteworthy that iodine isocyanate is a pseudohalogen and adds heterolytically. As a result of the electrophilic character of iodine isocyanate,[20] the iodine atom attacks the least substituted carbon atom, i.e. the adduct is formed "in conformity with the Markovnikov rule" (in contrast to the homolytic addition of *NN*-dichlorocarbamate).[21,22] The electrophilic addition of iodine isocyanate to a *cis*-alkene takes place *trans*-stereospecifically with formation of the *threo*-iodine isocyanate, which is converted into a carbamate without change of configuration. Treatment of this carbamate with base leads to a *cis*-aziridine, i.e. an intramolecular nucleophilic substitution takes place with inversion of configuration. A *trans*-aziridine is obtained similarly, albeit with lower yields than in the case of the *cis*-aziridine, from a *trans*-alkene via the *erythro*-iodine isocyanate.[19]

Homolytic addition of *NN*-dichlorocarbamates to alkyl-substituted alkenes proceeds non-stereospecifically with formation of a mixture of *erythro*- and *threo*-isomers[15] regardless of the geometrical configuration of the alkene. The lack of stereo-specificity in the UV-initiated addition of *N*-chlorourethane to but-2-ene is associated with the impossibility of the formation of a bridged structure.[23]

The most thorough information concerning the effect of steric factors on the rate of addition of *NN*-dichlorocarbamates to alkenes has been obtained in a study of its reactions with isomeric hexenes. Hex-1-ene reacts in less than 1 h quantitatively with formation of only the adduct. 2-Methylpent-2-ene is even more reactive, i.e. the electron-donating effect of the methyl group at the double bond overcomes its steric effect. 2,3-Dimethylbut-1-ene reacts much more slowly. 3,3-Dimethylbut-1-ene reacts on being refluxed for 4–5 h, while in the case of 2,3-dimethylbut-2-ene the addition to the double bond is not observed at all. Furthermore, the number of hydrogen atoms subjected to allylic attack changes simultaneously with the change in the steric parameters. Whereas hex-1-ene forms predominantly the 1,2-adduct with *NN*-dichlorourethane, 2,3-dimethylbut-1-ene and 2,3-dimethylbut-2-ene afford the allylic monochlorination products in 25 and 45% yields respectively.[24] Thus the yields of the main products diminish and those of side products increase with increase in the number of allyl hydrogen atoms.[25] As stated above, at low temperatures 1,2-addition predominates over the abstraction of an allyl hydrogen atom.[19]

The interaction of unsaturated compounds with *N*-halogeno-carbamates, which proceeds without the use of initiators (transition metal salts) or UV irradiation has all the features of a spontaneously initiated free-radical chain reaction, the sequence of the stages of which can be represented as folllows:



An inducation period is observed in this reaction and is followed by a rapid exothermic process; light accelerates the latter while free-radical reaction inhibitors retard it; the addition takes place also non-stereospecifically and contrary to the Markovnikov rule, the yields of the adducts diminish, and the yields of the side products (urethane, monochlorourethane) increase with increase in the number and activity of allyl hydrogen atoms. It is noteworthy that the radicals formed in the initiation stage are capable of abstracting an allyl hydrogen atom. This results in the appearance of a stable allyl radical, which subsequently participates in chain propagation.[15,19] The addition reactions are not then accompanied by vinyl polymerisation. Consequently in the formation of the primary radical, the monoadduct is produced at a rate much higher than the rate at which the polymerisation chain can be propagated. A concerted but non-synchronous molecularly induced homolysis (four-centre attack), in which the transition state is of a free-radical type, has therefore been proposed for the reaction considered. However, the impossibility of achieving the stereospecific addition to *trans*-hex-3-ene and stilbene constitutes evidence against the fully concerted homolysis.[24]

The reactions of alkenes with *NN*-dihalogenoarenesulphonamides are of considerable interest. Likhosherstov and co-workers[26–29] were the first to describe the interaction of *NN*-dichloroarene-sulphonamides with but-2-ene and isobutene in the presence of alcohols, phenols, or lower carboxylic acids in order to obtain β-chloroesters. In the reaction with but-2-ene, two racemic diastereoisomeric forms of *N*-(β-chlorobutyl)benzenesulphonamide and the corresponding aziridines were isolated as side products. The mode and mechanism of the addition reaction were not determined. The authors assumed that the reactions which they investigated are heterolytic.

There have been several communications containing contradictory data concerning the mode and mechanism of the addition of *N*-mono- and *NN*-di-halogenoarenesulphonamides to alkenes. In one of these communications,[30] it has been stated that *N*-bromo-*N*-methylarenesulphonamides add to alkenes and give rise to products in which the bromine atom occupies the same position as in the normal addition, i.e. in accordance with the Markovnikov rule, of HBr to these alkenes:

$$CH_3—CH=CH_2 + BrN(CH_3)SO_2Ar \rightarrow CH_3—CH(Br)CH_2—N(CH_3)SO_2Ar.$$

On the other hand, *NN*-dibromoarenesulphonamides add in the reverse order. However, here no account was taken of the different polarisations of the bromine atom in HBr and *N*-bromoamides. The structure of the product was demonstrated by a series of chemical conversions into known compounds.

In their reaction with propene, *NN*-dichloroarenesulphonamides give rise to two isomers, (III) and (IV), in proportions of 85 : 15.[31]

$$CH_3—CH=CH_2 + Cl_2NSO_2R \rightarrow \begin{cases} CH_3—CH(Cl)CH_2—N(Cl)SO_2R, & (III) \\ ClCH_2—CH(CH_3)N(Cl)SO_2R, & (IV) \end{cases}$$

It has been suggested that compound (III) is formed by a radical mechanism, similarly to the addition of *NN*-dichlorocarbamate,[31] while compound (IV) adds via the competing ionic mechanism. On the other hand, the product (IV) can be obtained, according to the authors, also via a radical mechanism, since the difference between the stabilities of the two possible radicals in the first chain propagation stage is not very great.

The reaction with isobutene proceeds quite differently. Mainly the allylic chlorination product (V) was isolated, its amount being equivalent to that of the benzenesulphonamide isolated. The formation of compound (VI) (in a low yield) takes place, according to the authors, via the cyclic chloronium intermediate (VII), i.e. via an ionic mechanism:

$$(CH_3)_2C=CH_2 + Cl_2NSO_2C_6H_5 \rightarrow (CH_3)_2C(Cl)CH_2^+ \text{ (VII)} + C_6H_5SO_2\bar{N}Cl \rightarrow$$

$$\rightarrow ClCH_2—C(CH_3)=CH_2 \text{ (V)} + C_6H_5SO_2NHCl,$$

$$2\,C_6H_5SO_2NHCl \rightleftharpoons C_6H_5SO_2NCl_2 + C_6H_5SO_2NH_2,$$

$$(CH_3)_2C(Cl)CH_2^+ \text{ (VII)} + C_6H_5SO_2NH_2 \rightarrow C_6H_5SO_2NHC(CH_3)_2CH_2Cl + H^+ \text{ (VI)}.$$

Another communication describes the oxygen-inhibited radical addition of *NN*-dichloroarenesulphonamide to ethylene and hex-1-ene. In contrast to the example described above, the amide radical attacks the less substituted, i.e. the terminal, carbon atom.[32] However, an ionic reaction pathway involving atmospheric oxygen, in which a mixture of products with the opposite orientation is formed, is also possible.

The attack on the more substituted carbon atom by the amide radical in the reaction of *NN*-dibromoarenesulphonamide with 2,3-dimethylbut-1-ene and 2-methylpent-2-ene shows that *NN*-dibromoarenesulphonamide is less sensitive to steric factors than *NN*-dichlorocarbamate.[33] However, the structure of the adducts was not rigorously demonstrated.

