Russian Journal of Organic Chemistry, Vol. 37, No. 3, 2001, pp. 297–317. Translated from Zhurnal Organicheskoi Khimii, Vol. 37, No. 3, 2001, pp. 327–346.

N-Halo Reagents. Synthesis and Reactions of *N*-Halocarboxamides

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Received October 27, 1999

Abstract—The review summarizes published data on the synthesis and reactivity of *N*-halocarboxamides.

I. INTRODUCTION

Among numerous compounds, which possess an N–Hlg bond and are generically called *N-halo reagents*, *N*-halocarboxamides attract attention due to their accessibility and high reactivity. The high reactivity of *N*-halocarboxamides originates from the presence of very labile N–Hlg bond and versatile modes of its splitting. Depending on the conditions, cleavage of the N–Hlg bond in carboxamides could give rise to various highly reactive intermediates such as halogen radicals, halogen cations, aminyl anions, nitrenes, etc. As a result, *N*-halocarboxamides are capable of participating in various radical and ionic processes involving both the halogen and the nitrogen atom. The most important reactions are halogenation, halohydroxylation, addition at multiple bonds, acylamination, oxidative imination, and some other processes. These reactions have found wide application in fine organic synthesis for preparation of halogen derivatives, carbonyl compounds, halohydrins, imino derivatives of sulfur, selenium, and phosphorus, acylamino compounds, and other valuable products. Some products turned out to be biologically active substances [1–4], complexing agents [5], inhibitors of acid corrosion [6], and electrolytic additives [7]. *N*-Halocarboxamides are also important for the chemistry of natural compounds; they are used

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as mild and selective oxidants for transformation of hydroxy group into carbonyl (e.g., in the synthesis of steroids [8]), as well as halogenating [9, 10] and halohydroxylating agents [11, 12].

The chemistry of *N*-halocarboxamides was the subject of review articles [13, 14], where the data reported until 1970 were covered. However, since that time numerous new data appeared, which are summarized in the present review.

II. METHODS OF SYNTHESIS OF *N*-HALOCARBOXAMIDES

All known synthetic routes to *N*-halocarboxamides are based on halogenation of carboxamides with various halogenating agents.

II.1. Halogenation with Halogens

Elemental halogens (except for fluorine) are most frequently used for halogenation of carboxamides, and the reaction follows ionic mechanism. *N*-Monosubstituted and unsubstituted carboxamides relatively readily react with iodine, bromine, and chlorine to give the corresponding *N*-halo derivatives [15]:

$$R^1CONHR^2 + X_2 \longrightarrow R^1CONXR^2 + HX$$

R^1 = Alk, Ar; R^2 = Alk, Ar, H; X = Cl, Br, I.

The reaction is reversible; polar solvents, e.g., water, favor formation of the target products. It was presumed [16] that primary attack by halogen on the carbonyl oxygen atom is followed by O→N-rearrangement:

$$R^1CONHR^2 \overset{Cl_2}{\rightleftharpoons} \left[R^1-\overset{OCl}{\overset{|}{C}}=\overset{+}{N}HR^2\right]Cl^- \rightleftharpoons \left[R^1-\overset{O}{\overset{\|}{C}}-\overset{+}{N}HR^2Cl\right]Cl^- \rightleftharpoons R^1CONClR^2 + HCl$$

In some cases *C*-halo derivatives are also formed as a result of decomposition of *N*-halocarboxamides in acid medium with liberation of cationic halogen species which then attacks other atoms of the amide. In order to suppress this process the reaction can be performed in a buffer solution. Otsuki *et al.* [17] reported on the synthesis of *N*,*N*-dichlorobenzamide by chlorination of benzamide with chlorine in aqueous medium in the presence of acetate buffer. Gaseous fluorine reacts with carboxamides to afford mixtures of C- and N-fluorinated products which are likely to be formed via radical processes [18]. However, these reactions were not studied in detail, and they are not used for preparative purpose.

II.2. Halogenation with Metal Hypohalites

Metal hypohalites are more convenient reagents for preparation of *N*-halocarboxamides, as compared to molecular halogens. In reactions with metal hypohalites, the concurrent C-halogenation is less probable. *N*-Halocarboxamides are usually obtained by adding an equimolar amount of sodium hydroxide to a mixture of molecular halogen and carboxamide [19] or by adding an equimolar amount of preliminarily prepared hypohalite solution to carboxamide [20].

$$RCONH_2 \xrightarrow{NaOX} RCONHX$$

R = H, Me, CH_2Br, CH_2F, $CHCl_2$, CCl_3, CF_3, Et; X = Cl, Br.

Excess alkali should be avoided, for *N*-halocarboxamides possessing an N–H moiety can undergo Hofmann rearrangement in alkaline medium; *N*-substituted *N*-halocarboxamides can undergo hydrolysis with formation of the initial amide. Hardy and Robson [21] studied the mechanism of halogenation of *N*-methylbenzamide with sodium hypochlorite. The reaction begins with attack by hypochlorite ion on the carbonyl oxygen atom, which involves transition state **A** and gives *O*-chloro derivative as intermediate. The latter undergoes O→N rearrangement to afford the final *N*-chloroamide:

$$PhCONHMe + OCl^- \rightleftharpoons \left[Ph-\overset{O-Cl}{\overset{|}{C}}=\overset{+}{N}(Me)-H\ \ O^-\right]$$

A

$$\overset{-OH^-}{\underset{OH^-}{\rightleftharpoons}} Ph-\overset{OCl}{\overset{|}{C}}=NMe \rightleftharpoons Ph-\overset{O}{\overset{\|}{C}}-NClMe$$

II.3. Halogenation with Alkyl Hypohalites

A large number of *N*-chlorocarboxamides were synthesized by the action of *tert*-butyl hypochlorite on the corresponding amide in an organic solvent (MeOH, *t*-BuOH, CCl_4, etc.) [22–25]. These reactions are carried out by adding an equimolar amount of

tert-butyl hypochlorite to a solution of an amide in appropriate solvent, and the mixture is kept for 10–20 h in the dark.

$$R^1CONHR^2 \xrightarrow{t\text{-BuOCl}} R^1CONClR^2$$

R^1 = Me, Ph, CH_2Cl, CH_2Br, MeNH, EtNH; R^2 = H, Ph, MeO, $PhCH_2O$.

Reactions of N-unsubstituted carboxamides with 2 equiv of *t*-BuOCl yield the corresponding *N*,*N*-dichlorocarboxamides [22]. Insofar as *tert*-butyl hypoiodite is unstable, *N*-iodocarboxamides are obtained by reaction of carboxamides with *tert*-butyl hypochlorite in the presence of iodine [26, 27] or mercury diiodide [27] in CCl_4.

$$RCONH_2 \xrightarrow{t\text{-BuOCl } (I_2 \text{ or } HgI_2)} RCONHI$$

R = H, Me, CH_2Cl, CH_2Br, Ph, 4-MeC_6H_4, 4-$NO_2C_6H_4$.

Barton *et al.* [28] studied fluorination of carboxamides with trifluoromethyl hypofluorite. The authors succeeded in obtaining *N*-fluoro derivatives from aliphatic carboxamides, but reactions with excess trifluoromethyl hypofluorite resulted in further fluorination to afford mixtures of various fluorinated products.

$$R^1CONHR^2 \xrightarrow{CF_3OF} R^1CONFR^2$$

$$\xrightarrow{CF_3OF} R^1C\overset{+}{O}NF_2R^2\cdot F_3CO^-$$

$$\longrightarrow R^1COF + R^2NF_2 + R^1COOCF_3$$

Reactions of CF_3OF with aromatic carboxamides led to fluorination of the aromatic ring.

II.4. Halogenation with Other Halogenating Agents

Kajigaeshi *et al.* [29] desribed a convenient procedure for preparation of *N*-bromocarboxamides using sodium bromite as brominating agent. A concentrated aqueous solution of sodium bromite was added to a solution of carboxamide in acetic acid to obtain 81–97% of the corresponding *N*-bromo derivative.

$$RCONH_2 \xrightarrow{NaBrO_2} RCONHBr$$

R = C_7H_{15}, C_9H_{19}, $C_{11}H_{23}$, $C_{13}H_{27}$, $C_{15}H_{31}$, $PhCH_2$, Ph, 4-MeC_6H_4, 4-$NO_2C_6H_4$, 4-ClC_6H_4.

A series of *N*-bromocarboxamides was prepared by treatment of carboxamides with benzyltrimethylammonium tribromide [30]:

$$RCONH_2 + Me_3(PhCH_2)\overset{+}{N}\cdot Br_3^- \xrightarrow{NaOH} RCONHBr$$

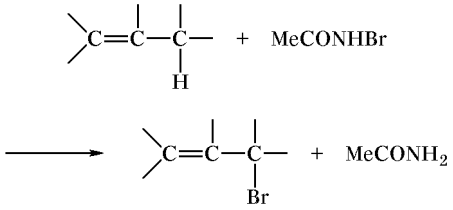
$$+ Me_3(PhCH_2)\overset{+}{N}\cdot Br^- + NaBr + H_2O$$

R = Bu, C_5H_{11}, $C_{13}H_{27}$, Ph, 4-ClC_6H_4, 4-BrC_6H_4, 3-$NO_2C_6H_4$, 4-$NO_2C_6H_4$.

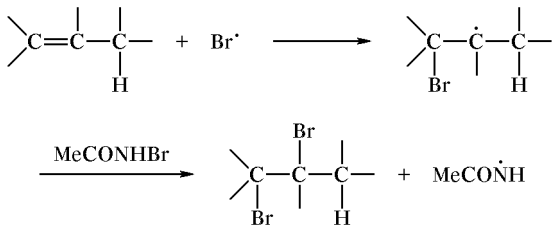
III. REACTIONS OF *N*-HALOCARBOXAMIDES

III.1. Halogenation

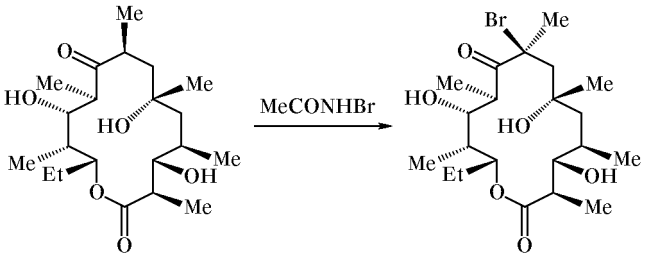
Some *N*-chlorocarboxamides, e.g., *N*-chloro-*p*-nitroacetanilide and *N*,*p*-dichloroacetanilide, are capable of chlorinating unsaturated compounds at the allylic position [13]. However, these compounds have not found wide application as halogenating agents. *N*-Bromoacetamide is a well known halogenating agent which is widely used for replacement of allylic hydrogen atom in unsaturated compounds by bromine [8, 15, 31].



