139. S.S.Batsanov and L.I.Gorogotskaya, Zhur.Neorg.Khim., 4, 62 (1959). [Russ.J.Inorg.Chem., 24 (1959)].
140. S.S.Batsanov and E.D.Ruchkin, Zhur.Neorg.Khim., 4, 1728 (1959) [Russ.J.Inorg.Chem., 779 (1959)].
141. S.S.Batsanov and N.R.Serebryanaya, Izv.Vys.Ucheb. Zaved., Khim.i Khim.Tekhnol., 3, 980 (1960).
142. S.S.Batsanov and Yu.A.Litvin, Izv.Sibir.Otd.Akad.Nauk SSSR, No.5, 49 (1962).
143. S.S.Batsanov and L.I.Abaulina, Izv.Sibir.Otd.Akad.Nauk SSSR, No.10, 67 (1961).
144. S.S.Batsanov, N.A.Shestakova, and L.A.Khripin, Dokl. Akad.Nauk SSSR, 152, 606 (1963).
145. S.S.Batsanov, L.M.Doronina, and N.V.Podberezskaya, Dokl.Akad.Nauk SSSR, 154, 624 (1964).
146. S.S.Batsanov and V.I.Rigin, Dokl.Akad.Nauk SSSR, 158, 1355 (1964).
147. S.S.Batsanov, N.V.Podberezskaya, and L.A.Khripin, Izv. Akad.Nauk SSSR, Ser.Khim., 209 (1965).
148. S.S.Batsanov and E.D.Ruchkin, Zhur.Neorg.Khim., 10, 2602 (1965) [Russ.J.Inorg.Chem., 1415 (1965)].
149. S.S.Batsanov and V.I.Rigin, Dokl.Akad.Nauk SSSR, 167, 89 (1966).
150. K.Fajans, J.Phys.Chem., 55, 1107 (1951).
151. W.Huckel, J.prakt.Chem., 5, 105 (1957).
152. S.S.Batsanov, Zhur.Fiz.Khim., 34, 937 (1960) [Russ.J. Phys.Chem., 444 (1960)].
153. Ya.K.Syrkin, Uspekhi Khim., 31, 397 (1962) [Russ.Chem. Rev., 197 (1962)].
154. S.S.Batsanov, Zhur.Fiz.Khim., 37, 1418 (1963) [Russ.J. Phys.Chem., 761 (1963)].
155. V.P.Spiridonov and V.M.Tatevskii, Zhur.Fiz.Khim., 37, 994, 1236, 1583, 1973 (1963) [Russ.J.Phys.Chem., 522, 661, 848, 1070 (1963)].
156. G.V.Bykov, Zhur.Fiz.Khim., 39, 1289 (1965) [Russ.J. Phys.Chem., 688 (1965)].
157. S.S.Batsanov, see Ref.126, p.63.
158. C.A.Coulson, "Valence" (Translated into Russian), Inostr. Lit., Moscow, 1965.

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Methods of Preparation and Chemical Properties of Aliphatic Halogenonitro-compounds

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The review deals with the literature on the nitrohalogenation of unsaturated compounds by addition to the latter of nitryl and nitrosyl halides and by the reaction of the unsaturated compounds with mixtures of nitrogen tetroxide and halogens. The condensation of nitro-alkanes with halogeno-carbonyl compounds, the nitration of halogeno-derivatives of aliphatic hydrocarbons, and the halogenation of nitro-compounds have also been described. Work on the reaction of polyhalogeno-alkanes with metal nitrites and the replacement of a carboxy-group by a halogen and a nitro-group have been reviewed. Dehydrohalogenation, dehalogenation, and also reactions involving the substitution of the halogen atoms have been examined in the analysis of the chemical properties of halogenonitro-compounds. The review also deals with work on the reactions of halogenonitro-compounds with participation of the nitro-group. A brief report is given on the applications of halogenonitro-compounds.

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I. INTRODUCTION

Among aliphatic nitro-compounds considerable interest attaches to halogenonitro-compounds in which there are two or three reaction centres: the halogen atom, the nitro-group, and, for substances with a primary or a secondary nitro-group, two or one "mobile" hydrogen atom. The presence of several reaction centres permits a wide range of reactions with these compounds.

Despite their undoubted interest, the chemistry of halogenonitro-compounds has not been reviewed so far. The present review presents a compilation of data on the syn

thesis and chemical properties of halogenonitro-compounds excluding α-halogenonitro-compounds. The latter, containing a halogen and a nitro-group at the same carbon atom, constitute a fairly large group of substances, which differs sharply in methods of preparation and properties from halogenonitro-compounds in which the halogen and the nitro-group are attached to different carbon atoms[1].

II. METHODS OF PREPARATION OF HALOGENONITRO-COMPOUNDS

1. NITROHALOGENATION OF UNSATURATED COMPOUND

a. Addition of Nitryl Halides to Unsaturated Compounds

Nitrohalogenation with nitryl chloride and fluoride only has been described[2-15] and the possibility of the addition of nitryl fluoride has been demonstrated in only one study[16]:

$$CF_3-C(R)=CF-OR' + FNO_2 \rightarrow \begin{matrix} CF_3 \\ \diagdown \\ R \end{matrix}\!\!>C(NO_2)-CF_2-OR' ,$$

where R = F or CF_3 and R′ = alkyl.