The reaction of *NN*-dichloroarenesulphonamide with *cis*- and *trans*-but-2-enes is not sensitive to radical process inhibitors and proceeds equally well both in the dark in an oxygen atmosphere and in nitrogen under the usual illumination. The *trans*-stereospecific addition via the ionic mechanism leads, according to the authors, to the formation of a new type of β-chloroalkyliminosulphonate derivative (VIII) together with the β-chloroalkanesulphonamide adduct:[34]

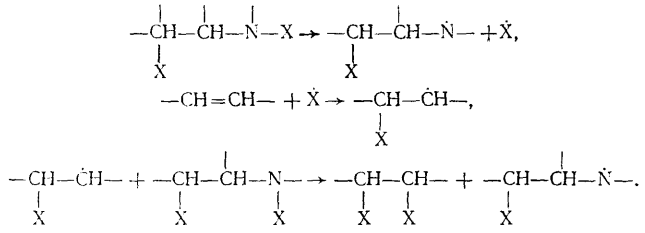
$$CH_3CH=CHCH_3 \xrightarrow[2)\ Na_2SO_3]{1)\ Cl_2NSO_2C_6H_5} \begin{cases} CH_3CH(Cl)CH(NHSO_2C_6H_5)CH_3, \\ CH_3CH(Cl)CH(CH_3)O—S(=O)(=NH)—C_6H_5 \text{ (VIII)} \end{cases}$$

The intermediate bridged chloronium ion is attacked either by the nitrogen atom or the oxygen atom of the *N*-chlorobenzene-sulphonamide anion. The high nucleophilicity of the oxygen atom is in this case completely unusual and conflicts with the available literature data on this problem.[34]

The *trans*-stereoselectivity of the addition of *NN*-dibromoarene-sulphonamide has been demonstrated in reactions with *cis*- and *trans*-hex-3-enes, *cis*-hept-2-ene, etc.[35] The formation of dibromo-derivatives and bromohydrins together with monoadducts has been observed:

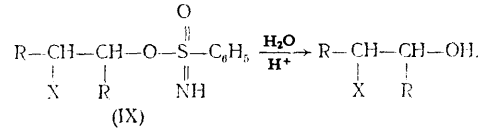
$$C_2H_5CH(Br)CH(NHSO_2C_6H_5)C_2H_5, \quad C_2H_5CH(Br)CH(Br)C_2H_5, \quad C_2H_5CH(Br)CH(OH)C_2H_5.$$

Judging from the observed stereoselectivity, the reaction proceeds via an ionic mechanism. The formation of dibromo-derivatives is a result of the radical reaction of *N*-bromo-*N*(β-bromoalkyl)-arenesulphonamide with a second substrate molecule:



It is striking that, as in the case of cyclohexene, allylic bromination products were not detected in the reaction.

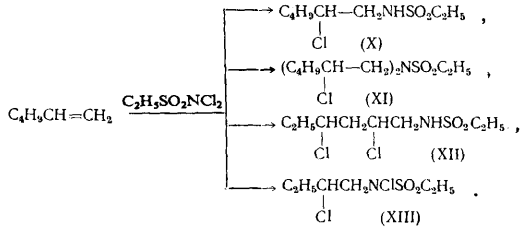
The elucidation of the pathways leading to the formation of bromohydrins was difficult. One of the possible pathways, namely the attack by water on the intermediate bromonium ion, is unlikely since the reaction is carried out under anhydrous conditions and the decomposition with bisulphite is performed in the complete absence of the alkene. An alternative possibility involves the hydrolysis of the iminosulphonate derivative (IX) which might have been formed in a reaction similar to that examined above:[34]



(IX)

However, all attempts to isolate compound (IX) were unsuccessful and a final conclusion about the mechanism of the formation of bromohydrins was not reached.

In the photoinitiated addition of *N*-chloro-*N*-methyl- and *NN*-dichloro-ethanesulphonamide to hex-1-ene, the nitrogen atom is attached to the terminal carbon atom of the alkene.[36] The formation of the products (X)–(XII) is described by the usual free-radical addition mechanism. Under these conditions, competition is observed between the abstraction of the allyl hydrogen atom from hex-1-ene and the rearrangement of the adduct (XIII) formed initially to (XII):



In a somewhat later study by the same workers,[37] it was observed that the mode of addition depends on the reaction conditions, while the yields vary with the alkene/*N*-chlorosulphonamide molar ratio. The data in Table 1 indicate a high regioselectivity of the addition only in photoinitiation. Under the usual illumination, the process competes with the radical reaction. The latter is slightly inhibited by oxygen and benzoquinone. It is of interest that virtually equal amounts of products with opposite orientations are obtained in a nitrogen atmosphere.

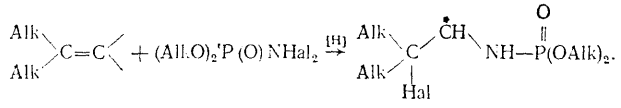
Table 1. The yields of the isomeric adducts in the reaction of *NN*-dichloroethanesulphonamide with hex-1-ene.[36,37]

Reaction conditions	1:1 adduct, %	
	C_4H_9–CH–CH_2Cl | $HNSO_2C_2H_5$	C_4H_9CH–CH_2 | | Cl $HNSO_2C_2H_5$
Photoinitiation, N_2	traces	100
Normal illumination	60	40
O_2 atmosphere, in the dark	67	33
In the presenceof $AlCl_3$	69	31
In the presenceof *p*-benzoquinone	68	32
Normal illumination, N_2	55	45

Rearrangements resembling the Hoffmann–Loeffler reaction for *N*-halogenoamides have been investigated in relation to *N*-alkyl-*N*-chloroarenesulphonamides[38] and *N*-chloroalkane sulphonamides[39] on photoinitiation or heat treatment.

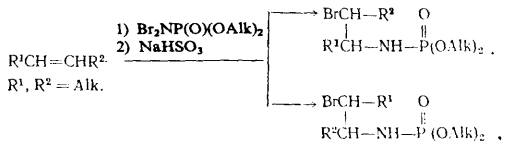
Thus there is no unanimity among investigators concerning the mechanism and order of the addition of *NN*-dihalogeno-sulphonamides to alkenes, which apparently depend both on the experimental conditions and on the nature of the halogen and the structure of the alkene. The wide variety of conditions under which the reactions were carried out and hence the wide range of products, which are in addition obtained via different mechanisms, preclude the comparison of the results of experiments of different workers.

The addition of *NN*-dichloro- and *NN*-dibromophosphoramidates to a series of alkenes with a terminal double bond has been studied recently.[40–45] The reactions take place in boiling benzene or methylene chloride or on photochemical initiation, depending on the reactivities of the reagents:



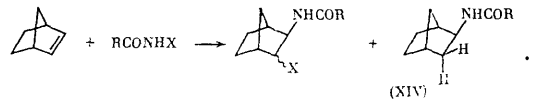
As in the example described above, the reaction of *NN*-dichloro-phosphoramidates is regiospecific and takes place with formation of a product in which the addition has taken place contrary to the Markovnikov rule. A radical mechanism has been proposed.

The heterolytic addition of *NN*-dibromophosphoramidate takes place in the presence of stoichiometric amounts of boron trifluoride etherate with formation of a mixture of products with opposite orientations:



III. Alicyclic alkenes

The regiospecificity of *N*-halogenoamides in the presence of chromium(II) chloride can be illustrated in relation to 1-methylcyclohexene and norbornene.[11] As might have been expected, the amido-group attacks the less substituted carbon atom. A small amount (up to 7%) of the 1,2-adduct with the opposite mode of addition was detected in the case of *N*-chlorocarbamate and *N*-bromoacetamide. The amide radical attacks norbornene exclusively in the *exo*-position in conformity with the generally accepted mechanism of the free-radical addition to norbornene:



An appreciable amount of the 1-*H*-adduct (XIV) was isolated in the above reaction, in contrast to the reaction involving 1-methylcyclohexene, which does not afford the 1,*H*-adduct even if the other reactant is *N*-chloroacetamide, producing the greatest amount of this adduct in its reactions with other alkenes. The ratio of the 1,2- and 1,*H*-adducts increases for cyclohexene and norbornene when R is varied in the sequence $CH_3 < CH_2Cl < OC_2H_5$.