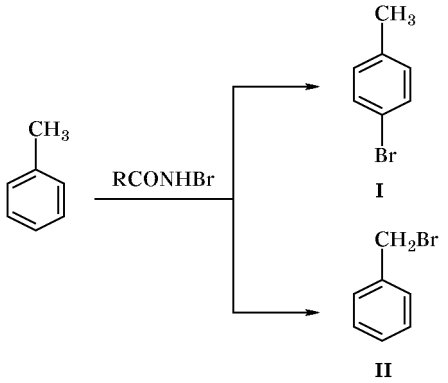
On the other hand, reactions of some unsaturated compounds with *N*-bromoacetamide were accompanied by formation of dibromo derivatives, which is an essential drawback in the application of this reagent. It was shown [13] that allylic bromination of unsaturated compounds with *N*-bromoacetamide can be accelerated by heating or UV irradiation. This means that the process follows a radical path. The formation of dibromo derivatives is the result of addition of bromine radical at the C=C bond.



Auricchio *et al.* [10] described bromination with *N*-bromoacetamide of erythronolide B; the product was the corresponding 8-bromo derivative.

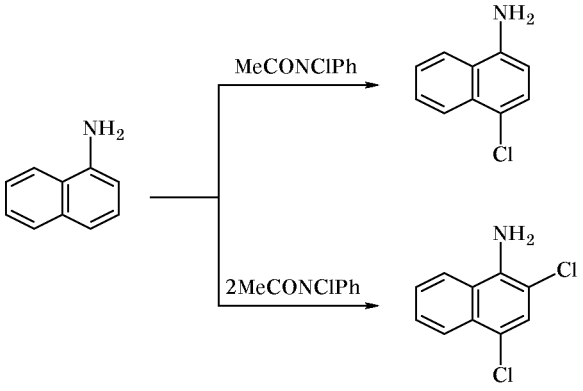


Depending on the nature of *N*-bromocarboxamide, bromination of toluene can occur both at the aromatic ring and at the side chain [13].

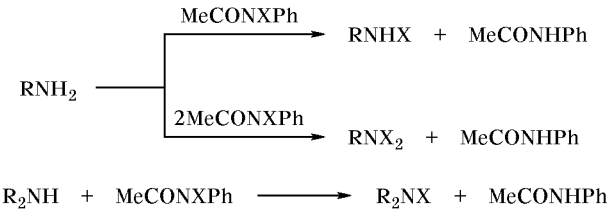


I:**II**: R = Me, 0:100; R = CCl_3, 17:83; R = CH_2Cl, 62:38; R = $CHCl_2$, 82:18; R = CF_3, 88:12.

It was presumed that the bromination at the aromatic ring follows ionic mechanism, whereas the reaction at the side chain is a radical process. Thus *N*-bromocarboxamides containing electron-acceptor substituents are more prone to react by ionic mechanism due to their ability to generate bromine cation. The chlorination of α-naphthylamine with *N*-chloroacetanilide was also reported [13]. The reaction is facile; depending on the reactant ratio, either mono- or dichloro derivative is formed.



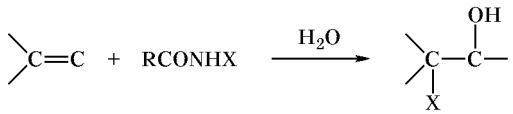
Exchange reactions of *N*-halocarboxamides with primary and secondary aliphatic amines lead to formation of *N*-haloamines [8, 13].



R = Alk; X = Cl, Br.

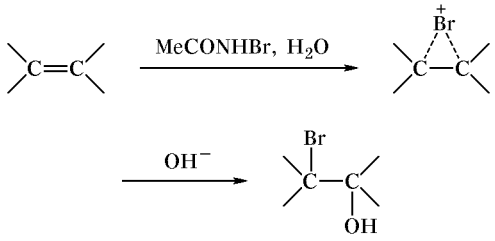
III.2. Halohydroxylation of Unsaturated Compounds

N-Halocarboxamides react with olefins in aqueous medium to give products of addition of halogen and hydroxy group at the double bond [8, 32]:



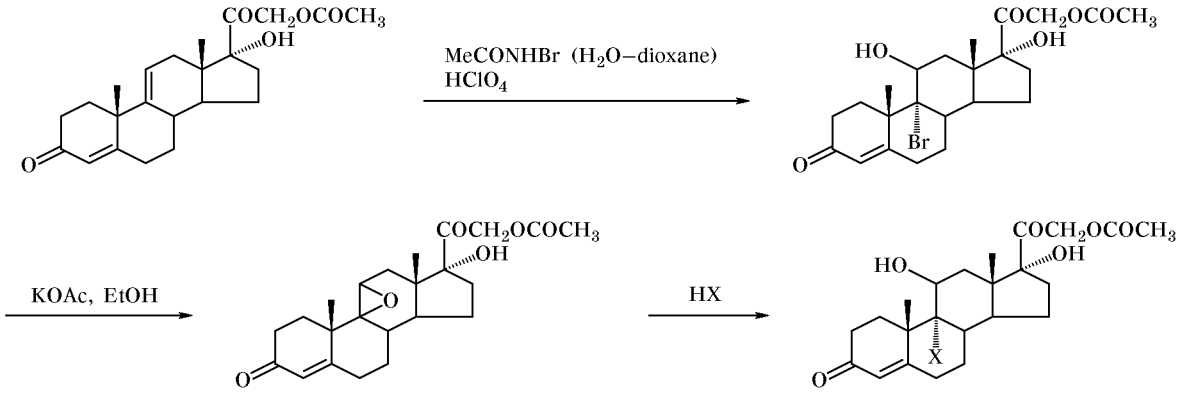
X = Cl, Br.

Reactions of olefins with *N*-bromoacetamide in aqueous medium (bromohydroxylation) were studied in most detail. As a rule, these reactions are carried out in mixtures of water with organic solvents (such as acetone, dioxane, pyridine, *tert*-butyl alcohol, etc.) in order to make the reaction mixture homogeneous and hence to facilitate the process. Here, the reactive species was presumed [32] to be hypobromous acid which is formed *in situ* by reaction of *N*-bromoacetamide with water. Bromohydroxylation of olefins with *N*-bromoacetamide is catalyzed by $HClO_4$ which favors generation of hypobromous acid. The reaction is generally characterized by high regioselectivity; it is likely to involve cyclic bromonium intermediate:



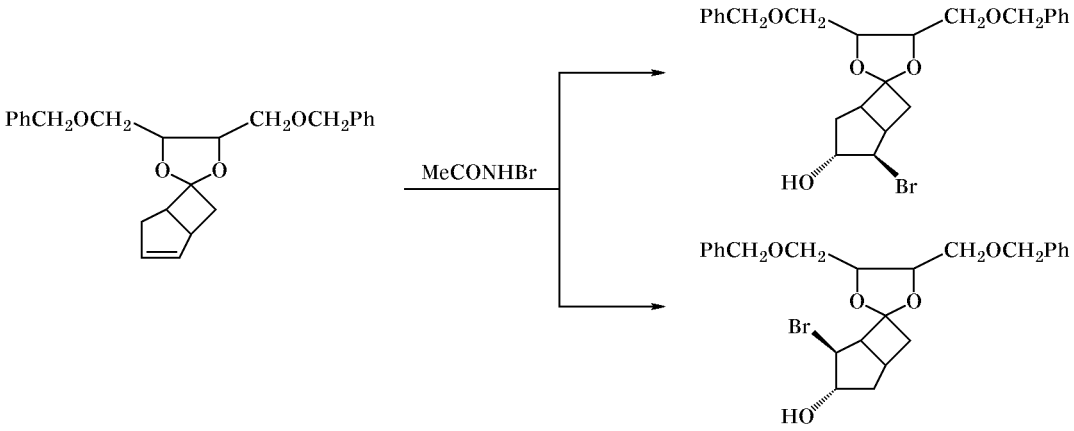
N-Bromoacetamide reacts with olefins in anhydrous alcohols to give alkoxy bromides, while in glacial acetic acid acetoxy bromo derivatives are formed [8],

Scheme 1.



X = Cl, I.

Scheme 2.

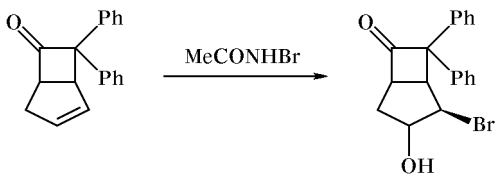


in keeping with the proposed mechanism. This reaction is widely used in the chemistry of natural compounds, e.g., in the synthesis of steroids [8]. In the bromohydroxylation of steroidal 9(11)-C=C bond bromine adds to $C^{9(9\alpha)}$, and hydroxy group, to $C^{11(11\beta)}$. As an example, Scheme 1 illustrates the synthesis of 9α-halohydrocortisones, where the key stage is bromohydroxylation with *N*-bromoacetamide of 21-acetoxy-17α-hydroxy-$\Delta^{4,9(11)}$-pregnadiene-3,20-dione. The yield of 5α-bromo-6β-hydroxy steroids considerably increases when the reaction is performed in dimethoxymethane instead of dioxane [33]. Sondheimer and Wife [34] described the synthesis of acetylbufalin through bromohydroxylation of 1,4-dehydroacetylbufalin with *N*-bromoacetamide.

Turuta *et al.* [35] obtained 9α-bromo-17α-ethynyl-11β,17β-dihydroxyandrost-4-en-3-one in 83% yield by bromohydroxylation of 17α-ethynyl-17β-hydroxyandrosta-4,9-dien-3-one with *N*-bromoacetamide. The same authors accomplished a multistep synthesis of 16α,17α-epoxycorticosterone, the initial step being bromohydroxylation of androsta-3,17-diene-4,9-dione with *N*-bromoacetamide [36].

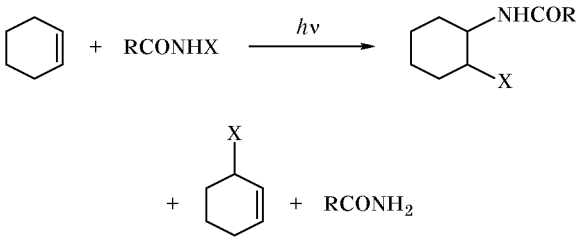
The bromohydroxylation of bicyclo[3.2.0]hept-2-ene-6-spiro-2′-[4′,5′-bis(benzyloxymethyl)]-1,3-dioxolane with *N*-bromoacetamide in acetone–water (4:1) at 20°C yields a mixture of two isomeric bromohydrins [37] (Scheme 2).