Many investigators are inclined to believe that nitryl chloride adds to unsaturated compounds by a free-radical mechanism, although it is also capable of heterolytic dissociation[3,12,14]:

$$NO_2^+ + Cl^- \rightleftarrows NO_2Cl \rightleftarrows NO_2^{\cdot} + Cl^{\cdot}$$
$$\downarrow\uparrow$$
$$NO_2^- + Cl^+ .$$

However, in weakly polar media nitryl chloride largely dissociates with formation of free radicals[12]. This can account for the finding that, in the chloronitro-compounds formed, the nitro-group is attached to the terminal carbon atom of the double bond regardless of the electronic properties of the substituents:

$$R-CH=CH_2 \xrightarrow{NO_2^{\cdot}} R-\dot{C}H-CH_2-CH_2NO_2$$
$$R-\dot{C}H-CH_2NO_2 \xrightarrow{NO_2Cl} R-CHCl-CH_2NO_2 + NO_2^{\cdot} ,$$

where R = alkyl, CH_3OCO, CN, COOH, $C(=O)Cl$, or a halogen.

The primary attack by the chlorine atom leads to the formation of dichlorides. There exist contradictory data on the reaction of styrene with nitryl chloride[2,3]. Steinkopf and Kühnel[2] isolated 2-chloro-1-nitro-1-phenylethane as the reaction product, but later Goddard[3] repeated the reaction and obtained 1,2-dichlorophenylethane and β-nitrostyrene, the formation of which takes place, in his view, according to the mechanism

$$C_6H_5-CH=CH_2 \xrightarrow{NO_2Cl} [C_6H_5-CHCl-CH_2NO_2] \xrightarrow{-HCl} C_6H_5-CH=CHNO_2 .$$

The isolation in a number of cases of 2-chloro-nitrites and pseudonitrosites[5,9] is evidence that either nitryl chloride reacts partially by a heterolytic mechanism or the $NO_2^{\cdot}$ radical attacks the carbon atom with formation of the $-\overset{|}{C}-ONO$ bond.

The addition of nitryl chloride to acetylenic hydrocarbons can serve as a convenient method for the synthesis of unsaturated halogenonitro-compounds[11,14,15]:

$$RC\equiv CR' + NO_2Cl \rightarrow RCCl=CNO_2R' ,$$

where R = C_2H_5, C_4H_9, C_6H_5, or Cl and R′ = C_2H_5, C_4H_9, C_6H_5, Cl, or H.

In addition to α-chloro-β-nitrostyrene, Freeman and Emmons[14] isolated $\alpha\alpha$-dichloroacetophenone from the products of the reaction of phenylacetylene and nitryl chloride and proposed a probable mechanism for its formation:

$$C_6H_5-C\equiv CH \xrightarrow{NO_2} C_6H_5-\dot{C}=CHNO_2 \xrightarrow{NO_2Cl} C_6H_5CCl=CHNO_2$$
$$C_6H_5-C\equiv CH \xrightarrow{NO_2Cl} C_6H_5-\dot{C}=CHCl \xrightarrow{NO_2^{\cdot}} C_6H_5-\overset{ONO}{\overset{|}{C}}=CHCl \xrightarrow{NO_2Cl}$$
$$\rightarrow \left[C_6H_5-\overset{ONO}{\overset{|}{C}}-CHCl_2\right] \rightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-CHCl_2 .$$

The reaction of nitryl chloride with diene hydrocarbons has been little investigated[4,17]. When nitryl chloride was allowed to react with divinyl, isoprene, piperylene, and chloroprene, the products of the 1,4-addition of NO_2Cl and the products of their isomerisation with migration of the double bond towards the nitro-group were obtained together with dichlorides.

b. Reaction of Nitrosyl Halides with Unsaturated Compounds

Nitrosyl chloride adds to ethylenic hydrocarbons in accordance with the Markovnikov rule[18-37]. The primary product of the addition reaction, an unstable monomeric nitrosochloro-derivative, can react further in three principal ways[29]: (1) it can condense to a relatively stable dimer; (2) it can be oxidised to chloronitro-compounds; (3) it can isomerise to the oxime of a chloro-aldehyde (or ketone):

$$\left[\begin{matrix} \diagdown \\ C-CH \\ \diagup \end{matrix}\!\!\begin{matrix} Cl \\ NO \end{matrix}\right]_2 \rightleftarrows \begin{matrix} \diagdown \\ C-CH \\ \diagup \end{matrix}\!\!\begin{matrix} Cl \\ NO \end{matrix} \rightarrow \begin{matrix} \diagdown \\ C-CH \\ \diagup \end{matrix}\!\!\begin{matrix} Cl \\ NO_2 \end{matrix}$$
$$\downarrow$$
$$\left[Cl-\overset{|}{C}-CH-N=\overset{\downarrow}{N}-CH-\overset{|}{C}-Cl\right] \qquad \begin{matrix} \diagdown \\ C-C=NOH \\ \diagup \end{matrix}\!\!\begin{matrix} | \\ Cl \end{matrix}$$
$$\begin{matrix} | & | \\ O & O \end{matrix}$$

The mode of reaction depends on the structure of the initial hydrocarbon and its chloronitroso-derivative. The second and third processes, oxidation and isomerisation, depend on the first—the capacity of the monomeric chloronitro-compounds to be converted into the dimer and on the stability of the dimeric form.

The presence of electron-acceptor atoms and groups at the carbon atom adjacent to the nitroso-group reduces the electron density of the –N=N– bond and favours the dissociation of the dimer into monomeric molecules, and, conversely, electron-donor substituents increase the stability of the dimer.