The reaction involving ionic bromination by *N*-bromocarbamate, competing with the 1,2-addition, has been noted only for cyclohexene. According to the authors, in this instance the brominating agent is *NN*-dibromocarbamate arising as a result of the disproportionation of the initial reagent:

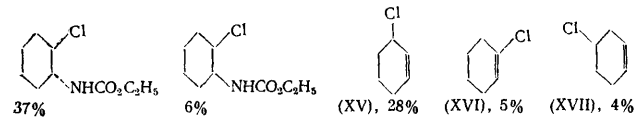
$$2ROCONHBr \rightleftharpoons ROCONBr_2 + ROCONH_2.$$

For *N*-bromoamides, this equilibrium is displaced to the left and the yields of the adducts are comparable to those for *N*-chlorocarbamates. Norbornene is unique in the series of monoolefins: in its reactions with *N*-chloroamides, it gives rise predominantly to the 1,*H*-adducts. On the other hand, in the reactions with *N*-bromo-amides, norbornene and cyclohexene afford comparable amounts of the 1,*H*-adducts. In the reactions involving the addition of *N*-halogenoamides to 1-methylcyclohexene and norbornene, the ratio of the *cis*- and *trans*-isomers increases in the sequence $CH_3 < CH_2Cl < OC_2H_5$. It is greater for *N*-chloroamides than for *N*-bromoamides and differs from the sequence observed for the reaction with cyclohexene. The addition to 1-methylcyclohexene is more stereoselective and that to norbornene is less stereoselective than the addition to cyclohexene. *N*-Alkyl-*N*-halogenocarbamates do not form 1,2- or 1,*H*-adducts in their reactions with cyclohexene. Small amounts of bicyclohexenyl (5%) and the corresponding alkyl carbamates have been isolated in such reactions. Table 2, compiled on the basis of the results of Driguez et al.,[11] summarises the relations examined above.

The UV-initiated addition of *N*-chlorocarbamates to cyclic alkenes proceeds with formation of a mixture of *cis*- and *trans*-products in proportions of 7 : 1. The predominance of the *cis*-configuration is a fairly rare phenomenon in radical addition reactions.[17]

The interaction of *NN*-dichlorocarbamate with cyclopentene can serve as an example of a *cis*-stereospecific radical reaction. In contrast to cyclohexenes, for five-membered cyclic alkenes there is a possibility of an intramolecular 1,3-transfer of a chlorine atom in the radical formed initially. On heating, the *cis*-isomer is converted into the *trans*-isomer.[46]

In contrast to the reaction examined above,[11] the *trans*-isomer predominates in the UV-initiated addition of *N*-chlorourethane to norbornene. It is noteworthy that the *cis*- and *trans*-isomers were isolated in this instance and the demonstration of the structure was based on the chemical conversion of the adducts into known compounds and also of the analysis of the ^1H NMR spectra of the isomers and their reaction products.[47] The overall yield of the adducts was high (93%) and the *trans*/*cis* ratio was 1.95, rising to 2.45 when a radical addition initiator was used. The reaction of *NN*-dichlorocarbamate with cyclohexene produces a complex mixture of products:[15]



In addition to the above set of products, monochlorourethane was detected in another study (4–5%).[48] It is of interest to compare this reaction with the chlorination of cyclohexene, where the products (XVIII), (XV), and (XVII) are obtained in proportions of 2 : 1 : 0.6, the formation of compounds (XV) and (XVIII) being the result of both radical reactions and the competing ionic reactions:

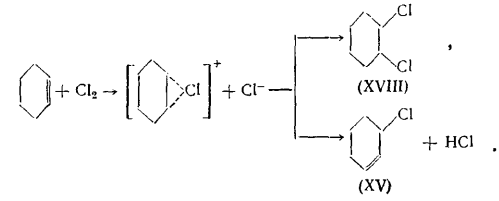


Table 2. The yields (%) of the products of the addition of *N*-halogenoamides to cyclohexene, 1-methylcyclohexene, and norbornene.[11]

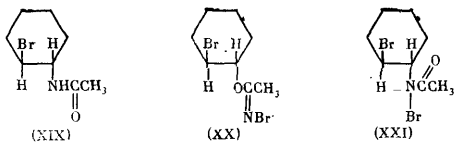
N-Halogenoamide	1-Methylcyclohexene		Norbornene			Cyclohexene		
	cis + *trans*	*cis*/*trans*	*cis* + *trans*	*cis*/*trans*	(XIV)	*cis* + *trans*	*cis*/*trans*	1,H
$CH_3CH_2OCONHCl$	80	25	41	5.8	54	87	6.7	6
$CH_3CONHCl$	74	6.4	1.6	*cis* only	93	34	2.1	36
$ClCH_2CONHCl$	77	5.5	33	2.8	55	75	2.0	13
$CH_3CH_2OCONHBr$	75	2.0	76	1.9	2	71	1.5	10.5
$CH_3CONHBr$	60	2.0	91	1.0	4	67	1.1	9
$ClCH_2CONHBr$	77	2.5	88	1.8	2.5	74	1.3	4

The mechanism of the formation of the product (XVII) in the reaction with *NN*-dichlorocarbamate is therefore not very clear. It could have been obtained as a result of the elimination of a hydrogen chloride molecule from the dihalogeno-derivative (XVIII), which, however, was not detected in the reaction with *NN*-dichlorocarbamate. The mechanism of the formation of

compound (XVI) as well as other chlorocyclohexenes was not discussed by Foglia and Swern[15] and Bal'on and Moskaleva.[48] On the other hand, it has been suggested that the 1,2-adduct is formed via free-radical mechanism.

In contrast to the addition of *N*-chloroamides to olefins, including alicyclic olefins, *N*-bromo- and *NN*-dibromo-carbamates add to cyclohexene stereospecifically (mainly by *trans*-addition). The structure of the product obtained was demonstrated by analysing the ^{1}H NMR spectra and by converting it into 8,9-*cis*-perhydrobenzoxazol-2-one. It had been established earlier that only the corresponding *trans*-compounds are capable of entering into similar reactions.[49] The lack of any side products whatever, in contrast to other reactions of *N*-bromocarbamate with alkenes, is striking.[11,15] The products of allylic bromination were not observed either on treating cyclohexene with *N*-bromo-acetamide.[50] Nevertheless, it is well known that bromoamides show a greater tendency than chloroamides to undergo allylic halogenation reactions and are used as specific brominating agents.[51,52] One of these widely used reagents is, for example, *N*-bromosuccinimide.[53] However, for *N*-bromosuccinimide also, experimental conditions have been found under which it (and *N*-chlorosuccinimide) add to cyclohexenes, producing adducts in yields up to 20%.[12]

The photoinitiated reaction of cyclohexene with *N*-bromo-acetamide, already mentioned above, is completely unexpected. Together with the formation of only 1% of the 1,2-*trans*-adduct (XIX), 36% of the *trans*-adduct (XX) and the isomeric product (XXI) were obtained:[50]



The *N*-bromoamidyl radical is generated via reactions (2) and (3), which are followed by the rapid reactions (4) and (5). The last of these explains, according to the authors, the absence of dibromo-derivatives and unsaturated bromo-derivatives as well as the formation of the products of the reaction of *NN*-dibromoacetamide with cyclohexene:

$$CH_3CONHBr \rightarrow CH_3CO\dot{N}H + \dot{B}r, \quad (1)$$

$$CH_3CO\dot{N}H + CH_3CONHBr \rightarrow CH_3CONH_2 + CH_3CO\dot{N}Br, \quad (2)$$

$$\dot{B}r + CH_3CONHBr \rightarrow CH_3CO\dot{N}Br + HBr, \quad (3)$$

$$HBr + CH_3CONHBr \rightarrow Br_2 + CH_3CONH_2, \quad (4)$$

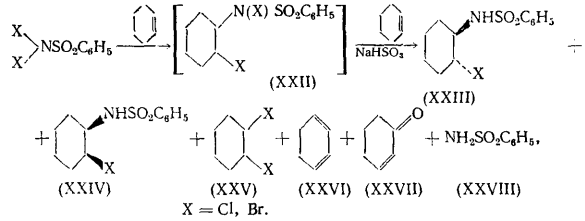
$$Br_2 + CH_3CO\dot{N}Br \rightarrow \dot{B}r + CH_3CONBr_2, \quad (5)$$

$$CH_3CO\dot{N}Br + CH_3CONHBr \rightarrow CH_3CONBr_2 + CH_3CO\dot{N}H. \quad (6)$$

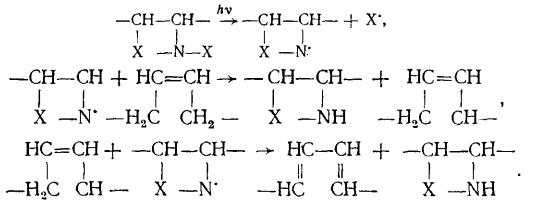
We may note that *N*-chloroiminosulphonates similar to compound (XX) are formed in the reaction of but-2-ene with chloramine B via an ionic pathway. The set of equations (1)–(6) quoted by the authors do not explain, in our view, the observed distribution of the yields of the products and leave open the question of both the reaction mechanism and of the "brominating" properties of mono- and dibromo-acetamides.