Transformation of unsaturated bicyclic ketone into the corresponding bromohydrin by the action of *N*-bromoacetamide is the key stage in the chemical–enzymatic synthesis of carbocyclic analog of Oxetanocin A [38].



III.3. Haloacylamination of Unsaturated Compounds

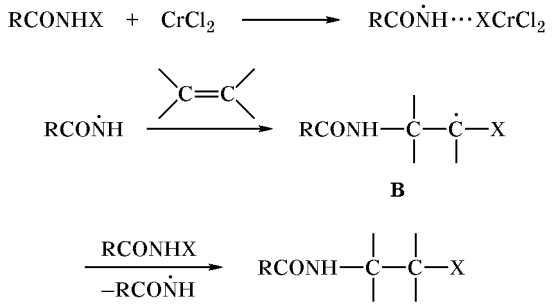
Simultaneous introduction of a halogen atom and acylamino group into unsaturated compounds can be effected through addition of *N*-halocarboxamides at the multiple bond. These reactions were considered in detail in [39, 40]; therefore, the present review contains only the main points and also some published data which were not covered. Two procedures were developed to accomplish addition of *N*-halocarboxamides to alkenes. The first of these involves photolysis of a mixture of *N*-halocarboxamide and alkene in an organic solvent [41–43]. The major side process is allylic halogenation which leads to formation of 3-haloalkenes and amides. A detailed study of the photolytic reaction was performed with the addition *N*-halocarboxamides to cyclohexene as an example.



R = Alk, Ar; X = Cl, Br.

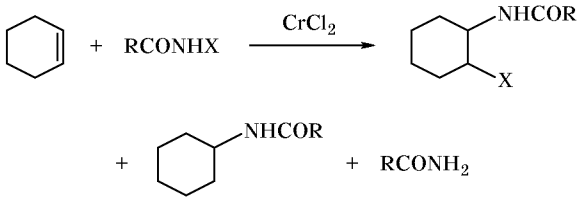
The yield of the *cis*- and *trans*-adducts ranges from 25 to 99% when the reaction is carried out at –70 to 20°C in methylene chloride or chloroform–methanol [41–43, 44]. In nitromethane as solvent the yield is about 53% [43], and in benzene, 42% [43]. Lowering the temperature favors formation of the addition products. Also, the natures of the halogen X and radical R in the initial *N*-halocarboxamide are important. Mirskova *et al.* reported [39] that the yield of the 1,2-adduct increases in the following R series: *t*-Bu < Pr < Et < Me < CH_2CH_2Cl < CH_2Br < CH_2Cl < CH_2F < $CHCl_2$ < CCl_3 < CF_3 (from 37 to 99%, the *cis* isomer prevailing. This series was explained [39] in terms of increase in the electrophilic character of the RCONH radical on introduction of electron-acceptor substituents R. The rate of addition of *N*-bromocarboxamides (reaction time 4–5.5 h) is higher than the rate of addition of *N*-chloro analogs (21–53 h), but in the former case the yield of 1,2-adducts is smaller [41, 43]. Photochemical addition of *N*-substituted *N*-halocarboxamides $R^1CON(X)R^2$ (R^2 = Alk, Ac) to alkenes is difficult to occur, and the yields of the adducts are low [42, 43, 45]. Here, the major products are the corresponding amides and haloalkenes formed by allylic halogenation.

The second procedure for addition of *N*-halocarboxamides to alkenes utilizes chromium(II) chloride as catalyst [44, 46–48]. As well as photochemical addition, the process follows radical mechanism and involves RCONH radicals [46, 49].



X = Cl, Br.

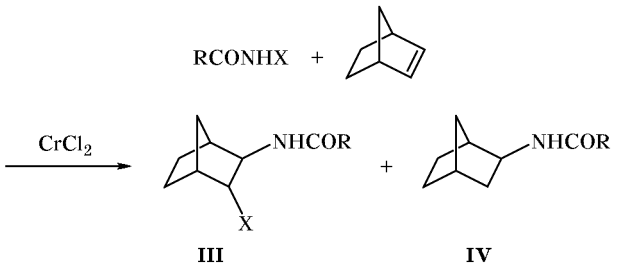
Apart from allylic halogenation, the reaction is accompanied by formation of 1*H*-adduct via reduction of radical adduct **B** with chromium(II) chloride. The addition of *N*-halocarboxamides to cyclohexene in chloroform–methanol at –78 to 20°C leads to formation of several products.



R = Alk, Ar; X = Cl, Br.

The yield of isomeric adducts ranges from 34 to 88% [44, 46, 47, 49]. In reactions with *N*-chlorocarboxamides, the nature of the R radical in the reagent is important. The yield of a mixture of the *cis*- and *trans*-adducts increases from 34 to 78% in the following series of R: Me < NH_2 < CCl_3 < CH_2Cl < CF_3 [36]; simultaneously, the yield of 1*H*-adducts falls from 36 to 2%. In the addition of *N*-bromocarboxamides the nature of the R radical only slightly affects the yield of the adduct, but the reaction is accompanied by electrophilic bromination [46].

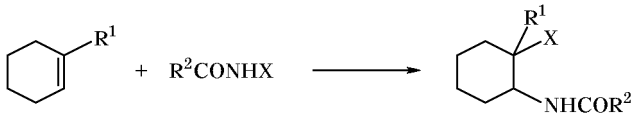
Catalytic addition of *N*-halocarboxamides to norbornene results in formation of two products whose yield also depends on the R radical in the initial *N*-halocarboxamide [46].



III **IV**

X = Cl, Br; R = Me: **III**, 2%; **IV**, 83%;
R = CH_2Cl: **III**, 33%; **IV**, 55%.

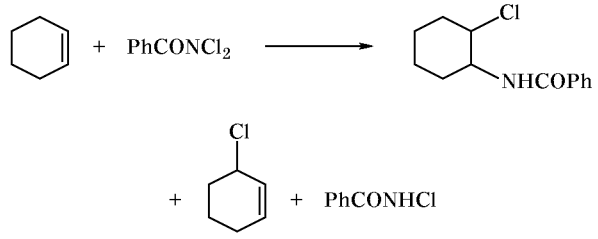
N-Halocarboxamides react with some cyclohexene derivatives to give 35 to 87% of isomeric *cis*/*trans*-adducts [41, 44, 46, 47]. These data indicate high regioselectivity of both photochemical and catalytic addition of *N*-halocarboxamides to alkenes.



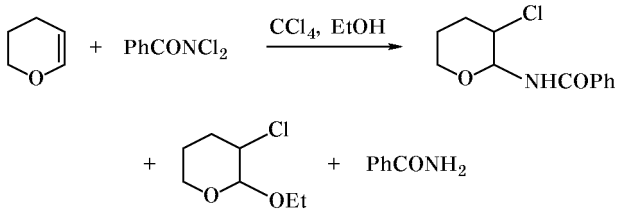
R^1 = Me, MeO, MeCO, Cl; R^2 = Me, CH_2Cl, CF_3;
X = Cl, Br.

High regioselectivity is also inherent to the addition of *N*-halocarboxamides to 1-octene [42, 45], 1,1-diethoxyethene [43], 1-hexene [50], 3,3-dimethyl-1-butene [50], 1-dodecene [42, 46], cyclohexadiene, and norbornadiene [43, 46, 49].

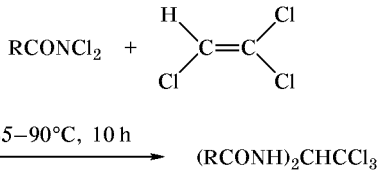
Unlike *N*-monochloro derivatives, *N*,*N*-dichlorobenzamides react with styrene to form only addition products at the double bond, *N*-(2-chloro-2-phenylethyl)amides (75–92%) [51]. According to [17], the reaction of *N*,*N*-dichlorobenzamide with cyclohexene results in formation of three products.



N,*N*-Dichlorobenzamide reacts with dihydropyran in CCl_4; subsequent heating for a short time of the primary products in alcohol leads to formation of *cis*- and *trans*-2-benzamido-3-chlorotetrahydropyran, 3-chloro-2-ethoxytetrahydropyran, and benzamide [52]. Presumably, one of the primary products is 2,3-dichlorotetrahydropyran.

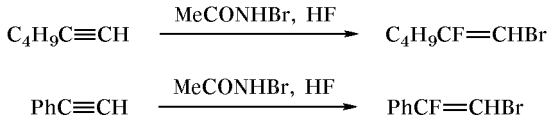


Reactions of *N*,*N*-dichlorocarboxamides with trichloroethylene in the absence of oxygen yield 1,1-bis(acylamino)-2,2,2-trichloroethanes [53] which, in keeping with the data of [54], are products of further transformation of the initially formed Schiff bases.

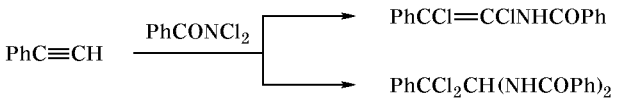


R = Me, Ph.

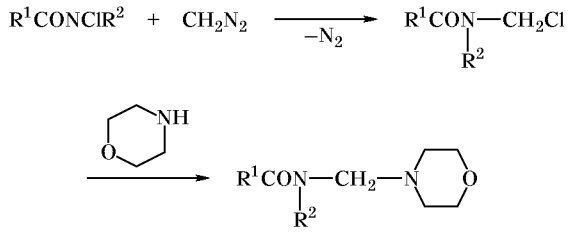
Reactions of *N*-halocarboxamides with acetylenic hydrocarbons have been studied to a considerably lesser extent. It was noted [32] that *N*-bromoacetamide reacts with terminal alkynes in the presence of hydrogen fluoride to afford bromofluoroalkenes generally having *trans* configuration. The bromine atom adds preferentially to the terminal carbon atom. The presence of electron-acceptor groups in the initial alkyne hinders the reaction.



The addition of *N*,*N*-dichlorobenzamide to phenylacetylene, followed by treatment of the reaction mixture with a solution of sodium hydrogen sulfite, leads to formation of two products: *N*-(1,2-dichlorostyryl)-benzamide (68.5%) and 1,1-dichloro-2,2-bis(benzoylamino)-1-phenylethane (12.7%) [55].