As a rule the reaction mixture contains products formed by all three reactions. However, depending on the structure of the initial olefin, one or other product predominates. The nature of the product depends on the relative rate of addition of nitrosyl chloride (NOCl) to the olefin and the oxidation of the product to a chloronitro-compound and a dichloro-derivative. If the oxidation is faster than the addition, the main reaction product is the chloronitro-compound. Thus, symmetrical and asymmetric alkylethylenes, and particularly polyalkylethylenes, yield mainly crystalline dimeric chloronitroso-derivatives and only small amounts of chloronitro-compounds. Trimethylethylene, isobutene[38,39], 2,2,3-trimethylbut-3-ene[29], 1-methylcyclohexene, 1-ethylcyclohexene, but-2-ene[30], pent-2-enyl-2-methylbut-1-ene, 2-(*p*-tolyl)propene[29], and

tetramethylethylene[40] react in this way. The chloronitro- and dichloro-compounds are the main products of the reaction of nitrosyl chloride with monosubstituted alkylethylenes—isopropylethylene[21], pent-1-ene, hex-1-ene, hept-1-ene, and 2,2-dimethylbut-3-ene[29]. If in an asymmetrically disubstituted ethylene one of the substituents has electron-acceptor properties, the chloro-derivative and the dichloro-compound predominate in the reaction products. This has been demonstrated for α-methylstyrene[41].

The addition of nitrosyl chloride takes place in accordance with the polarisation of the double bond. Allyl chloride, vinyl chloride, trichloroethylene[19], 2-chloropropene[33], methyl methacrylate, 3,3,3-trichloromethylpropene, 2-nitropropene[34], and methyl acrylate[35] react in this way.

The conversion of chloronitroso-compounds into chloronitro-compounds probably takes place via a stage involving the formation of diazo-nitrates, for example[29]:

$$CH_3{-}CX{=}CH_2 \xrightarrow{NOCl} CH_3CX(NO){-}CH_2Cl \xrightarrow{2NOCl} CH_3{-}CX(N_2ONO_2){-}CH_2Cl + 2Cl;$$

$$CH_3{-}CX(N_2ONO_2){-}CH_2Cl \xrightarrow{NOCl} CH_3{-}CXCl{-}CH_2Cl + N_2 + 2NO_2;$$

$$CH_3{-}CX{=}CH_2 + NO_2^{\cdot} \rightarrow CH_3{-}\dot{C}X{-}CH_2NO_2 \xrightarrow{NOCl(Cl)} CH_3{-}CXCl{-}CH_2NO_2;$$

where X = Cl, $COOCH_3$, NO_2, or CCl_3.

When 2,2-dimethylpent-3-ene reacts with nitrosyl chloride, a mixture of chloronitro-products is formed[31]:

$$CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}{-}CH{=}CH{-}CH_3 + NOCl \rightarrow \begin{cases} (CH_3)_3C{-}CHNO_2{-}CHCl{-}CH_3 \\ (CH_3)_3C{-}CHCl{-}CHNO_2{-}CH_3 \end{cases}.$$

Nitrosyl chloride reacts with tetrafluoroethylene, chlorotrifluoroethylene, and the asymmetric dichlorodifluoroethylene with formation of nitro-compounds when the mixture is passed through a heated glass tube[25]:

	Yield
$CF_2{=}CF_2 \xrightarrow[NOCl]{50^\circ} CF_2ClCF_2NO_2$,	63%
$CF_2{=}CFCl \xrightarrow[NOCl]{100^\circ} CF_2ClCFClNO_2$,	67%
$CF_2{=}CCl_2 \xrightarrow[NOCl]{100^\circ} CF_2ClCCl_2NO_2$.	57%

The same products are formed when the reaction is carried out in a sealed tube[18,23] or in an autoclave at room temperature[26].

When nitrosyl chloride, tetrafluoroethylene, and chlorotrifluoroethylene were passed through a tube over ferric chloride at 45°C, nitroso-compounds, dichloro-compounds, chloronitro-compounds, and dinitro-compounds were isolated[37]. Similar results were obtained when nitric oxide (NO) was used instead of nitrosyl chloride[32,42]. Probably in this case the first reaction stage is the formation of nitrosyl chloride from nitric oxide and ferric chloride.

The addition of nitrosyl bromide and fluoride to unsaturated compounds has been investigated to a lesser extent. Only one reaction of nitrosyl bromide is known[24-26]:

$$CF_2{=}CF_2 + NOBr \rightarrow CF_2NO_2CF_2Br.$$

Tetra- and tri-fluoroethylene, and vinylidene fluoride readily react with nitrosyl fluoride, but nitro-compounds were not found among the products. Perfluoropropene reacts with nitrosyl fluoride only at 150°C. In the presence of calcium sulphate as the catalyst the yield of nitroalkanes is slight and without catalyst radical nitration products are formed exclusively[43].

Degradation products were obtained from perfluorobut-2-ene and nitrosyl fluoride at 200°C: $CF_3CF_2NO_2$, CF_3NO_2, etc.[44]

Depending on the molar ratio of the reactants, diene hydrocarbons combine with one or two molecules of nitrosyl chloride[22]. Thus diallyl reacts with nitrosyl chloride to form 5-chloro-6-nitrohexene, 2,5-dichloro-1,6-dinitrohexane, and also 5,6-dichlorohex-1-ene and 1,2,5,6-tetrachlorohexane, i.e. the double bonds react completely independently of one another and the addition of nitrosyl chloride takes place as with monosubstituted olefins. Butadiene behaves similarly:

$$CH_2{=}CH{-}CH{=}CH_2 \begin{cases} \xrightarrow{+NOCl} CH_2{=}CH{-}CHCl{-}CH_2NO_2 \\ \xrightarrow{+2\,NOCl} CH_2NO_2{-}CHCl{-}CHCl{-}CH_2NO_2 \end{cases}.$$

Nitrochlorination of acetylene derivatives with nitrosyl chloride permits the synthesis of a wide variety of 1,2-chloronitro-alkenes in a single stage:

$$RC{\equiv}CR' \xrightarrow{NOCl} \underset{Cl\ \ NO}{RC{=}CR'} \xrightarrow{O} \underset{R\ \ R'}{ClC{=}CNO_2}.$$