Asymmetrically substituted cyclohexenes have been investigated in the reaction involving the addition of iodine isocyanates.[54] It has been established that 1-ethyl-, 1-isopropyl-, and 1-phenyl-1-(α-naphthyl)cyclohex-1-enes react smoothly with formation of α-iodo-β-isocyanato-derivatives "in accordance with the Markovnikov rule". On acid hydrolysis, the adducts give rise to the corresponding salts of β-iodoamines in 30–40% yield. Among similar reactions, we may note the addition of iodine isocyanate to Δ^1-dihydronaphthalene.[55] Urea derivatives, aziridines, iodine carbamates, as well as amine hydrochlorides have been obtained from products of similar reactions (β-iodoisocyanates).

As already stated above, the addition of *NN*-dihalogeno-sulphonamides to alkenes proceeds via a free-radical or ionic mechanism depending on the experimental conditions. The reactions of cyclohexene with *NN*-dihalogenoarenesulphonamides afford similar sets of products for *NN*-dichloro- and *NN*-dibromo-benzenesulphonamides:[56–58]



Two reaction steps have been proposed: the intermediate (XXII) is formed in the first step and subsequently interacts with new cyclohexene molecules, giving rise to the reaction products indicated above. This hypothesis is confirmed by the results of the study of the reaction of compound (XXII) [obtained by brominating the adduct (XXIII) in the presence of alkali] with cyclohexene: the products (XXIV)–(XXVIII) are formed. On this basis, the authors postulated the absence of adducts in the reaction of *N*-alkyl-*N*-halogenobenzenesulphonamides with cyclohexene, which was in fact the case. The authors explain the formation of the dihalogeno-derivative (XXV) by invoking the well known mechanism of the bromination by *N*-bromosuccinimide.[59] However, the formation of cyclohexadiene via the free-radical abstraction of a hydrogen atom from the cyclohexenyl radical appears unlikely:



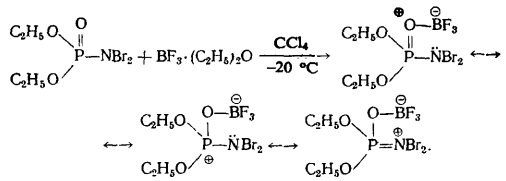
Thus the mechanism of the formation of cyclohexadiene and especially of cyclohexenone (XXVII) as well as the absence of products of allylic bromination from the reaction mixtures remain unexplained. On the other hand, competition between the halogen atom and the sulphonamide radical, which depends on their relative reactivities, can lead to the preferential formation of allylic bromination products and not products resulting from the addition of the halogen molecule. In confirmation of this, one may quote the results of a study of the reaction of *NN*-dichlorobenzene-sulphonamide with cyclohexene at 20 °C. A product of type (XXII)

was obtained (the reaction is non-stereospecific). It reacts with boiling carbon tetrachloride with a mixed cyclohexene molecule, affording the product of the allylic chlorination of cyclohexene together with compounds (XXIII) and (XXIV).[60] This course of the process is the opposite of the reactions described above.[56]

Two studies[61,62] were devoted to the reactions involving the addition of *NN*-dibromobenzenesulphonamides to norbornene and a series of bicyclic olefins, which occur, according to the authors, via an ionic mechanism. The principal pathway involved the formation of a nortricyclene bromo-derivative together with adducts, among which dibromo-derivatives and bromohydrins were detected. This was also observed in the reaction, discussed previously, of aliphatic alkenes, with *NN*-dibromobenzenesulphonamide and also in the reaction of *NN*-dichlorocarbamate with norbornene, which results in the formation of 3-chloronortricyclene in 45% yield.[15]

The reactions in which alkenes are subjected to *cis*-stereospecific hydroxyamination by chloramine T in the presence of catalytic amounts of osmium tetrachloride have been investigated vigorously in recent years.[63] In the above study, certain synthetic possibilities of this reaction and the practical applications of the product were investigated.

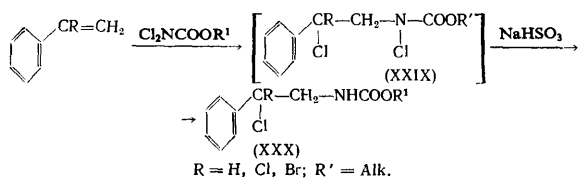
The ionic addition of *NN*-dibromophosphoramidate to cycloalkenes has been studied in relation to indene, cyclopentene, etc. The process has a *trans*-stereospecific character and proceeds rapidly at low temperatures without an induction period, in contrast to the radical reactions described above. Boron trifluoride etherate plays the role of an ionising agent for the dibromophosphoramidate molecule.[45] The electrophilic character of the bromine atom in the complex form leads to the heterolytic cleavage of the N–Br bond and ionic addition to the double bond.



IV. Arylalkenes

The reactions involving the addition of *N*-halogenoamides to aromatic alkenes exhibit the same features as the reactions with aliphatic and alicyclic alkenes.

As was to be expected, the addition of *NN*-dichlorocarbamate to styrene leads to the formation of the monoadduct (XXX) in which the carbamate group is attached to the less substituted carbon atom:[15]



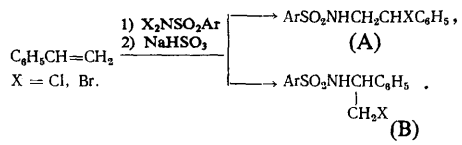
In this reaction it was possible to isolate the intermediate (XXIX).[48,64] Interesting series of reactions have been carried out in order to obtain various styrenes with functional group substituents.[65,66] These reactions as well as the synthesis of 5-alkyl-2-oxazolidinones from the adducts undoubtedly indicate that the carbamate group occupies the terminal position.[15,64] The addition of *NN*-dichlorourethane to bromostyrene proceeds similarly. The use of catalytic amounts of copper powder increases the yield of the adduct from 30 to 90%.[67]

In its reaction with *trans*-stilbene, dichlorocarbamate gives rise to an 11:9 mixture of the *erythro*- and *threo*-forms. The substances synthesised have been used to obtain 2-chloro-1,2-diphenylethyl isocyanate, 2-chloro-1,2-diphenylethylamine, 2,3-diphenylaziridine, and *NN*-disubstituted amides.[68]

The high regio- and stereo-specificities of the addition of *N*-bromocarbamates to styrene (a nitrogen-containing radical attacks the carbon atom, forming *trans*-adducts) has been demonstrated.[48]

The reactions of aromatic alkenes with *NN*-dihalogenoarenesulphonamides are of greatest interest, as for the olefins described above. The mechanism and mode of addition have been the subject of studies.

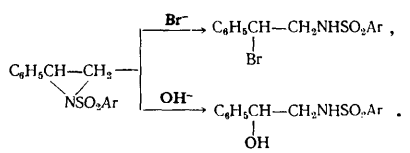
In the reaction with styrene, there is a possibility, in principle, of the formation of two isomers (A) and (B), which was already noted in one of the first studies on the addition of *N*-bromo-*N*-methylbenzenesulphonamide:[69]



The addition of dichloroarenesulphonamide to styrene in an inert gas atmosphere without an initiator leads to compound (A), while in the presence of equimolar amounts of aluminium chloride the product is compound (B). The authors believe that compound (A) is formed by a free-radical mechanism, while compound (B) is produced by an ionic mechanism via the complex $Cl^+[AlCl_3(NClSO_2Ar)]^-$ formed initially.[70]

A group of Soviet chemists have also shown that compound (A) is formed by a radical mechanism in a nitrogen atmosphere. However, in the presence of atmospheric oxygen, the reaction proceeds via an ionic pathway and the higher-melting adduct (B) is obtained.[71,72]

Japanese workers state that the reaction with styrene yields larger amounts of the product (A) formed "contrary to the Markovnikov rule" than in reactions with alkenes, where approximately equal amounts of adducts involving the opposite modes of addition were found in the case of *NN*-dichloroarenesulphonamides.[73] At the same time, it has been discovered that the reaction of *NN*-dibromoarenesulphonamide with styrene in the absence of catalysts gives rise to the product (B),[74] in contrast to *N*-bromo-*N*-methylarenesulphonamides, which, as for aliphatic alkenes, afford adducts formed contrary to the Markovnikov rule.[30] This can be illustrated by the formation of a bisadduct as a result of the addition of the brominated product (B) to a new styrene molecule. It is of interest to note that the opening of the ring of the aziridine obtained from compound (B) leads to the formation of a product in which the disposition of the substituents is the opposite to that in the initial compound.[68] This has also been noted in other studies:[75,76]



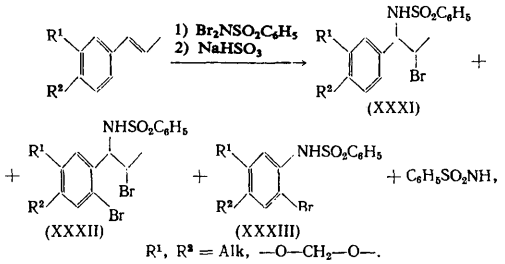
The adducts obtained were reduced to the corresponding amines, demonstrating rigorously thereby that the sulphonamide group occupies the initial position.