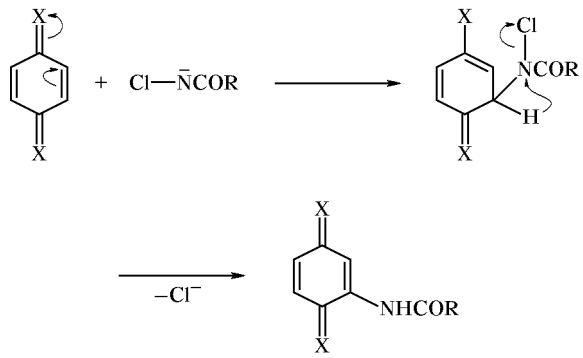
Orazi *et al.* [56] reported on the addition of *N*-chlorocarboxamides to diazomethane with formation of *N*-(chloromethyl)carboxamides. The chlorine atom in the latter can be replaced by various nucleophiles, e.g., by morpholino group.



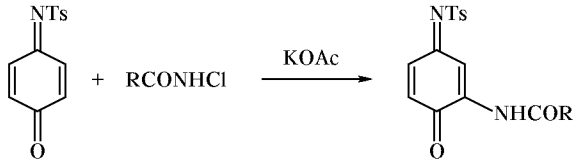
R^1 = Alk; R^2 = H, Alk.

III.4. Acylamination of Quinoid Compounds

Anions generated from *N*-chlorocarboxamides by the action of bases are capable of participating in nucleophilic substitution of hydrogen at an electron-deficient carbon atom in quinoid systems. Here, the replaced hydrogen atom adds to the nitrogen, and chloride ion is a leaving group.

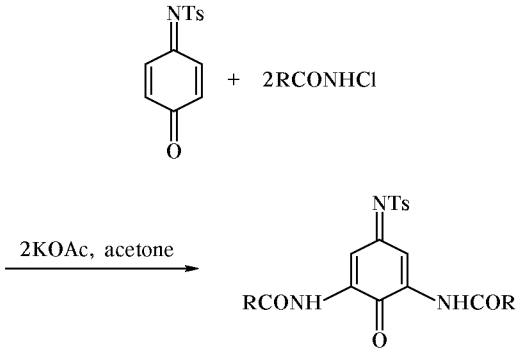


For example, equimolar amounts of *N*-*p*-tolylsulfonyl-1,4-benzoquinonimine and *N*-chlorocarboxamide react in acetone or methanol in the presence of potassium acetate to give the corresponding 2-acylamino derivatives [57, 58].



R = Me, Ph, 4-MeC_6H_4, 4-$NO_2C_6H_4$.

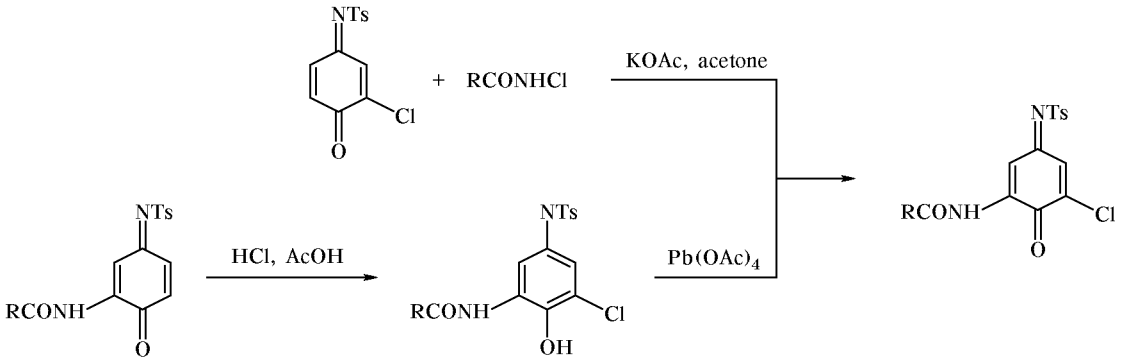
In the presence of excess *N*-chlorocarboxamide 2,6-bis(acylamino) derivatives are obtained [57, 58].



Acylamination of 2-chloro-*N*-*p*-tolylsulfonyl-1,4-benzoquinonimine results in introduction of the acylamino group into position *6*. The structure of the product was proved by independent synthesis [57, 59] (Scheme 3). Further treatment of this product with excess *N*-chlorocarboxamide leads to formation of 3,6-bis(acylamino) derivatives [59] (Scheme 4).

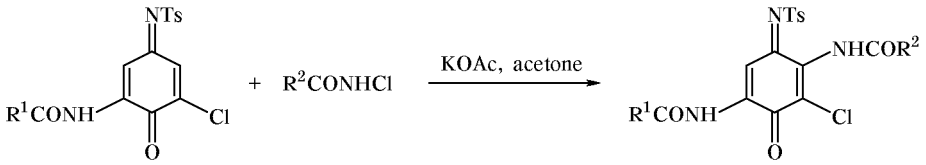
Bezverkhii *et al.* [60] described acylamination of *N*-arylsulfonyl-1,4-naphthoquinonimines in acetone in the presence of an equimolar amount of triethylamine. The reaction yielded the corresponding 2-acylamino-*N*-arylsulfonyl-1,4-naphthoquinonimines (Scheme 5). According to [60], *N*,*N*′-bis(phenylsulfonyl)-1,4-naph-

Scheme 3.



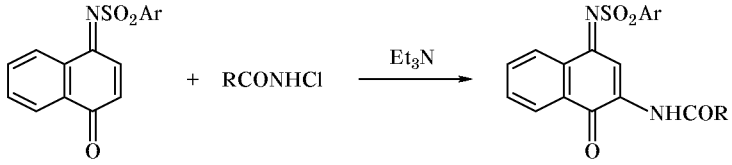
R = H, Ph, 4-MeC_6H_4.

Scheme 4.



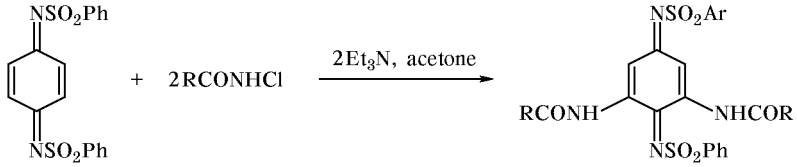
R^1 = Ph, 4-MeC_6H_4; R^2 = H, 4-MeC_6H_4.

Scheme 5.



Ar = Ph, 4-MeC_6H_4, 4-$NO_2C_6H_4$; R = Ph.

Scheme 6.

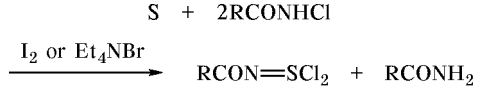


R = Ph, 4-ClC_6H_4.

thoquinonediimine cannot be involved in this reaction since the predominant *syn* isomer is sterically hindered for attack by *N*-chlorocarboxamide anion. On the other hand, *N*,*N*′-bis(phenylsulfonyl)-1,4-benzoquinonediimine relatively readily undergoes acylamination to form 2,5-bis(acylamino) derivatives [61] (Scheme 6).

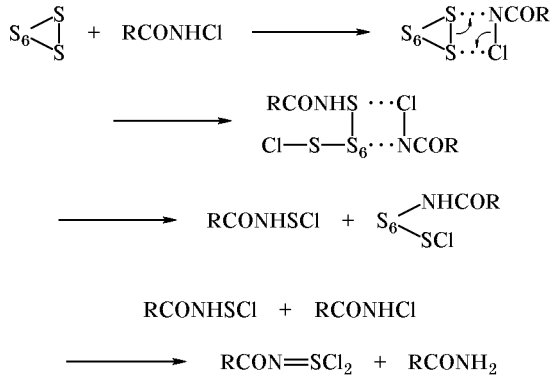
III.5. Oxidative Imination of Sulfur and Sulfur Compounds

III.5.1. Oxidative imination of sulfur and inorganic sulfur compounds. Elemental sulfur relatively readily reacts with *N*-halocarboxamides to form different products, depending on the reaction conditions and the nature of the halogen and acyl radical. Reactions of sulfur with *N*-chlorocarboxamides at a ratio of 1:2 yield acyliminosulfur dichlorides and carboxamides [62–64].



R = *t*-Bu, CH_2Cl, Ph, 4-MeC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4.

These reactions occur in an inert organic solvent (such as carbon tetrachloride, dichloroethane, benzene, etc.) at room temperature or on slight heating and require the presence of a catalytic amount of iodine or tetraethylammonium bromide. No appreciable effect of UV irradiation or peroxide initiators is observed. It was presumed [64] that sulfur and *N*-chlorocarboxamide initially form a ionic complex which decomposes via cleavage of the S–S bond. The subsequent reaction with *N*-chlorocarboxamide leads to formation of acylaminosulfenyl chloride which is then converted into acyliminosulfur dichloride.



According to [64], the reactivity of *N*-chlorocarboxamides toward sulfur decreases with increase in the electron-acceptor power of the acyl radical. When R is an electron-donor group (*t*-Bu, 4-MeC_6H_4, or Ph), the reaction occurs relatively readily at 20°C. When R = 4-ClC_6H_4 or 4-BrC_6H_4, the reaction mixture should be heated at 30–40°C. *N*-Chloro-*p*-nitrobenzamide does not react with sulfur at 20°C, and on prolonged heating *N*,*N*′-bis(*p*-nitrobenzoyl)sulfur diimide is formed. In this case, the reaction was presumed [64] to involve intermediate formation of *p*-nitrobenzoylaminosulfenyl chloride which then reacts with the second *N*-chloro amide molecule to give aminosulfinimidoyl chloride. The latter is converted into *N*,*N*′-bis(*p*-nitrobenzoyl)sulfur diimide via loss of hydrogen chloride molecule.

$$S + 4\text{-}O_2NC_6H_4CONHCl \longrightarrow [4\text{-}O_2NC_6H_4CONHSCl]$$

$$\xrightarrow{4\text{-}O_2NC_6H_4CONHCl} 4\text{-}O_2NC_6H_4CONHS(Cl)=NCOC_6H_4NO_2\text{-}4$$

$$\longrightarrow (4\text{-}O_2NC_6H_4CON=)_2S$$

N-Chlorotrichloroacetamide reacts with sulfur by a similar scheme, but the final product is *N*,*N*′-bis(trichloroacetyl)amidosulfinimidoyl chloride [64].

$$S + 2CCl_3CONHCl \xrightarrow{40\text{–}50^\circ C,\ CCl_4} CCl_3CONH{-}S(Cl){=}NCOCCl_3$$

The halogen nature essentially affects the structure of products formed by reactions of sulfur with *N*-halocarboxamides. *N*-Bromocarboxamides react with sulfur to form *N*,*N*′-thiobis(acylamines) which are likely [65] to result from decomposition of intermediate acylaminosulfenyl bromides.

$$2S + 2RCONHBr \longrightarrow 2[RCONHSBr] \longrightarrow (RCONH)_2S$$

R = Me, 4-MeC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 4-$NO_2C_6H_4$, 2,4-$Cl_2C_6H_3$.