Perrot and Berger[27] obtained α-chloro-β-nitrostyrene and its derivatives from phenylacetylene and nitrosyl chloride:

$$RC_6H_4C{\equiv}CH + NOCl \rightarrow RC_6H_4C(Cl){=}CHNO_2,$$

where R = H, p-CH_3, o- and p-Cl, or m-NO_2 and p-NO_2.

c. Nitrohalogenation of Saturated Compounds by Nitrogen Tetroxide–Halogen Mixtures

The structure of the products of the nitrohalogenation of olefins by N_2O_4–X_2 (X = Cl, Br, or I) in many ways depends on the reaction conditions, the structure of the initial olefin, and the nature of the halogen[45-52]. When the reaction is carried out in the vapour phase, free-radical processes predominate[47,53], since under these conditions N_2O_4 and X_2 dissociate into radicals: $N_2O_4 \rightleftharpoons 2NO_2^{\cdot}$, $X_2 \rightleftharpoons X^{\cdot} + X^{\cdot}$. The radical initiating the reaction can be either $NO_2^{\cdot}$ or $X^{\cdot}$ (the capacity for this decreases in the series Cl → Br → I). In the chloronitration of propene and butene at 260–275°C, the products are 1-chloro-2-nitro-alkanes[52] (the chlorine atom is more reactive):

$$R{-}CH{=}CH_2 + Cl^{\cdot} \rightarrow R\dot{C}HCH_2Cl,$$

$$R{-}\dot{C}HCH_2Cl + NO_2^{\cdot} \rightarrow RCHNO_2CH_2Cl,$$

$$R{-}\dot{C}HCH_2Cl + Cl_2 \rightarrow RCHClCH_2Cl + Cl^{\cdot}.$$

Vinyl chloride and bromide react with N_2O_4–Cl_2 and N_2O_4–Br_2 mixtures in different ways when the reaction temperature is raised from 250° to 325°C:[47]

$$CH_2{=}CHR + NO_2^{\cdot} \xrightarrow{255^\circ} CH_2NO_2\dot{C}HR$$

$$CH_2NO_2\dot{C}HR + X_2 \rightarrow CH_2NO_2CHRX$$

$$CH_2{=}CHR + X^{\cdot} \xrightarrow{325^\circ} CH_2X{-}\dot{C}HR$$

$$CH_2X{-}\dot{C}HR + NO_2^{\cdot} \rightarrow CH_2X{-}CHRNO_2$$

where R = Cl, Br. The different reactions can be accounted for by a change in the reactivity of the $NO_2^{\cdot}$ and $X^{\cdot}$ radicals with increasing temperature.

Sometimes a change in the relative proportions of the reactants (the olefin and the N_2O_4–X_2 mixture) leads to a change in the mode of addition[48]:

$$CH_2{=}CHCl \xrightarrow{N_2O_4+Br_2} \begin{cases} \rightarrow CH_2BrCHClNO_2 \\ \rightarrow CHClBrCH_2NO_2 \end{cases}.$$

Liquid-phase nitrohalogenation of unsaturated compounds takes place as a rule by a radical mechanism[45-50]. The reaction is then initiated by the $NO_2^{\cdot}$ radical:

$$>C=C< + NO_2^{\cdot} \rightarrow -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}NO_2 \ .$$

The nitroalkyl radical formed is "captured" by the halogen:

$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}NO_2 + X_2 \rightarrow -\overset{|}{\underset{X}{C}}-\overset{|}{\underset{|}{C}}NO_2 + X^{\cdot} \ .$$

For example,

$$CH_3-CH=CH_2 + N_2O_4 + I_2 \rightarrow CH_3-CHI-CH_2NO_2 \ ,$$
$$CH_3COO-CH=CH_2 + N_2O_4 + I_2 \rightarrow CH_3COOCHI-CH_2NO_2 \ ,$$
$$C_6H_5-CH=CH_2 + N_2O_4 + I_2 \rightarrow C_6H_5-CHI-CH_2NO_2 \ .$$

The free-radical mechanism explains particularly satisfactorily the reactions of fluoro-olefins with a mixture of N_2O_4 and I_2:[48,49]

$$N_2O_4 \rightarrow 2NO_2^{\cdot} \ ,$$

$$CF_2=CHX + NO_2 \rightarrow NO_2CHX\dot{C}F_2 + O_2NCF_2\dot{C}HX$$
$$\downarrow I_2 \qquad\qquad \downarrow I_2$$
$$O_2NCHXCF_2I + I^{\cdot} \quad O_2NCF_2CHXI + I^{\cdot} \ ,$$

$$CHX=CF_2 + ONO^{\cdot} \rightarrow CHX-CF_2ONO \xrightarrow{I_2} ICHX-CF_2ONO \rightarrow ICHX-COOH \ ,$$

where X = H, F, or perfluoroalkyl.

Bachman and Logan[51] carried out the reaction of ethylene, propene, and butenes with N_2O_4–I_2 and N_2O_4–Br_2 mixtures in the presence of an excess of nitrogen tetroxide and and isolated halogeno-nitrates, the formation of which they believe to be due to an ionic mechanism:

$$R-CH=CH_2 + Br_2 \rightarrow R-\overset{+}{C}H-CH_2Br + Br^- \ ,$$
$$R-\overset{+}{C}H-CH_2Br + N_2O_4 \rightarrow R-CHONO_2CH_2Br + NO^+ \ .$$

Stevens and Emmons[45] explain this finding by the presence of a large excess of nitrogen tetroxide in the reaction.