The ionic telomerisation of styrene by *NN*-dichloro-*p*-chlorobenzenesulphonamide leads to telomers of the following type:[77]

$$n\text{-ClC}_6\text{H}_4\text{SO}_2\text{NH}(\text{C}_8\text{H}_8)_n\text{Cl},\quad n = 1, 2, 3;$$

$$n\text{-ClC}_6\text{H}_4\text{SO}_2\text{N}\begin{matrix}(\text{C}_8\text{H}_8)_m\text{Cl}\\(\text{C}_8\text{H}_8)_{n-m}\text{Cl}\end{matrix}\quad n = 2, 5, 6, 14;\ m = 1\ .$$

The addition of *NN*-dibromoarenesulphonamide to propenylbenzene derivatives proceeds *trans*-stereospecifically with formation of a mixture of products (XXXI)–(XXXIII):



R^1, R^2 = Alk, —O—CH_2—O—.

The formation of the product (XXIII) as a result of the elimination of the C_3 fragment from the adduct (XXXI), which occurs for 3,4-dialkoxypropenylbenzene, is of greatest interest according to the authors.[76,78] The fate of the C_3 fragment was not investigated. In the similar reaction with safrole (R^1, R^2 = —O—CH_2—O—) the products of the rearrangement predominate over the normal adducts for any reactant ratios.[79] The rearrangement proceeds via the phenonium ion (migration of the methylenedioxyphenyl group to the electron-deficient β-carbon atom of the safrole chain). Safrole and the rearranged products are brominated by an excess of *NN*-dibromoarenesulphonamide or the molecular bromine formed from it.

Thus *NN*-dibromoarenesulphonamides as a rule differ from their chloro-substituted analogues or *NN*-dichlorocarbamate in the mode of addition, which in the case of non-aromatic olefins depends on the experimental conditions.

NN-Dichlorophosphoramidates add to styrene and its analogues contrary to the Markovnikov rule, non-stereospecifically, and by the radical mechanism.[44,80] A vinyl chlorination product is also formed in the reaction of 1,1-di(*p*-methoxyphenyl)ethylene. *trans*-Stilbene reacts in the course of several hours, affording a low yield of adducts (33.5%). The products of allylic chlorination or vinyl polymerisation were not detected in the reactions with styrene, (*E*)- and (*Z*)-1-phenylpropenes and α-methyl styrene. In the presence of equimolar amounts of boron trifluoride etherate, adducts are formed in accordance with the Markovnikov rule (by an ionic mechanism).[45]

V. Substituted alkenes

1. Halogenoalkenes

The addition of *N*-chlorocarbamate to 1-chlorocyclohexene in the presence of chromium(II) chloride leads to smaller amounts of the 1,2- and 1,*H*-adducts than in the case of cyclohexene.[11]

Vinylidene chloride combines with *NN*-dichlorocarbamate fairly rapidly, giving good yields of the adducts,[24,81] which can be explained, according to the authors, by the stabilisation of the $CCl_2CH_2N(Cl)CCOR$ group as a result of the possibility of the delocalisation of the unpaired electron over the two chlorine atoms, which compensates to a large extent for their electron-accepting effect. Treatment of the adduct with alcoholic alkali leads to the formation of *N*-(1-alkoxy-2,2-dichloroethyl)-carbamic acid esters:

$$\dot{C}Cl_3CH_2NHCOR \xrightarrow[CH_3OH]{KOH} [CCl_2{=}CHNHCOR \rightleftarrows CHCl_2CH{=}NCOR] \rightarrow CHCl_2CH(OCH_3)NHCOOR.$$

The increased reactivity of dichlorovinylamides is attributed to the possible enamide–*N*-acylimine tautomerism and the high reactivity of the *N*-acylimine form in nucleophilic addition reactions.[81]

When *NN*-dichlorourethanes are heated with trichloroethylene,[82] the adduct formed initially with the carbamate group at the less substituted carbon atom is readily dechlorinated, being converted into the *N*-acylimine:

$$CCl_2{=}CHCl + Cl_2NCOOR \rightarrow [CCl_3CHClN(Cl)COOR] \xrightarrow[-Cl_2]{30\ ^\circ C} \underset{(XXXIV)}{} \rightarrow CCl_3CH{=}NCOOR.$$
(XXXV)

Together with the liberation of chlorine, the formation of pentachloroethane was detected in the given reaction[83] and the bisadduct $(C_2H_5OCONH)_2CHCCl_3$ was isolated. It is suggested, in contrast to the data of Mirskova et al.,[83] that the adduct (XXXIV) is not formed under the reaction conditions, while the azomethine (XXXV), isolated in the form of compound (XXXVI), is obtained as a result of the elimination of a chlorine atom from the radical (C) generated in the first stage of chain propagation:

$$C_2H_5OCONCl_2 \rightarrow C_2H_5OCO\dot{N}Cl + \dot{C}l,$$
$$C_2H_5OCO\dot{N}Cl + CHCl{=}CCl_2 \rightarrow C_2H_5OCON(Cl)CHCl{-}\dot{C}Cl_2,$$
(C)

$$(C) \rightarrow C_2H_5OCO\dot{N}CHClCCl_3 \xrightarrow{-\dot{C}l} C_2H_5OCON{=}CHCCl_3,$$
(XXXV)

$$(C) \xrightarrow{-\dot{C}l} C_2H_5OCONClCH{=}CCl_2 \rightarrow C_2H_5OCON{=}CHCCl_3,$$
(D) (XXXV)

$$(D) \xrightarrow{C_2H_5OCONCl_2} (C_2H_5OCONCl)_2CHCCl_3 \xrightarrow{H_2O} \rightarrow (C_2H_5OCONH)_2CHCCl_3 \xrightarrow{H_2O} C_2H_5O\overset{O}{\overset{\|}{C}}NH\overset{OH}{\overset{|}{C}}HCCl_3.$$
(XXXVI)

Chloral imines are obtained from trichloroethylene and *NN*-dichloroacetamide or *NN*-dichlorobenzamide, also with the intermediate formation of a type (C) radical-adduct, its rearrangement, the 1,3-migration of a chlorine atom, and the elimination of chlorine from the α-position.[84] Trichloroethylene reacts in the same way with *NN*-dichloroarenesulphonamides.[85–88] The saturated adducts $CCl_3CHClNClSO_2Ar$ are not formed under any reaction conditions. The reaction is accompanied by the liberation of chlorine and leads to trichloroethylidenearenesulphonamides.

The influence of Lewis acids on the mode of reaction of *NN*-dichloroarenesulphonamides with trichloroethylene and on the yield of its products[88] has also been studied. It has been shown that, in the presence of $SnCl_4$ or $AlCl_3$ under conditions ruling out to the maximum extent the free-radical reaction, the interaction of the above reactants proceeds in the same way as under the conditions of thermal and photochemical initiation.

The mechanism has been studied by CINP and EPR and the presence of radical stages in the photochemical reaction of *NN*-dichlorobenzenesulphonamide and *NN*-dichlorourethane with trichloroethylene was demonstrated.[89] The possible pathways leading to the formation of the final products were suggested.