In turn, *N*,*N*′-thiobis(acylamines) can react with *N*-chlorocarboxamides to afford amidosulfinimidoyl chlorides [65].

$$(PhCONH)_2S + PhCONHCl \longrightarrow PhCONH{-}S(Cl){=}NCOPh + PhCONH_2$$

Acyliminosulfur dichlorides were obtained by reactions of sulfur with *N*,*N*-dichlorocarboxamides in anhydrous organic solvents (benzene, carbon tetrachloride, dichloroethane, etc.) in the presence of catalysts (I_2, $FeCl_3$, $AlCl_3$, Et_4NBr) [66, 67].

$$S + RCONCl_2 \xrightarrow{\text{Catalyst, } 20^\circ C} RCON{=}SCl_2$$

R = 4-ClC_6H_4, 2,4-$Cl_2C_6H_3$, C_6F_5.

Under more severe conditions, the same reaction with excess *N*,*N*-dichlorocarboxamide yields *N*,*N*′-diacylsulfur diimides [68].

$$S + 2RCONCl_2 \xrightarrow{70\text{–}80^\circ C} (RCON{=})_2S$$

Sulfur(I) chloride readily undergoes oxidative imination with *N*-chlorocarboxamides [64]. The reaction occurs at 20–25°C in inert organic solvents.

$$S_2Cl_2 + 4RCONHCl \longrightarrow 2RCON{=}SCl_2 + 2RCONH_2 + Cl_2$$

R = CH_2Cl, 4-ClC_6H_4, 4-BrC_6H_4.

The initial stage of the process is cleavage of the S–S bond with formation of acylaminosulfenyl chloride and sulfur(II) chloride; the reaction of the latter with *N*-chlorocarboxamide affords acyliminosulfur dichloride.

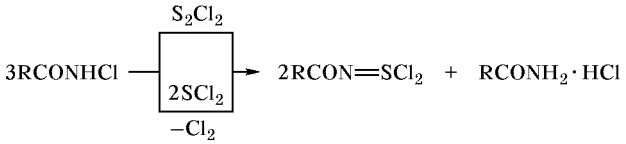
$$S_2Cl_2 + RCONHCl \longrightarrow RCONHSCl + SCl_2$$

$$SCl_2 + RCONHCl \longrightarrow [RCONHSCl_3] \longrightarrow RCON{=}SCl_2 + HCl$$

$$RCONHCl + HCl \longrightarrow RCONH_2 + Cl_2$$

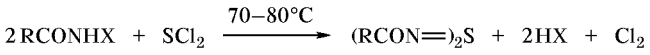
The proposed mechanism was confirmed experimentally, namely by oxidative imination of sulfur(II) chloride with *N*-chlorocarboxamides at a reactant ratio of 1:2 [64]. Intermediate acylaminosulfur trichloride loses hydrogen chloride molecule which adds to strongly basic amides to form salts. In this case, the scheme of oxidative imination of sulfur(I) and sulfur(II) chlorides with *N*-chloracarboxamides looks as shown in Scheme 7. *N*-Bromocarboxamides react with sulfur(I) and sulfur(II) chlorides in a similar way [65]. It was noted [64, 65] that heating of *N*-chloro- or *N*-bromocarboxamides with sulfur(II) chloride at

Scheme 7.



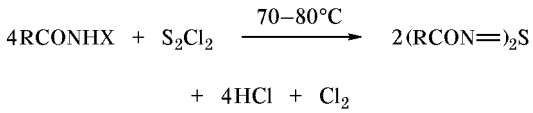
R = *t*-Bu, Ph, 4-MeC_6H_4.

a ratio of 2:1 leads to formation of the corresponding sulfur diimides.

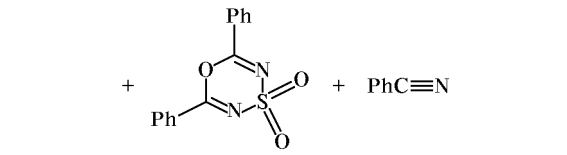


R = Ph, 4-ClC_6H_4; X = Cl, Br.

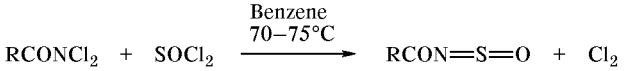
Sulfur diimides are also formed on prolonged heating of *N*-chlorocarboxamides with sulfur(I) chloride at a ratio of 4:1 [64].



Levchenko *et al.* [69] studied reactions of *N*-chloro- and *N*,*N*-dichlorocarboxamides with thionyl chloride. The authors found that heating of *N*-chlorobenzamide with thionyl chloride in CCl_4 yields a mixture of *N*,*N*-dibenzoylsulfamide, 2,6-diphenyl-1,4,3,5-oxathiadiazine 4,4-dioxide, and benzonitrile [69].

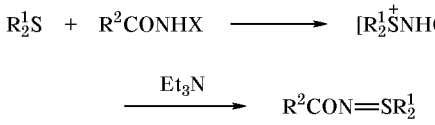


N-Sulfinylamides were obtained by reactions of *N*,*N*-dichlorocarboxamides with thionyl chloride in benzene at 70–75°C [70, 71].



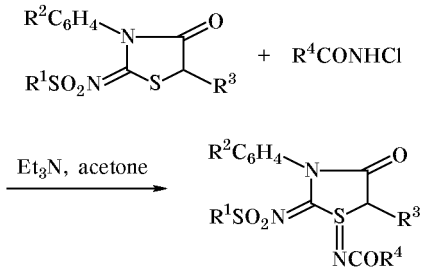
R = Ph, 4-$NO_2C_6H_4$.

III.5.2. Oxidative imination of sulfides and their analogs. Reactions of *N*-halocarboxamides with sulfides in inert organic solvents lead to formation of aminosulfonium salts [72] which are converted into *N*-acylsulfimides [73–76]. These reactions underlie a preparative procedure for synthesis of N-substituted sulfimides, which is frequently used in laboratory practice [77, 78].



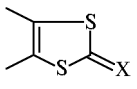
R^1 = Me, Et; R^1_2 = $(CH_2)_4$; R^2 = Me, CH_2Cl, CCl_3, Ph, 4-$MeOC_6H_4$, 4-MeC_6H_4; X = Cl, Br.

An analogous scheme is typical of reactions of *N*-halocarboxamides with some sulfur-containing heterocyclic compounds. For example, oxidative imination of 2-arylsulfonylimino-3-aryltetrahydrothiazol-4-ones with *N*-chlorocarboxamides yields the corresponding 1-acylimino derivatives [79].



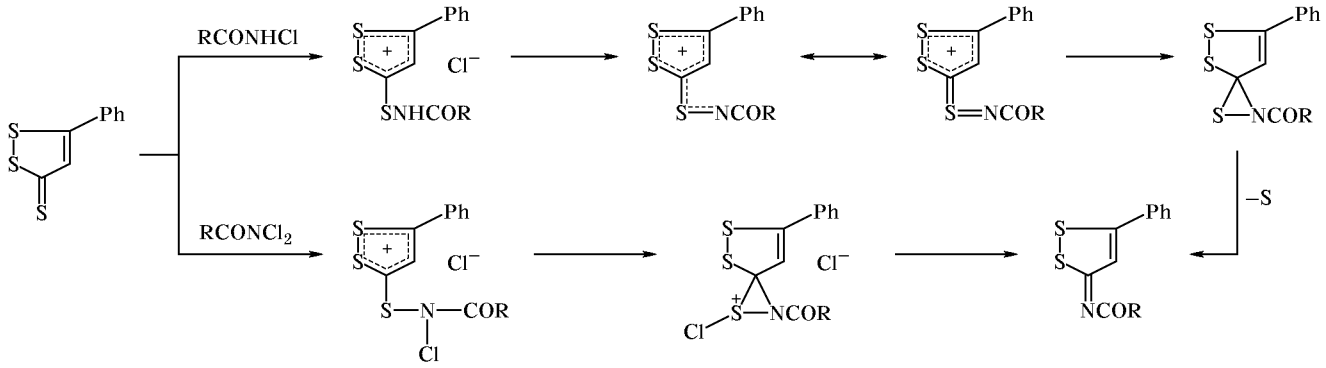
R^1 = Ph, 4-MeC_6H_4, 4-ClC_6H_4; R^2 = H, 4-Me; R^3 = Me, Et; R^4 = Me, Ph.

Oxidative imination with *N*-chloro- and *N*,*N*-dichlorocarboxamides of the thionic sulfur atom in 1,2-dithiole-3-thiones [80–83] and 1,3-dithiole-2-thiones was studied [84, 85]. 1,2-Dithiole-3-thiones give rise to unstable *N*-acylsulfimides which readily lose sulfur to afford acylimino derivatives (Scheme 8). Boberg *et al.* [84] isolated relatively stable *N*-(2-nitrobenzoyl)sulfimide from the reaction of *N*-chloro-2-nitrobenzamide with 4-phenyl-1,3-dithiole-2-thione (Scheme 9). On the other hand, reactions of *N*,*N*-dichlorocarboxamides with 1,3-dithiole-2-thiones could give analogs of the latter, depending on the conditions [85].

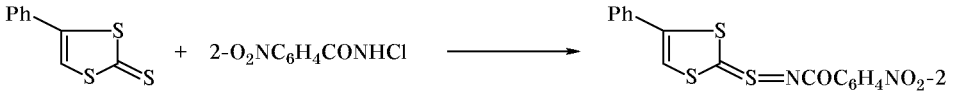


X = NCOAr, SO, O.

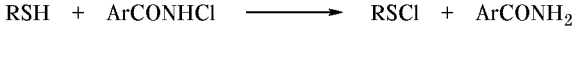
Scheme 8.



Scheme 9.

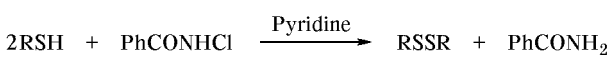


III.5.3. Oxidative imination of thiols. Reactions of *N*-chlorocarboxamides with thiols could give various products, depending on the reactant ratio and reaction conditions. *N*-Chlorocarboxamides were reported [86] to react with equimolar amounts of thiols in anhydrous organic solvents, yielding the corresponding sulfenyl chlorides and amides.