Diene hydrocarbons react with the N_2O_4–I_2 mixture by a 1,4-addition mechanism[46]:

$$CH_2=CH-CH=CH_2 \rightarrow CH_2NO_2-CH=CH-CH_2I \ .$$

With substituted butadienes, the attack by NO_2 radicals is directed preferentially to carbon atoms most highly enriched in electrons:

$$CH_2=\underset{|}{\underset{R}{C}}-CH=CH_2 \xrightarrow{N_2O_4+I_2} O_2N-CH_2-\underset{|}{\underset{R}{C}}=CH-CH_2I \ ,$$

where R = CH_3 or Cl.

2. CONDENSATION OF NITROALKANES WITH HALOGENO-CARBONYL COMPOUNDS

The condensation of nitro-alkanes with halogeno-carbonyl compounds has been investigated relatively little[54-73]. It was first studied by Henry[54], who allowed chloral hydrate to react with nitromethane in the presence of potassium carbonate[54]:

$$CCl_3CH(OH)_2 + CH_3NO_2 \rightarrow Cl_3CCH(OH)CH_2NO_2 \ .$$

Later it was repeated[55,57,63,67,73] and extended to chloral homologues (butylchloral and bromal[63]) and other nitro-alkanes (nitroethane, phenylnitromethane[56], and 1-nitro-propane[55]).

The condensation of chloral hydrate with nitromethane takes place with an almost quantitative yield but the reaction is somewhat less complete with other nitro-alkanes. When the reaction was carried out in the vapour phase, contrary results were obtained—a better yield with nitro-butane[58].

The condensation of mono- and dichloroacetaldehyde and bromoacetaldehyde takes place with greater difficulty[59-62]. Fluoro-substituted aldehydes also enter into the condensation reaction with nitro-alkanes in the presence of alkaline catalysts[59-66,68,69]:

$$RCF_2CH(OH)_2 + R'CH_2NO_2 \rightarrow RCF_2CH(OH)CH(NO_2)R' \ ,$$

where R = F or C_2F_5 and R′ = H, CH_3, or C_2H_5.

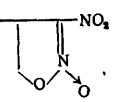
Of the halogeno-substituted ketones, only 1,1,1-trifluoroacetone[68], 1,1,1-trifluorobutan-2-one[66], and perfluoroacetone[70] have been investigated in the condensation with nitro-alkanes:

$$CF_3COR + CH_3NO_2 \rightarrow CF_3CR(OH)CH_2NO_2$$

where R = CH_3, C_2H_5, or CF_3.

When the potassium salt of dinitromethane is condensed with chloroacetaldehyde hydrate, the product of the spontaneous cyclisation, 4-hydroxy-3-nitroisoxazoline *N*-oxide, was obtained instead of the expected potassium salt of γ-chloro-β-hydroxydinitropropane:[72]

$$ClCH_2CHO + [HC(NO_2)_2]^-K^+ \rightarrow [ClCH_2CHOHC(NO_2)_2]^-K^+ \rightarrow$$



3. NITRATION OF HALOGENO-DERIVATIVES OF ALIPHATIC HYDROCARBONS

a. Nitration with Nitrogen Oxides

When nitric oxide acts on chlorotrifluoroethylene and hexafluoropropane, nitro-derivatives are obtained in small amounts[42]:

$O_2NCF_2CFClNO$, $O_2NCF_2CFCl_2$, $O_2NCF_2CFClNO_2$, $CF_3CF(NO)-CF_2NO_2$ и $CF_3CF(NO_2)CF_2NO_2$.

The addition of nitrogen dioxide to halogeno-olefins takes place by a free-radical mechanism with formation of dinitro-derivatives of halogeno-alkanes. This has been shown by numerous studies on the addition of nitrogen tetroxide to tribromoethylene[64], tetrachloro- and tetrabromoethylenes[65], tetrafluoroethylene[64,66-70], chlorotrifluoroethylene[24,66,71], and hexafluoropropene[69]. Together with halogenonitro-alkanes, the formation of halogenonitronitrites has been observed; on subsequent hydrolysis, the latter yield halogeno-substituted nitro-alcohols[74-87], nitrocarboxylic acids[78-80], or nitro-ketones[81].

In some cases the nitro-alcohol is formed preferentially[82-84]:

$$CH_2Cl-CH=CH_2 + N_2O_4 \rightarrow CH_2Cl-CH(OH)-CH_2NO_2 \ .$$
$$CH_2=\underset{|}{\underset{CH_2Cl}{C}}-CH_3 + N_2O_4 \rightarrow O_2NCH_2\underset{|}{\underset{CH_2Cl}{C}}(CH_3)OH$$

By allowing the complex $BF_3.N_2O_4$ to react with vinyl chloride at 0°C in chloroform, Bachman and Vogt[85] obtained 2,2-dichloronitroethane:

$$CH_2=CHCl + BF_3\cdot N_2O_4 \rightarrow Cl_2CHCH_2NO_2 \ .$$

They explained the formation of this product by the oxidative degradation of part of the vinyl chloride.

The nitration of perfluorobutadiene with N_2O_4 yields 1,4-dinitroperfluorobut-2-ene and 1-nitroperfluorobut-2-enyl nitrite[86]:

$$CF_2=CF-CF=CF_2 \longrightarrow O_2N-CF_2-CF=CF-CF_2-NO_2 \quad O_2N-CF_2-CF=CF-CF_2-ONO$$

On hydrolysis the nitrite is converted into γ-nitroperfluorobutyric acid and on treatment with alcohols or on ammonolysis it yields the esters of this acid or the amide.