1,1,2-Tribromo-1,2-dichloroethane has been detected, together with the liberation of gaseous chlorine and bromine, in the reaction of dichloroarenesulphonamide with tribromoethylene.[90] The rearrangement of the intermediate radical-adduct $C_6H_5SO_2NClCHBr\dot{C}Br_2$ (if it occurs) is achieved via the 1,3- and not the 1,2-migration of a chlorine atom. The elimination of a bromine atom with formation of the enamide $CBr_2=CHNClSO_2C_6H_5$ and its subsequent isomerisation appear to the authors to be less probable because of the greater ease of the homolytic dissociation of the N–Cl bond compared with C–Br.

In contrast to trichloro- and tribromo-ethylenes, vinylidene chloride[91] as well as other compounds containing the dichlorovinyl group[92] afford a 1 : 1 adduct with *NN*-dichloroarenesulphonamide, and in the last case the adducts obtained under ionic and radical conditions have the same structure (in contrast to the reaction of styrene).

The addition to ethylene, styrene, and allyl chloride of the product of the reaction of dichloroarenesulphonamide with vinylidene chloride has been investigated. Ionic reactions do not occur in this case and in the radical process the nitrogen atom adds to the styrene fragment contrary to the Markovnikov rule:

$$p\text{-}ClC_6H_4SO_2\overset{Cl}{\underset{|}{N}}CH_2CCl_3 + CH_2=CHR \rightarrow R\overset{Cl}{\underset{|}{C}}H-CH_2-\overset{SO_2C_6H_4Cl\text{-}p}{\underset{|}{N}}-CH_2CCl_3;$$
$$R = H,\ C_6H_5,\ CH_2Cl.$$

Such reactions proceed with much more difficulty than the analogous reactions with *NN*-dichloroarenesulphonamides.[94]

2. Alkenes with functional group substituents

The interactions of monochlorourethanes [in the presence of chromium(II) chloride] with methyl acrylate and methyl vinyl ketone do not afford 1,2-adducts.[11] A two fold excess of the reagent leads to the formation of small amounts of 1,*H*-adducts.

The yields of the products of the addition of *NN*-dichlorocarbamates to alkenes with functional group substituents are high regardless of whether electron-donating or electron-accepting groups adjoin the double bond. The polar effects of the substituents do, however, affect the rate of addition. The reaction of diethyl maleate with *NN*-dichlorocarbamate is slow (more than 30 h), while ethyl vinyl sulphone does not react even on refluxing in benzene for 72 h. Methyl acrylate reacts with dichlorocarbamate more slowly than does methyl vinyl ketone, while acrylonitrile reacts still more slowly.[24] In all these reactions, the carbamate group attacks the less substituted carbon atom; a free-radical mechanism of the addition reaction has been proposed. When they combine with *NN*-dichlorourethane on heating in benzene, vinyl ethers give rise to adducts with the opposite mode of addition (in accordance with the Markovnikov rule),[95] in contrast to vinyl acetate, which produces an adduct with the carbamate group in the terminal position regardless of the method of initiation.[24,96]

The use of a univalent copper salt or copper powder as the catalyst in the addition of *NN*-dichlorocarbamate to acrylic acid derivatives shortens the reaction from 4–5 h to 30–40 min and increases the yield and purity of the adducts.[97] It has been suggested that the reaction has a radical character:

$$AlkOCONCl_2 \xrightarrow[-CuCl]{Cu} AlkOCO\dot{N}Cl,$$
$$AlkOCONCl_2 \xrightarrow[-CuCl_2]{CuCl} AlkOCONCl \xrightarrow{CH_2=CHR}$$
$$\rightarrow AlkOCON(Cl)CH_2\dot{C}HR \xrightarrow[-CuCl]{CuCl_2} AlkOCON(Cl)CH_2CH(R)Cl\ .$$

It follows from the scheme presented that the copper(II) chloride formed in the initiation stage terminates the chain, which promotes, according to the authors,[98] an increase in the yield of the main reaction products. The formation of 5-alkyloxazolidinone, as in the case of aliphatic alkenes,[24] demonstrates the terminal position of the carbamate group.

NN-Dichloroarenesulphonamides add to the double bond in alkenes containing electron-accepting groups in the presence of peroxide catalysts or under UV irradiation.[71] The proposed initiation system (univalent copper salt and tetraethylammonium bromide) promotes an increase in the yield of adducts in these reactions and a decrease in the reaction time.[98] The role of the second additive (tetraethylammonium bromide) consists, in the authors' view, in generating the bromine atoms which initiate the addition reaction.

The reaction of *NN*-dichlorobenzenesulphonamide with alkyl 2,2-dichlorovinyl ketone results in the formation of 1,1-adducts $C_6H_5SO_2N(Cl)-CH(COAlk)CCl_3$, which are converted into *N*-(1-acyl-2,2,2-trichloroethyl)benzenesulphonamides on exposure to atmospheric moisture. On treatment with alkali the sulphonamides eliminate HCl and afford *N*-(1-acyl-2,2-dichlorovinyl)benzenesulphonamides:[99]

$$C_6H_5SO_2NHCH(COAlk)CCl_3 \xrightarrow{OH^-} C_6H_5SO_2\underset{H}{\underset{|}{N}}-\underset{CCl_2}{\underset{\|}{C}}-COAlk.$$

In conclusion, it is of interest to note that *NN*-dibromoarenesulphonamides, which add to asymmetric alkenes in accordance with the Markovnikov rule, in contrast to *NN*-dichlorourethane, react with αβ-unsaturated carboxylic acid esters similarly to *NN*-dichlorourethanes, in such a way that the bromine atom enters a position adjoining the carbonyl group ("contrary to the Markovnikov rule").

VI. Alkadienes

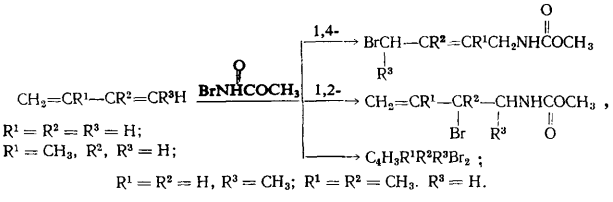
The order of the addition of various reagents to alkadienes depends greatly on their structure and its determination therefore permits additional conclusions concerning the reaction mechanism. On the other hand, the possibility of the formation in this case of a mixture of 1,2- and 1,4-isomers hinders the isolation and identification of the adducts.

The addition of various *N*-halogenoamides to buta-1,3-diene, isoprene, piperylene, cyclohexadiene, chloroprene, etc. has been investigated.

The photochemical decomposition of *N*-halogeneamides (including urethanes) is inhibited by cyclohexa-1,3-diene. After irradiation for 45 h, the reaction mixture still contains 94% of the active halogen.[25] On the other hand, the addition to norbornadiene proceeds readily and affords three isomeric 3,5-disubstituted nortricyclenes in 66% yield and 7% of the 1,2-adduct. Only linear adducts are formed in the photoinitiated addition of *N*-halogenoamides to non-conjugated dienes. In the reaction of cycloocta-1,5-diene, bicyclic derivatives — the products of the "transannular cycloaddition" of the primary radical — were not detected.[25]

NN-Dichlorocarbamates add to butadiene with formation of a mixture of the 1,4-*trans*-adduct (86%) and the 1,2-adduct (14%).[100] The reactions with chloroprene and 2,3-dimethylbuta-1,3-diene result in the exclusive formation of 1,4-adducts. In the case of isoprene, the 1,4-adduct $ClH_2C-C(CH_3)=CHCH_2NHCOOR$ was isolated (selectivity 85%). The formation of the products of the reverse 4,1-addition has also been postulated from ^1H NMR data. A mixture of three isomeric adducts, the 1,2-adduct (26%), the 1,4-adduct (44%), and the 4,1-adduct (30%), is formed in the reaction of *NN*-dichlorocarbamate with piperylene.[100]

The *trans*-1,4-adducts are formed predominantly in all cases in the interaction of *N*-bromocarbamates with conjugated alkadienes under the same conditions as for *NN*-dichlorocarbamates[100] (Table 3):



Dibromo-derivatives, whose formation may be induced by the disproportionation of the reagent with formation of carbamate and *NN*-dibromocarbamate, were identified as side products. The *NN*-dibromocarbamate functions as a brominating agent (as in the formation of dibromo-derivatives in the reactions of *N*-bromocarbamates with alkenes).[11]

Table 3. The isomeric composition of the products of the addition of *N*-halogenocarbamates to alkadienes.[100,101]

Hydrocarbon	$Cl_3NCOOCH_3$*			$BrHNCOOCH_3$		
	1,4-	4,1-	1,2-	1,4-	1,2-	dibromo-derivatives
$H_2C=CH-CH=CH_2$	90	—	10	70	20	10
$H_2C=C(CH_3)C(CH_3)=CH_2$	100	—	—	68	—	32
$H_2C=C(CH_3)CH=CH_2$	85	15		71	—	24
$H_2C=CH-CH=CH-CH_3$	44	30	26	66**	8	24

* According to the results of Daniher and Butler.[100]
** 1,4- and 4,1-isomers in proportions of ~1 : 1.