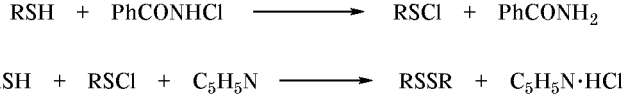
R = Ph, 4-MeC_6H_4; Ar = Ph, 4-MeC_6H_4.

The reaction of *N*-chlorocarboxamides with 2 equiv of thiols in the presence of pyridine leads to formation of disulfides and amides [86].

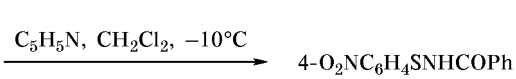


R = Ph, 4-MeC_6H_4.

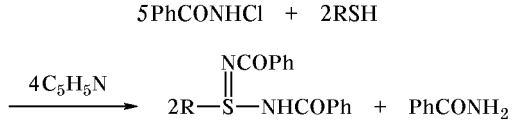
The following reaction scheme was presumed [86]:



In the presence of pyridine the rate of the second reaction is higher; therefore, the resulting sulfenyl chloride rapidly react with thiols. In the absence of a base, the first process is faster, and sulfenyl chloride can be isolated from the reaction mixture. With insufficient or equimolar amount of thiol in the presence of a base amide can react with sulfenyl chloride to afford *N*-acylsulfenamide. An example is the reaction of *N*-chlorobenzamide with an equimolar amount of *p*-nitrobenzenethiol in the presence of pyridine.

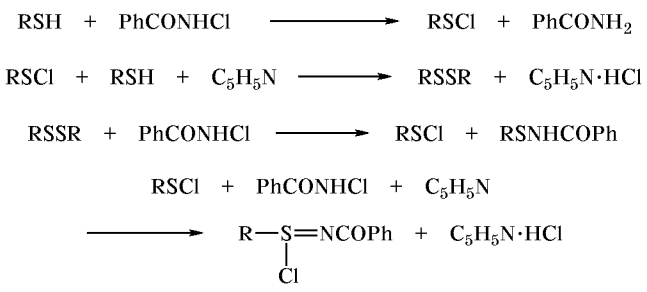


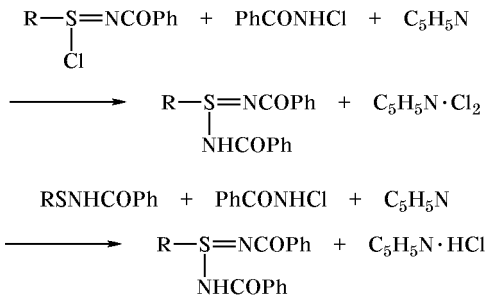
N-Chlorocarboxamides were shown to react with thiols at a ratio of 5:2 in anhydrous organic solvents in the presence of pyridine, yielding *N*,*N*′-diacylsulfinimidamides [86–88].



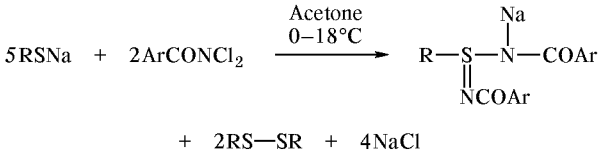
R = Me, Bu, C_5H_{11}, C_7H_{13}, Ph, 4-MeC_6H_4, 4-$NO_2C_6H_4$.

The following mechanism was proposed for the above transformations [89]:



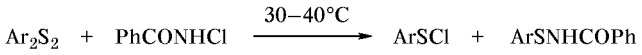


Oxidative imination of sodium thiolates with *N*,*N*-dichlorocarboxamides gives *N*,*N*′-diacylsulfinimidamide sodium salts [90, 91].



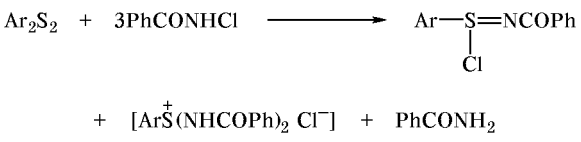
R = C_5H_{11}, Ph, 4-MeC_6H_4, 8-quinolyl, 4-mercapto-8-quinolyl;
Ar = Ph, 2-ClC_6H_4, 2-BrC_6H_4.

III.5.4. Oxidative imination of disulfides. Reactions of *N*-chlorocarboxamides with disulfides also lead to formation of different products, depending on the reactant ratio and conditions. *N*-Chlorocarboxamides react with disulfides at a ratio of 1:1 in inert organic solvents (CCl_4, benzol) to afford sulfenyl chlorides and *N*-acylsulfenamides in high yields [92].



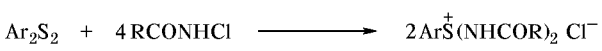
Ar = 4-ClC_6H_4, 4-$NO_2C_6H_4$, 3-$NO_2C_6H_4$.

Reactions of disulfides with 3 equiv of *N*-chlorocarboxamides yield mainly *N*-acylsulfinimidoyl chlorides [93]. Also, aminosulfonium salts and amides are formed in a small yield (15–20%).



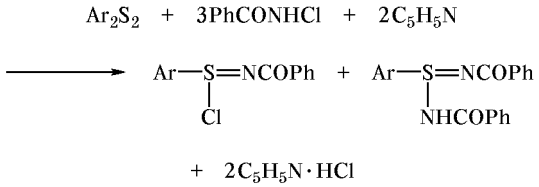
Ar = 4-ClC_6H_4.

Aminosulfonium salts are formed as the major products in reactions of disulfides with *N*-chlorocarboxamides at a ratio of 1:4 [93].

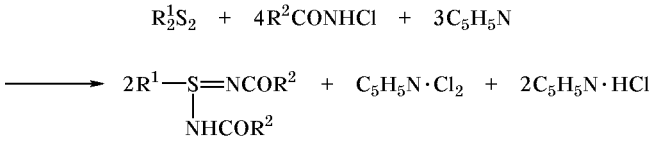


Ar = 4-ClC_6H_4, 4-$NO_2C_6H_4$; R = Me, Ph.

N-Benzoylarenesulfinimidoyl chlorides and *N*,*N*′-dibenzoylarenesulfinimidamides are formed by reaction of diaryl disulfides with 3 equiv of *N*-chlorobenzamide in the presence of pyridine [93].

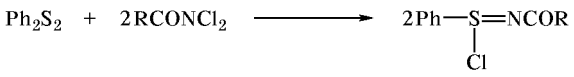


Reactions of disulfides with *N*-chlorocarboxamides at a ratio of 1:4 in the presence of pyridine give *N*,*N*′-diacylsulfinimidamides in relatively high yields [87, 93].



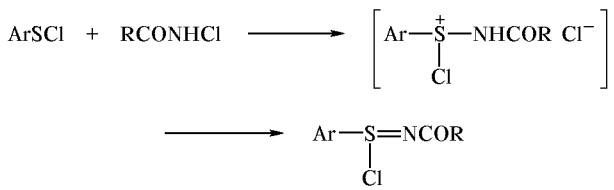
R^1 = Me, Bu, C_5H_{11}, C_7H_{15}, Ph, 4-MeC_6H_4, 4-ClC_6H_4, 4-$NO_2C_6H_4$; R^2 = Me, Ph.

N-(*p*-Chlorobenzoyl)benzenesulfinimidoyl chloride was obtained by reaction of diphenyl disulfide with 2 equiv of *N*,*N*,*p*-trichlorobenzamide [90].



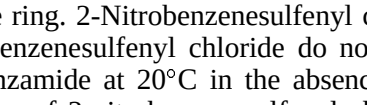
R = 4-ClC_6H_4.

III.5.5. Oxidative imination of sulfenyl and sulfinyl chlorides. *N*-Chlorocarboxamides react with equimolar amounts of arenesulfenyl chlorides in dry inert organic solvents (benzene, carbon tetrachloride, etc.) to afford *N*-acylarenesulfinimidoyl chlorides [94]. It was presumed [94] that the reaction involves intermediate formation of aryl(acylamino)chlorosulfonium chlorides which are converted into the final products via elimination of hydrogen chloride.

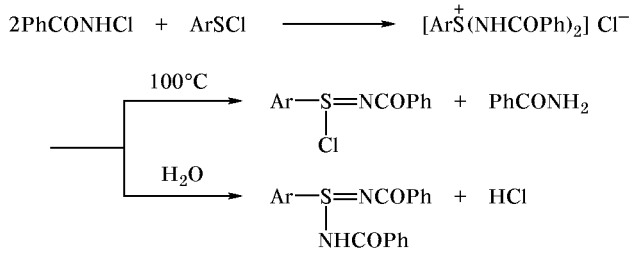


Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4; R = Me, Ph.

The reaction is hindered when arenesulfenyl chloride contains an electron-acceptor substituent in the benzene ring. 2-Nitrobenzenesulfenyl chloride and 2,4-dinitrobenzenesulfenyl chloride do not react with *N*-chlorobenzamide at 20°C in the absence of a base [94]. Heating of 2-nitrobenzenesulfenyl chloride with *N*-chlorobenzamide in benzene leads to formation of *N*-benzoyl-2-nitrobenzenesulfenamide.

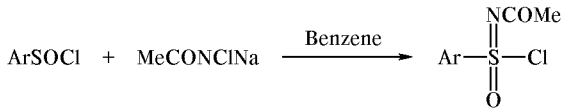


Reactions of *N*-chlorobenzamide with arenesulfenyl chlorides in benzene at 20°C (reactant ratio 2:1) yield mainly arylbis(benzoylamino)sulfonium chlorides. The latter decompose on heating into *N*-benzoylarenesulfinimidoyl chlorides and benzamide, whereas treatment with water gives rise to *N*,*N*′-dibenzoylarenesulfinimidamides [94].



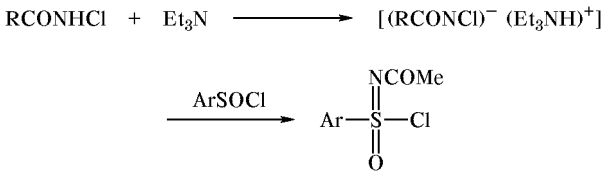
Ar = Ph, 4-MeC_6H_4.

Oxidative acylimination of arenesulfinyl chlorides is an important preparative route to *N*-acylarenesulfonimidoyl chlorides. The synthesis can be accomplished by the action of *N*-chlorocarboxamide sodium salts on arenesulfinyl chlorides [95].