Under the action of nitrogen oxides, halogenoacetylenes are converted into halogenonitro- and halogenodinitroethylenes[87-89]:

$$IC\equiv CI + N_2O_4 \rightarrow IC(NO_2)=C(NO_2)I,$$
$$IC\equiv CI + N_2O_3 \rightarrow I_2C=C(I)NO_2,$$
$$ClC\equiv CCl + N_2O_4 \xrightarrow{(C_2H_5)_2O} ClCH=C(Cl)NO_2.$$

Products of the substitution of halogen and hydrogen atoms were obtained in the nitration with N_2O_4 of 2,3-dibromopropene[90] and dichloroethylene[91] respectively:

$$CH_2=C(Br)-CH_2Br \rightarrow CH_2=C(Br)-CH_2NO_2$$
$$(CHCl)_2 \rightarrow NO_2CCl=CHCl.$$

b. Nitration of Halogeno-Alkenes and Halogeno-Alkanes with Nitric and Other Acids

The nitration of halogeno-alkenes with nitric acid or its mixtures with other acids takes place by an ionic mechanism and leads to the formation of products resulting both from the addition of the NO_2 group and the substitution of hydrogen or halogen atoms. In the latter case halogenonitro-alkenes are formed. The nitration process is complicated by side reactions involving oxidation. When a mixture of concentrated nitric and sulphuric acids reacts with tetrachloroethylene, tetrachloro-1,2-dinitroethane is formed[92]:

$$Cl_2C=CCl_2 + HNO_3 \xrightarrow[H_2SO_4]{} O_2NCCl_2CCl_2NO_2.$$

By nitrating 1,1,5-trichloropent-1-ene or 1,1-dichloropent-1-ene with nitric acid, Zakharkin[10] obtained both mono- and di-nitro-derivatives:

$$Cl_2C=CHCH_2CH_2CH_2Cl + HNO_3 \rightarrow Cl_2CCH(NO_2)CH_2CH_2CH_2Cl + Cl_2C(NO_2)CH(NO_2)CH_2CH_2CH_2Cl,$$
$$Cl_2C=CHC_3H_7 + HNO_3 \rightarrow Cl_2CCH(NO_2)C_2H_7 + Cl_2C(NO_2)CH(NO_2)C_3H_7$$

He believes that the formation of 1,1,1-trichloro-2-nitroalkanes can be explained by the reaction of hydrochloric acid (formed in the oxidation of the $Cl_2C=CH$ group) with nitric acid ($HNO_3 + HCl \rightarrow NOCl + Cl_2 + H_2O$)—the addition of nitrosyl chloride and the oxidation of the resulting products; the formation of nitryl chloride by the reaction of hydrochloric and nitric acids and its subsequent addition to the double bond cannot be excluded.

On being refluxed with an excess of nitric acid, dichloroethylene is converted into trichloronitroethylene in a good yield[93]. Under the action of fuming nitric acid or its mixtures with sulphuric acid, tetraiodoethylene yields 1,2,2-tri-iodonitroethylene[87].

Kooijman and Overhoff[94] nitrated chloro-olefins with nitric acid in such a way that the double bond in the initial olefins was not affected:

$$CH_2=C(CH_3)CH_2Cl + HNO_3 \rightarrow O_2NCH=C(CH_3)CH_2Cl.$$

A method of nitration of olefins with a mixture of sodium nitrite and dilute sulphuric acid has been patented[95,96]:

$$CH_2=C(CRR^1X)-CHR^2R^3 + NaNO_2 \xrightarrow{H_2SO_4} CH_2=C(CRR^1X)-CR^2R^3NO_2,$$

where R, R^1, R^2, and R^3 = H or alkyl and X = halogen.

The reaction of 2,3-dibromopropene with nitric acid in dichloroethane at 40–50°C yields a mixture of these products[97]:

$$BrCH_2C(Br)=CH_2 + HNO_3 \rightarrow (NO_2)_2CCH_2Br + (NO_2)_2CHCH_2Br + BrCH_2C(NO_2)(Br)-COOH.$$

Martynov and coworkers[98-102] obtained the products of the oxidation of halogeno-olefins with the nitrating mixture. They isolated halogenonitro-acids and their chlorides.

Nitrofluorination of olefins and their halogeno-derivatives with a mixture of nitric acid and anhydrous hydrogen fluoride can serve as one of the methods of preparation of fluoronitro-alkanes:

$$HF + HNO_3 \rightleftarrows O_2N^+ + 2F^- + H_2O^+$$
$$>C=C< + O_2N^+ \rightarrow \left[>C(NO_2)-\overset{+}{C}<\right] F^- \rightarrow >C(NO_2)-C(F)<.$$

This reaction was achieved for the first time with tetrafluoroethylene[103]:

$$CF_2=CF_2 + HNO_3 + HF \rightarrow CF_3CF_2NO_2.$$

The study of the nitrofluorination of asymmetric halogeno-olefins showed that the mode of addition is determined by the polarity of the double bond[103-106]:

$$CHCl=CH_2 \xrightarrow{HF+HNO_3} CHFCl-CH_2NO_2,$$
$$CF_2=CFCF_3 \xrightarrow{HNO_3+HF} (CF_3)_2CFNO_2,$$
$$CH_2=CHCOOCH_3 \xrightarrow{HF+HNO_3} CH_2F-CH(NO_2)COOCH_3 + CH_2OH-CHNO_2-COOCH_3.$$

The nitration of saturated hydrocarbons and their derivatives was first investigated by Konovalov. By heating a mixture of dilute nitric acid with 1-chloro-2-methylpropane or 1-chloro-3-methylbutane in sealed tubes, he obtained the corresponding mononitro-derivatives, the nitro-group substituting the hydrogen at the tertiary carbon atom[107,108]:

$$(CH_3)_2CH(CH_2)_nCl + HNO_3 \rightarrow (CH_3)_2C(NO_2)(CH_2)_nCl,$$

where n = 1, 2.