Thus the regio- and stereo-specificity of the addition of *N*-bromocarbamate hardly differs from that for *NN*-dichlorocarbamate. The reaction is not inhibited by oxygen (in contrast to the addition of dichlorocarbamate), while the ratio of the isomers depends little on the experimental conditions. A decrease in temperature promotes the formation of small amounts of dibromo-derivatives. The low selectivity of the addition reaction in the case of piperylene can be explained by the approximately equal stabilities of the two allyl radicals formed. The complete absence from the reaction mixtures of products resulting from chlorination and substitution of hydrogen atoms is noteworthy.[101]

The reactions of iodine isocyanate with alkadienes have also been investigated.[102] Aliphatic alkadienes with isolated double bonds combine with two moles of iodine isocyanate per mole of the substrate, in contrast to conjugated alkadienes which afford 1,4-mono-adducts; when the adducts are treated with methanol, the corresponding iodine carbamates are produced. Methylallene also combines slowly with one mole of iodine isocyanate; the structure of the adduct has not been demonstrated. With the exception of cycloocta-1,3-diene, alicyclic alkadienes react extremely rapidly, similarly to alkadienes with isolated multiple bonds. Contrary to expectation, cyclohexa-1,4-diene combines with only one mole of iodine isocyanate. Analysis of the ^1H NMR and IR spectra led to a tricyclic structure being attributed to the products of the addition of one mole of iodine isocyanate to norbornadiene.

NN-Dichloroarenesulphonamides add readily and exothermically to buta-1,3-diene and chloroprene. 1,4-Adducts are then formed in high yields.[31] The oxygen-inhibited reaction proceeds via a free-radical mechanism, like the addition of *NN*-dichlorocarbamate.

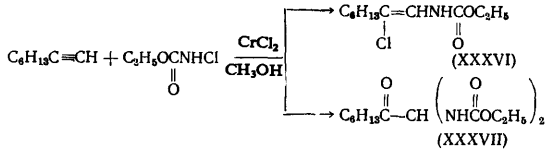
In their reactions with *NN*-dihalogenoarenesulphonamides (but not with dichlorocarbamate), alka-1,4-dienes afford, together with open-chain products, small amounts of cyclic adducts, mainly pyrrolidine derivatives. However, cyclohexa-1,4-diene does not form an azabicyclic compound, in contrast to *cis,cis*-cycloocta-1,5-diene, which produces such a compound in its reaction with *NN*-dibromotoluene-*p*-sulphonamide.[103] 1,4-Diphenylbuta-1,3-diene reacts with *NN*-dibromobenzenesulphonamide to form a pyrrolidine derivative and 1,2,3,4-tetrabromo-1,4-diphenylbutane in low yields. The authors attributed a symmetrical structure to the cyclic products of the addition of *NN*-dibromobenzenesulphonamide to hexa-1,5-diene, which does not agree with the firmly established mode of addition of halogenoamides to alkenes.[104]

The addition of diethyl *NN*-dichlorophosphoramidate to conjugated alka-1,3-dienes (butadiene, isoprene, 2,3-dimethylbutadiene) proceeds regiospecifically with formation of an (*E*)-1,4-adduct. The addition to cyclohexa-1,3-diene takes place in the same way. *trans*-Piperylene, 4-methylpenta-1,3-diene, 2,5-dimethylhexa-2,4-diene, and 1,4-diphenylbuta-1,3-diene usually give rise to a mixture of products. As in the case of other *NN*-dichloroamides, the reaction proceeds via a free-radical mechanism.[105]

VII. Acetylenes

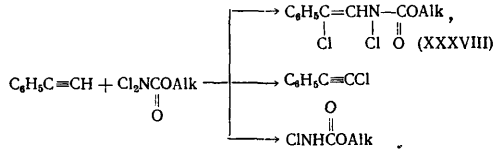
The reactions of acetylenes with *N*-halogenoamides have been least investigated. As a result of the high lability of enamines or enamides, obtained as a result of the addition reaction, the authors of the few studies which have been carried out succeeded in isolating either the products of further reactions or the true adducts in low yields. Only oct-1-yne and phenylacetylene were introduced into the reaction.

The addition of *N*-chlorocarbamate to oct-1-yne gives rise to a complex mixture of products, from which the adduct (XXXVI) and the *NN*-di(ethoxycarbonylamino)ketone (XXXVII), formed evidently as a result of the hydrolysis of the 2:1 adduct, were isolated. However, completely different proportions of the products (XXXVI) and (XXXVII) were obtained in two experiments (respectively 28 and 9% in one and traces and 13% in the other):

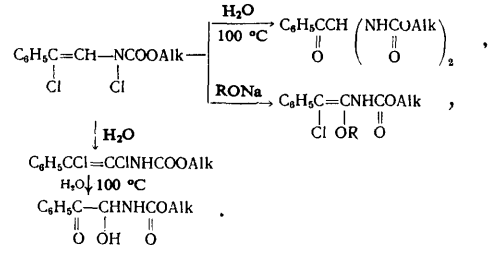


Unfortunately, the physicochemical constants and the methods used to isolate the above compounds are not quoted, which gives rise to some doubt as to the reliability of the results.[11]

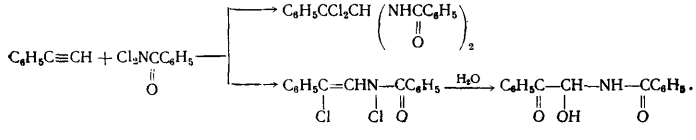
The addition of *NN*-dichloroamides to phenylacetylene has been studied:[106,107]



The *N*-chloro-*N*-(β-chlorostyryl)urethanes (XXXVIII) obtained are a mixture of geometrical isomers in proportions of 7:3; after storage for 24 h they rearrange to $C_6H_5CCl=CClNHCOOAlk$, which in our view is not an entirely usual behaviour. A number of chemical reactions of the compounds isolated demonstrate, according to the authors, the structure of the adducts formed initially:

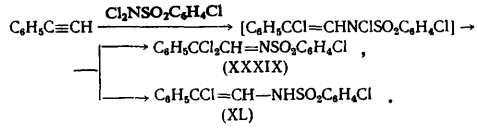


NN-Dichlorobenzamide adds in the same way to phenylacetylene:[108]



However, in both cases the hydrolysis and interaction of compound (XXXVIII) with sodium alkoxide are open to doubt. The lack of spectroscopic data for the NCl-adducts isolated and also the very high, in our view, chemical shift of the proton at the nitrogen atom in compound (XXXVIII) (9.05, 9.25 p.p.m.) suggest the possibility that the interaction of *NN*-dichloroamides with phenylacetylene proceeds differently than has been suggested.[106] *N*-Bromoamides have not been introduced into similar reactions.

The reaction of *NN*-dichloro-4-chlorobenzenesulphonamide with phenylacetylene afforded a high yield of the azomethine (XXXIX):[109]



Thus the previously uninvestigated "halogenotropism", i.e. the 1,3-migration of chlorine (most probably intramolecular) in the molecule of the NCl-adduct formed initially, occurs in this instance. Treatment of the reaction mixture with a solution of sodium bisulphite leads to a complex mixture of products, from which the adduct (XL) was isolated in a low yield (5%).

The addition of iodine isocyanate to acetylenes is complicated by the formation of diiodo-derivatives as side products. The pure reaction product cannot be obtained.[102] Ony the product derived from oct-4-yne by the addition of iodine isocyanate followed by treatment with methanol was isolated (yield 20%).