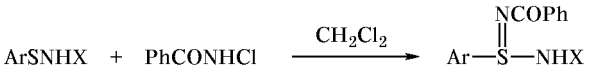
Ar = Ph, 4-MeC_6H_4.

However, this procedure has not found wide application, for some *N*-chlorocarboxamide sodium salts are unstable and difficult to obtain. Levchenko *et al.* [96] proposed to perform oxidative acylimination of arenesulfinyl chlorides with *N*-chlorocarboxamides in the presence of organic bases, such as triethylamine or pyridine. Organic base is slowly added to a cooled solution of a mixture of arenesulfinyl chloride and *N*-chlorocarboxamide. The first reaction stage is formation of a salt by *N*-chlorocarboxamide and tertiary amine, which then vigorously reacts with arenesulfinyl chloride to afford *N*-acylarenesulfonimidoyl chloride.



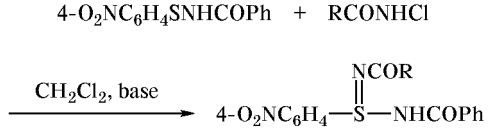
Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4, 2-$NO_2C_6H_4$, 4-$NO_2C_6H_4$;
R = Me, Ph, 3-$NO_2C_6H_4$.

III.5.6. Oxidative imination of sulfenamides. Oxidative imination of N-substituted sulfenamides with *N*-chlorocarboxamides is used as a preparative method for synthesis of *N*,*N*′-disubstituted sulfinimidamides with both similar and different groups on the nitrogen atoms. Here, the reactivity of sulfenamides is determined by nucleophilicity of the sulfur atom, which should be sufficient to be attacked by chlorine cation [97]. Therefore, electron-acceptor groups on the sulfur and nitrogen atoms in sulfenamide makes the reaction difficult or even impossible. Goerdeler and Doerk reported [98] that *N*-substituted arenesulfenamides ArSNHX possessing an electron-acceptor group X smoothly react with *N*-chlorobenzamide, yielding the corresponding *N*,*N*′-disubstituted arenesulfinimidamides.

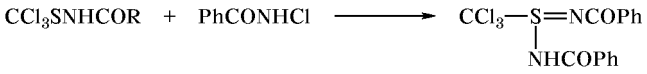


X = C(=NH)NH_2, C(=NH)Alk, C(=NH)SAlk, C(=NH)OAlk; Ar = Ph, 2-$NO_2C_6H_4$.

N-Acylarenesulfenamides react with *N*-chlorocarboxamides only in the presence of a base, such as pyridine, trimethylpyridine, triethylamine, or sodium methoxide [99].

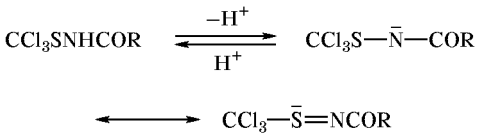


Oxidative imination of *N*-acyltrichloromethanesulfenamides with *N*-chlorobenzamide in a mixture of methanol with methylene chloride and pyridine as catalyst results in formation of *N*,*N*′-diacyltrichloromethanesulfinimidamides [100–102].

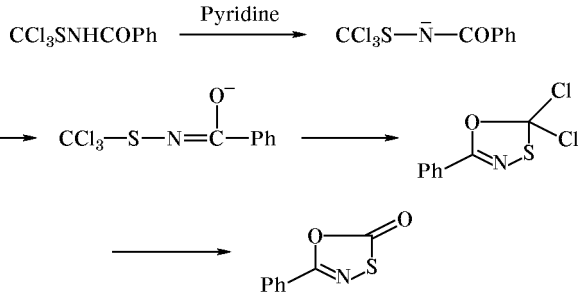


R = Bu, 4-MeC_6H_4.

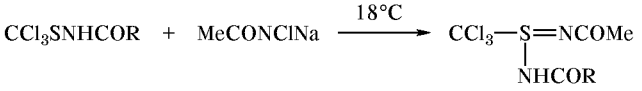
According to the data of UV spectroscopy [101], *N*-acyltrichloromethanesulfenamides are involved in the process as the corresponding N-anion in which the electron density on the sulfur atom is increased due to effect of the α-N-anionic center.



In the imination of *N*-acyltrichloromethanesulfenamides organic bases can promote a side process, namely cyclization of the *N*-acyltrichlormethanesulfenamide anion [100, 101].

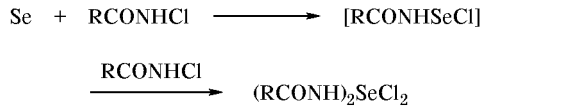


Imination of *N*-acyltrichloromethanesulfenamides with *N*-chlorocarboxamide sodium salts proceeds more smoothly [101].



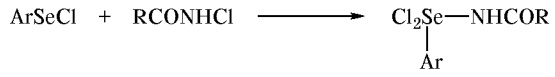
III.6. Oxidative Imination of Selenium and Selenium Compounds

Reactions of *N*-chlorocarboxamides with elemental selenium in carbon tetrachloride or methylene chloride at 20°C were reported to afford bis(acylamino)selenium dichlorides [103, 104]. The reaction involves intermediate formation of *N*-acylaminoselenenyl chlorides which then react with the second molecule of *N*-chlorocarboxamide. Depending on the initial *N*-chlorocarboxamide, the reaction takes from several hours to several days, and the yield of bis(acylamino)-selenium dichlorides is quantitative.



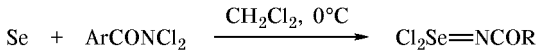
R = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-BrC_6H_4, 4-ClC_6H_4, 2,4-$Cl_2C_6H_3$.

Areneselenenyl chlorides react with *N*-chlorocarboxamides in a similar way, yielding aryl(acylamino)-selenium dichlorides [103, 104].



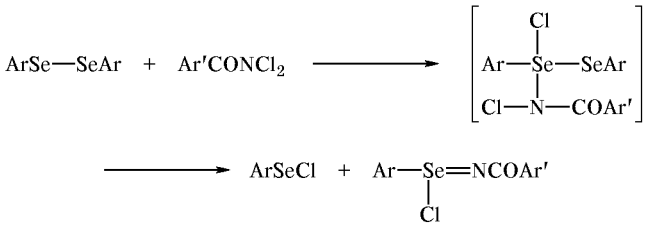
Ar = Ph, 4-$NO_2C_6H_4$, 4-ClC_6H_4; R = Ph, 4-MeC_6H_4, 4-BrC_6H_4, 4-ClC_6H_4, 4-$NO_2C_6H_4$.

Reactions of *N*,*N*-dichlorocarboxamides with elemental selenium follow the oxidative imination scheme and lead to formation of *N*-acyliminoselenium dichlorides [67, 105].



Ar = Ph, C_6F_5.

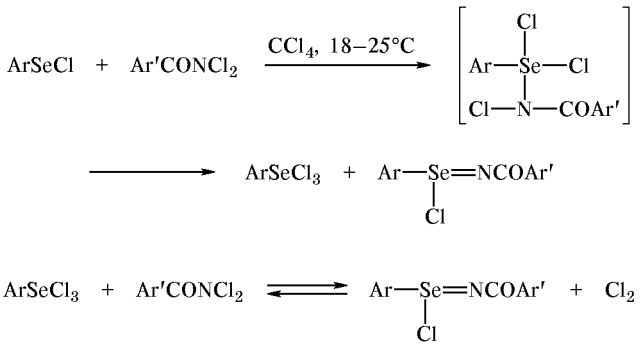
Reactions of *N*,*N*-dichlorocarboxamides with diaryl diselenides involve cleavage of the Se–Se bond and subsequent oxidative imination of the arylseleno fragments to give *N*-acylareneseleninimidoyl chlorides [106, 107]. The reaction occurs in CCl_4 at 5–10°C and is accompanied by heat evolution. Four-coordinate selenium compounds were presumed [106] to be intermediates; they decompose into areneselenenyl chloride and areneseleninimidoyl chloride.



Ar = Ph, 4-MeC_6H_4, 4-BrC_6H_4; Ar′ = Ph, 4-MeC_6H_4, 4-$NO_2C_6H_4$, 3,5-$(NO_2)_2C_6H_3$.

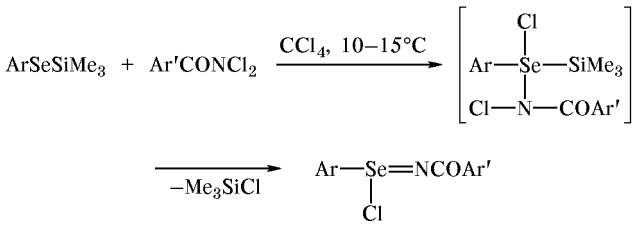
Areneselenenyl chlorides can in turn undergo imination by the action of *N*,*N*-dichlorocarboxamides to form *N*-acylareneseleninimidoyl chlorides [106]. This reaction is accompanied by formation of arylselenium trichlorides which react with *N*,*N*-dichloro-

carboxamides to give the same areneseleninimidoyl chlorides.



Ar = Ph, 4-MeC_6H_4, 4-BrC_6H_4; Ar′ = Ph, 4-MeC_6H_4, 4-$NO_2C_6H_4$, 3,5-$(NO_2)_2C_6H_3$.

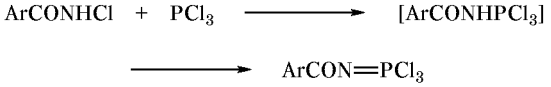
The latter reaction is reversible, and it is necessary to remove chlorine from the reaction mixture to displace the equilibrium toward the final product [106]. *N*-Acylareneseleninimidoyl chlorides are also formed by reactions of *N*,*N*-dichlorocarboxamides with aryl trimethylsilyl selenides [106].



Ar = Ph, 4-MeC_6H_4, 4-BrC_6H_4; Ar′ = Ph, 4-MeC_6H_4, 4-$NO_2C_6H_4$, 3,5-$(NO_2)_2C_6H_3$.

III.7. Oxidative Imination of Phosphorus Compounds

Reactions of *N*-chlorocarboxamides with phosphorus(III) chloride under reduced pressure lead to formation of *N*-acylphosphimidoyl trichlorides [108, 109] via elimination of HCl from unstable primary addition products.



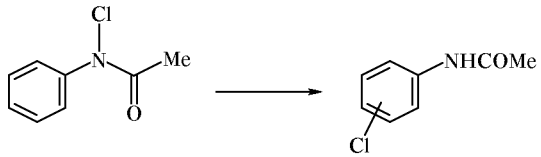
Ar = Ph, 4-BrC_6H_4.