Shechter and Conrad[109] achieved the vapour-phase nitration of 1,1,1-trifluoropropane at 437–462°C in the presence of oxygen and isolated 3,3,3-trifluoro-1-nitropropane. When the reaction was carried out at 395°C, a mixture of 3,3,3-trifluoro-1-nitropropane and 2,2,2-trifluoronitroethane was isolated in proportions of 3 : 2.[110]

Chloronitro-alkanes have been obtained by the action of a mixture of sulphuric acid and ammonium nitrate on the corresponding chloro-alkanes[111]:

$$RCH(Cl)CH_3 \xrightarrow[H_2SO_4]{NH_4NO_3} RCH(Cl)CH_2NO_2,$$

where R = CH_3 or C_2H_5.

4. HALOGENATION OF NITRO-COMPOUNDS

a. Halogenation of Nitro-Olefins

Unsaturated nitro-compounds (in solution) combine with chlorine or bromine at the double bonds in the cold or on heating, with formation of dihalogeno-derivatives[112-117]. The reaction involves a heterolytic mechanism:

$$RCH{=}C(NO_2)R' + X_2 \rightarrow RCH(X)C(X)(NO_2)R' .$$

When two electronegative substituents are present at the double bond, more severe conditions are required for the addition of the halogen. Thus chlorine adds to vicinal dinitro-olefins after the olefin has remained in contact for a long time with liquid chlorine in sunlight[115].

The double bond conjugated with the nitro-group in 1-nitrobutadiene[114] is deactivated and, when bromine reacts with 1-nitrobutadiene between −10° and 18°C, only one molecule of bromine adds to the olefin with formation of the dibromo-derivative in 99% yield:

$$NO_2CH{=}CH{-}CH{=}CH_2 + Br_2 \rightarrow NO_2CH{=}CHCHBrCH_2Br .$$

Since the nitro-group is a powerful electron acceptor, the electrophilic addition of bromine to β-nitrostyrene is difficult and therefore for this reaction to take place, the reaction mixture must be heated in chloroform[116].

b. Halogenation of Nitro-Alkanes

Riley and McBee[118,119] showed that the chlorination of nitro-alkanes in the absence of bases leads to the formation of β-chloronitro-alkanes. Bromination in the absence of base yields the same products as in the presence of bases, i.e. α-bromonitro-compounds are produced. The authors believe that substances such as phosphorus pentoxide favour the formation of the β-isomer by displacing the equilibrium of the reaction

$$RCH_2NO_2 \rightleftarrows RCH{=}N\begin{matrix}O\\ \diagup\\ \diagdown\\ OH\end{matrix} .$$

Riley and McBee explained the difference in the behaviour of chlorine and bromine by the fact that chlorine reacts very fast and the concentration of the nitronic acid is negligible, while bromination takes place slowly, and the conversion of the nitro-alkane into the aci-form takes place much more rapidly and therefore there is sufficient time for the aci-form to react with bromine with formation of α-bromonitro-alkane.

Sayles and Degering[120] described the chlorination of nitrobutane on irradiation with ultraviolet light in the presence of phosphorus pentoxide, the sole product according to their data being 4-chloro-1-nitrobutane:

$$CH_3CH_2CH_2CH_2NO_2 + Cl_2 \xrightarrow{P_2O_5} ClCH_2CH_2CH_2CH_2NO_2 .$$

However, in the chlorination of nitrobutane under analogous conditions Erm[121] obtained in addition 3-chloro-1-nitrobutane. He believes that the mode of reaction depends mainly on the intensity of the ultraviolet irradiation.

5. SUBSTITUTION OF A HALOGEN FOR THE HYDROXYL IN NITRO-ALCOHOLS

As in simple aliphatic alcohols, the hydroxy-group of nitro-alcohols can be replaced by a halogen when the latter reacts with the halides of phosphorus and sulphur acids[122-148]. This reaction is used to demonstrate the presence of the hydroxy-group in nitro-alcohols and for the preparation of halogenonitro-alkyls with a definite structure.

The substitution of the hydroxy-group of nitro-alcohols by a chlorine atom was first achieved by Henry[54,122-125], who treated the nitro-alcohols with phosphorus pentachloride:

$$RCH(NO_2)CH_2OH + PCl_5 \xrightarrow{K_2CO_3} RCH(NO_2)CH_2Cl ,$$

where R = H or CH_3, and

$$RCH(OH)CH_2NO_2 + PCl_5 \xrightarrow{K_2CO_3} RCHClCH_2NO_2 ,$$

where R = CH_3 or CCl_3. Other β-chloronitro-alkanes were prepared similarly[126-130].

The substitution of the hydroxy-groups in nitro-diols by halogens under the action of phosphorus pentachloride takes place with much greater difficulty[131,137], while with trihydric alcohols a mixture of chloro-derivatives of various degrees of substitution and of phosphoric acid esters of the nitro-alcohols is produced[133]. Kleinfeller[133] synthesised tri(bromomethyl)nitromethane by the bromination of nitroisobutylglycerol with elemental bromine in the presence of red phosphorus[133]. The nature of the side products formed in this process was similar to that in the chlorination reaction.

A more convenient method for the substitution of the hydroxy-group by a chlorine atom consists in the treatment of nitro-alcohols with thionyl chloride in the presence of pyridine. The following chloronitro-compounds have been obtained by this procedure: $ClCH_2CH_2NO_2$, $O_2NCH_2CHClCH_3$, $C_2H_5CH(NO_2)CH_2Cl$;[132] $CH_3C(Cl)(NO_2)CH_2Cl$, $O_2N(C_2H_5)C(CH_2Cl)_2$;[138] $O_2NC(CH_2Cl)_3$;[139] $CH_3C(NO_2)_2CH_2Cl$, $ClCH_2C(NO_2)_2CH_2Cl$;[148] $CH_2NO_2CHClCH_3$;[146] $(O_2N)_3CCH_2Cl$.[147]

In the study of the reaction of thionyl chloride with nitrodiols in the presence of pyridine, Novikov and coworkers[140] concluded that the chlorinating agent is a complex of thionyl chloride with pyridine, formed relatively slowly. Therefore, on rapid addition of $SOCl_2$ to the mixture of the diol and pyridine, there is not sufficient time for the formation of the complex and the reaction can lead to the formation of cyclic sulphites[133].