VIII. Alkenynes

The reactions involving the addition of *NN*-dihalogenoamides to conjugated alkenynes have been investigated in relation to vinylacetylene and its homologues.[101,109] The reactions of *NN*-dichlorocarbamates were performed in an argon atmosphere at a reduced temperature:

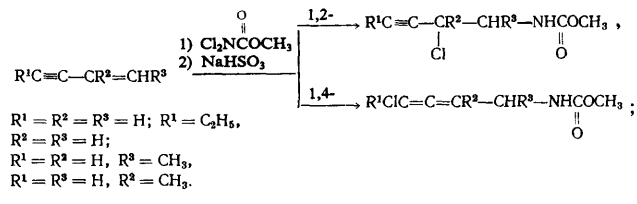


Table 4. The isomeric composition of the products of the addition of *N*-halogenocarbamates to alk-1-en-3-ynes.[101,112]

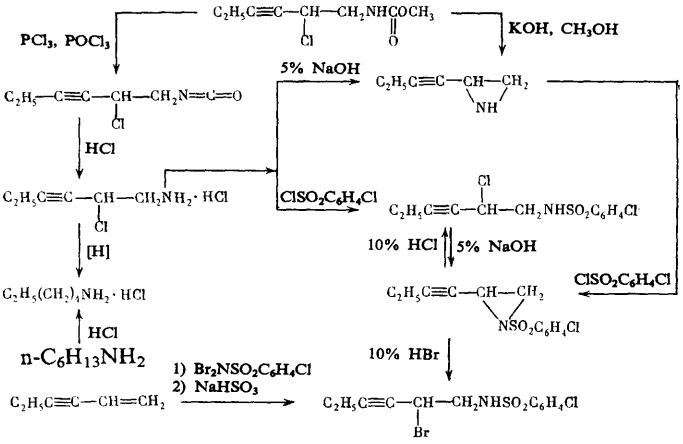
Hydrocarbon	$Cl_2NCOOCH_3$		$BrNHCOOCH_3$	
	1,2-	1,4-	1,2-	1,4-
$HC\equiv C-CH=CH_2$	30	70	70	30
$C_2H_5-C\equiv C-CH=CH_2$	100	—	95	5
$HC\equiv C-C(CH_3)=CH_2$	15	85	—	100
$HC\equiv C-CH=CH-CH_3$	60	40	20	80

It has been established that vinylacetylene and its closest homologues are attacked by *NN*-dichlorocarbamate only at the terminal atom of the ethylene bond and in the case of monosubstituted acetylenes the 1,4-adduct is formed preferentially. The amount of the 1,2-isomer in the case of propenylacetylene is

much greater than for isopropenyl- and vinyl-acetylenes. In the reaction of vinylethylacetylene, only the 1,2-adduct is formed (Table 4).

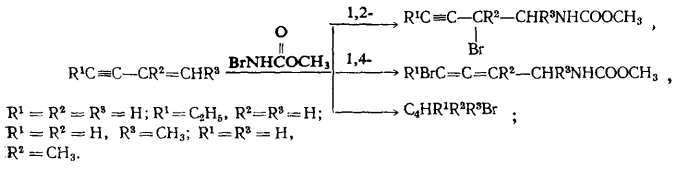
Attack by the carbamate group on the extreme ethylenic atom of the 1,3-enyne system was demonstrated in the last case not only from a study of the NMR spectra but also by means of chemical reactions (Scheme 1). The allenic (acetylenic) carbamates obtained do not isomerise to 1,3-dienes or acetylenes (allenes) either in the presence of copper(I) chloride or on treatment with alkali.

Scheme 1



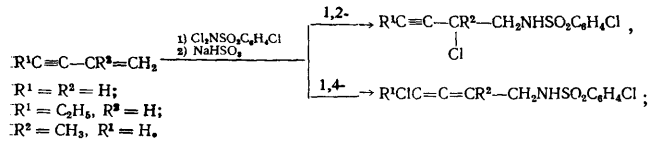
The inability of the compounds indicated to isomerise supports the view that the 1,2- and 1,4-isomers are obtained independently via a single mechanism, i.e. their addition reaction begins with attack by the carbamate group on the terminal ethylenic atom and not with attack by the chlorine atom on the extreme carbon atom of the triple bond with a subsequent allene–acetylene rearrangement.

In the reactions of *N*-bromocarbamate with alk-1-en-3-ynes, the amide moiety added to the ethylenic end of the molecule with rigorous selectivity, as in the reaction described above:[101]



However, the amount of 1,2-adducts in these reactions is smaller than in the reactions with *NN*-dichlorocarbamates. Vinylacetylene, for which the ratio of the isomers is reversed on replacement of *NN*-dichlorocarbamate by *N*-bromocarbamate, is an exception (Table 4). The reaction of *N*-bromocarbamate with alk-1-en-3-ynes results in the formation, as in the reaction with 1,3-dienes, of a considerable amount of dibromo-derivatives as side products (up to 25%) (the mechanism of this reaction was examined in detail above).

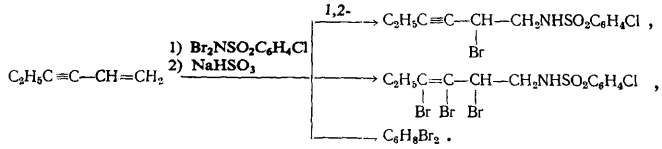
It has also been established that the regioselectivity of the addition of *NN*,4-trichlorobenzenesulphonamide to conjugated vinylacetylenes is similar to that for halogenocarbamates regardless of the experimental conditions:[109,110]



The terminal position of the sulphonamide group has been confirmed, apart from spectroscopic evidence, by a series of chemical reactions (presented in Scheme 1) in relation to 2-chloro-1-(4-chlorobenzenesulphonamido)hex-3-yne.

Trialkylsilyl-substituted vinylacetylenes combine with aromatic *NN*-dichlorosulphonamides at the double bond in the 1,4-position. The chlorine-containing adducts formed are unstable and are converted, already under the conditions of the addition reaction, into the corresponding alkadienyl(chloroalkynyl)sulphonamides. The addition is accompanied by the chlorination of the initial unsaturated compounds.[111]

The addition of *NN*-dibromo-4-chlorobenzenesulphonamide has been studied only in relation to vinylethylacetylene. The reaction mixture contained up to 40–45% of dibromo-derivatives, which were determined chromatographically. A tribromo-derivative was isolated from the reaction mixure as the main product. It was converted into the corresponding aziridine, which was also obtained by unambiguous synthesis. The monoadduct was identified by comparison with the authentic *N*-bromosulphonamide obtained as a result of the opening of the aziridine ring (Scheme 1):



Thus the view expressed in the literature that the order of the addition of *NN*-dihalogenoarenesulphonamides to unsaturated compounds depends on the experimental conditions and also that *NN*-dibromoarenesulphonamides add preferentially in accordance with the Markovnikov rule in reactions involving the addition of 4-chloro-*NN*-dibromobenzenesulphonamide to alk-1-ene-3-ynes has not been confirmed.[112] The structures of all the products obtained (the amide part of the reagent is attached exclusively or mainly to the extreme ethylenic atom) is convincing evidence in support of a radical reaction mechanism. This is also indicted by the absence of an appreciable influence of the solvent polarity on the mode of addition (the reaction with vinyl-acetylene was carried out in hexane, chloroform, and ether) and by the spontaneity and exothermicity of the process.[113] The amidyl radical formed as a result of the homolytic dissociation of the N–halogen bond attacks mainly the terminal atom of the double bond with formation of a more stable resonance-stabilised secondary propargyl radical. The attack on the terminal acetylenic atom with formation of a vinyl radical is less likely, since the electrophilic amidyl radical tends to attack the more nucleophilic double bond. Thus the preferential or exclusive formation of allenic or acetylenic isomers depends on the structure of the initial hydrocarbon and on the nature of the halogen in the reagent.

—o0o—

Summarising the analysis of the literature data for the addition of *N*-halogenoamides to unsaturated compounds, one may conclude that, despite some conflict between the results of the studies described, *N*-halogenamides can add to multiple bonds via both radical and ionic mechanisms depending on the conditions. In the former case, adducts are formed contrary to the Markovnikov rule, while in the latter the reaction proceeds in conformity with the Markovnikov rule. The most promising application of the reaction involving the addition of halogenoamides is the synthesis of aziridines.

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