The same reactions under atmospheric pressure yield the corresponding nitriles and phosphoryl chloride. *N*-Chlorocarboxamides were reported to react with triphenylphosphine [15] and triethylphosphine [110]; the products were triphenylphosphine oxide and triethylphosphine oxide, respectively. On the other hand, Petrenko [111] obtained the phosphonium salt $[Ph_3PNHCOPh]^+ Cl^-$ by reaction of *N*-chlorobenzamide with triphenylphosphine in anhydrous acetone at 18–35°C. An analogous salt was isolated in the reaction of *N*-chloroacetamide with triphenylarsine [112].

III.8. Rearrangements and Intramolecular Reactions of N-Halocarboxamides

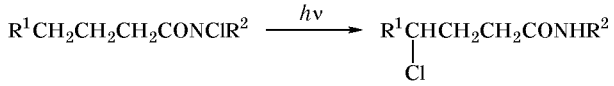
One of the most famous rearrangements typical of aliphatic *N*-halocarboxamides is the Hofmann rearrangement which occurs in the presence of bases and yields isocyanates [15]. The best results were obtained for *N*-bromocarboxamides in the presence of sodium methoxide [113].

Under certain conditions, *N*-aryl-*N*-chlorocarboxamides can undergo the Orton rearrangement, i.e., migration of the halogen atom to the *ortho*- or *para*-position of the aromatic ring [114].



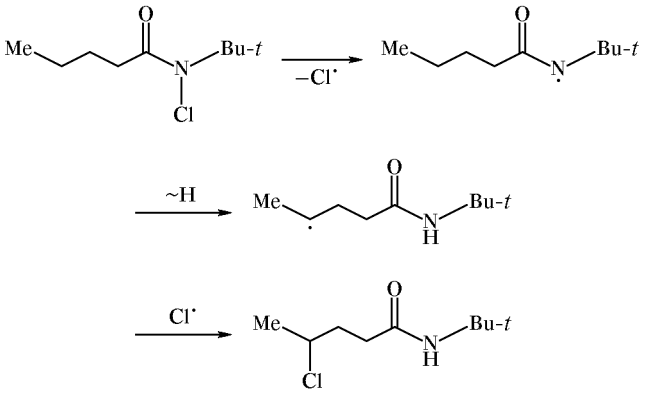
This rearrangement can be induced by UV irradiation or peroxide initiators (which favor homolytic dissociation of the N–Cl bond), as well as by the action of acetic and trichloroacetic acids in aprotic solvents or of halogenic acids in protic solvents [114].

N-Halo amides derived from aliphatic carboxylic acids having three or more methylene units give rise to the Hofmann–Leffler rearrangement under UV irradiation: the halogen atom migrates to the alkyl radical [115, 116].

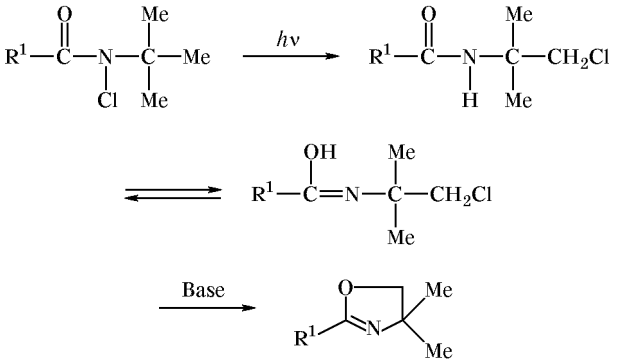


$R^1 = R^2$ = Alk.

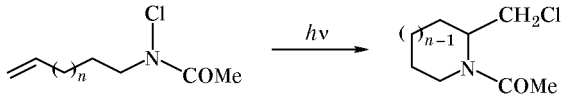
Of particular interest for organic synthesis is rearrangement involving halogen migration to the γ-position in *N*-halocarboxamides [15]. The yield of the product ranges from 50 to 70%, and the reaction is used as a method of functionalization of nonactivated γ-position.



UV irradiation (20°C) causes *N*-alkyl-*N*-chlorocarboxamides $R^1CON(R^2)Cl$ (R^2 = *t*-Bu, etc.) to undergo intramolecular rearrangement with migration of the chlorine atom to the R^1 radical and subsequent cyclization of the primary product into oxazole derivatives and other heterocyclic compounds [117, 118].

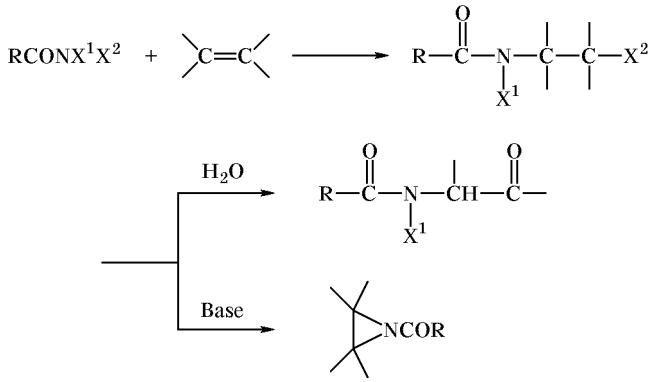


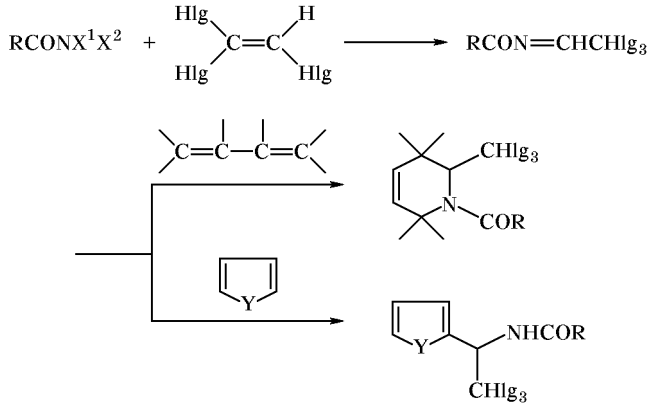
Intramolecular cyclization of unsaturated *N*-chlorocarboxamides under UV irradiation leads to formation of various nitrogen-containing heterocycles via addition at the double bond [44, 119–122].



IV. CONCLUSION

Reactions of *N*-halocarboxamides described in the present review illustrate great synthetic potential of these compounds and wide possibilities for using them by organic chemists. Various compounds formed thereby are widely used in fine organic synthesis and probably will find practical application in the nearest future. Among these, we can mention such highly reactive products as allyl halides and halohydrins resulting from allylic halogenation and halohydroxylation of unsaturated compounds; they are key intermediate products for introduction of an allyl group and oxirane ring. A great number of intermediate products for fine organic synthesis are available through addition of *N*-halo- and *N*,*N*-dihalocarboxamides to various unsaturated compounds, as shown in schemes given below [39].



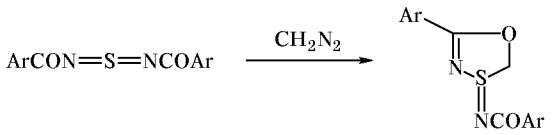


X^1 = H, Cl, Br; X^2 = Cl, Br; Y = S, O, NR^1 (R^1 = Alk).

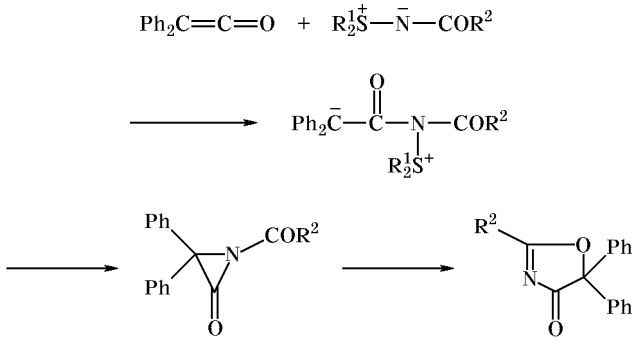
From the synthetic viewpoint, important are some products of oxidative imination of sulfur and sulfur compounds with *N*-halo- and *N*,*N*-dihalocarboxamides. These products were used to develop a series of procedures for preparation of various sulfur-containing compounds, including heterocyclic derivatives [123, 124]. For example, a preparative route to *N*,*N*′-thiobis(aroylamines) is based on the reduction of *N*,*N*′-bis(aroyl)sulfur diimides with benzenethiol [125, 126].

Levchenko and Dorokhova [127] described a new preparative synthesis of 3-aroylimino-5-aryl-2*H*-1,3,4-oxathiazoles by cycloaddition of singlet carbene

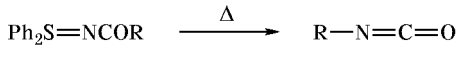
(generated from diazomethane) to the conjugate bond system of *N*,*N*′-bis(aroyl)sulfur diimides.



The ylide character of the S=N bond in *N*-acylsulfimides makes it possible to involve them in cycloaddition reactions with compounds possessing a cumulated or conjugated double bond system. Such transformation may be illustrated by the reaction of *N*-acylsulfimides with diphenylketene which leads to formation of 1,3-oxazol-4-one derivatives [128].



On the other hand, *N*-acylsulfimides give rise to various highly reactive intermediates which can be used in fine organic synthesis. [4+2]-Cycloaddition products derived from *N*-acylsulfimides and compounds having activated C=C bonds readily decompose to form sulfenamides [129]. Thermolysis of *N*-acylsulfimides in high-boiling organic solvents (with intermediate formation of acylnitrenes) underlies a procedure for preparation of isocyanates which are readily isolated from the reaction mixture [130, 131].



As a rule, isocyanates formed by the Hofmann rearrangement of *N*-halocarboxamides in aqueous alkali are readily hydrolyzed to amines under these conditions. The reaction can be used for preparation of amines, including those with cyclic structure which are difficult to obtain by other methods [132]. From the synthetic viewpoint, *N*-acylsulfinimidoyl chlorides and *N*-acylsulfonimidoyl chlorides are important products available through oxidative imination of sulfenyl and sulfinyl chlorides with *N*-chlorocarboxamides. The high lability of the S–Cl bond in these compounds makes them valuable reagents in the synthesis of other imino derivatives of sulfur [133, 134].

Thus reactions involving *N*-halocarboxamides lead to formation of important intermediate products for organic synthesis, which determines the high value of this class of *N*-halo reagents.

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