Halogenonitro-alkanes can be prepared from the acetals of nitro-alcohols by treating the latter with phosphorus pentachloride[141]:

$$RR^1C(NO_2)CHR^2OCHOR^3 \xrightarrow{PCl_5} RR^1C(NO_2)CH(R^2)Cl ,$$
$$\quad\quad\quad

6. DOUBLE DECOMPOSITION OF POLYHALOGENO-ALKENES WITH METAL NITRITES

Henry [54,149] achieved the synthesis of 2-chloronitroethane and 3-chloro-1-nitropropane by the reaction of silver nitrite with the corresponding $\alpha\omega$-chloroiodo-alkanes:

$$Cl(CH_2)_nI + AgNO_2 \rightarrow Cl(CH_2)_nNO_2,$$

where $n = 2$ or 3. A number of $\alpha\omega$-fluoronitro-alkanes have been synthesised by the reaction of the corresponding $\alpha\omega$-bromofluoro- or $\alpha\omega$-fluoroiodo-alkanes with silver nitrite [150]:

$$F(CH_2)_nX + AgNO_2 \rightarrow F(CH_2)_nNO_2,$$

where X = Br or I and $n = 3$, 4, 5, or 6.

Halogenonitro-alkanes can be obtained also from di-halogeno-derivatives in which both halogen atoms are identical. Thus Work carried out the reaction of silver nitrite with 1,5-dibromopentane [151] and 1,5-dibromo-3-propylpentane [152] at room temperature and obtained the corresponding $\alpha\omega$-bromonitro-alkanes:

$$RCH(CH_2CH_2Br)_2 + AgNO_2 \rightarrow NO_2CH_2CH_2CH(R)CH_2CH_2Br,$$

where R = H or C_3H_7. 2-Bromo-3-nitropropene was obtained similarly from 2,3-dibromopropene [90].

Freidlina et al. [153] obtained 1,1-dichloro-3-nitropropene from 1,1,3-trichloropropene and silver nitrite using the different reactivities of the chlorine atoms:

$$ClCH_2CH{=}CCl_2 + AgNO_2 \rightarrow NO_2CH_2CH{=}CCl_2.$$

A method for the preparation of halogeno nitro-compounds by the reaction of polyhalogeno-compounds with alkali or alkaline earth metal nitrites in aqueous ethanol was patented in 1944:[154]

$$ClCH_2CH_2Cl + MNO_2 \rightarrow O_2NCH_2CH_2Cl$$

$$ClCH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_2Cl + MNO_2 \rightarrow O_2NCH_2\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_2Cl.$$

7. REPLACEMENT OF A CARBOXY-GROUP BY A HALOGEN ATOM OR A NITRO-GROUP

Silver salts of *gem*-dinitro-carboxylic acids are converted into bromonitro-alkanes under the action of elemental bromine [155-157]. 4-bromo-2,2-dinitrobutane and 1,5-dibromo-3,3-dinitropentane have been obtained in this way:

$$CH_3\overset{\displaystyle NO_2}{\overset{|}{C}}(NO_2)CH_2CH_2COOAg \xrightarrow[CCl_4]{Br_2} CH_3\overset{\displaystyle NO_2}{\overset{|}{C}}(NO_2)CH_2CH_2Br,$$

$$AgOOCCH_2CH_2\overset{\displaystyle NO_2}{\overset{|}{C}}(NO_2)CH_2CH_2COOAg \xrightarrow[CCl_4]{Br_2} BrCH_2CH_2\overset{\displaystyle NO_2}{\overset{|}{C}}(NO_2)CH_2CH_2Br.$$

Scribner [158] showed that perfluoro-carboxylic acids are converted into nitroperfluoro-alkanes under the action of nitrogen dioxide:

$$C_7F_{15}COOH \xrightarrow{NO_2} C_6F_{13}NO_2 + C_7F_{16}NO_2.$$

8. SYNTHESIS OF γ-BROMODINITRO-COMPOUNDS

Novikov et al. [159] developed a new method for the synthesis of γ-bromodinitro-compounds, which consists in the reaction of the mercury-derivatives of nitro-alkanes with bromine:

$$(NO_2)_2CHCH_2CH_2HgCl + Br_2 \xrightarrow[\text{peroxide}]{\text{benzoyl}} (NO_2)_2CHCH_2CH_2Br + HgBrCl,$$

1-Bromo-3,3-dinitropropane, 1-bromo-2-methyl-3,3-dinitropropane, 1-bromo-3,3-dinitro-2-phenylpropane, 2-bromo-1-dinitromethylcyclopentane, and 2-bromo-1-dinitromethylcyclohexane have been obtained. The reaction involves a radical mechanism.

9. OTHER METHODS

When a stream of gaseous hydrogen chloride is passed through a mixture of β-nitro-alcohol and paraformaldehyde in concentrated hydrochloric acid, chloromethyl ethers of the β-nitro-alcohols are produced [160,161]:

$$R{-}\overset{\displaystyle R'}{\overset{|}{C}}(NO_2){-}CH_2OH + (CH_2O)_x + HCl \rightarrow R{-}\overset{\displaystyle R'}{\overset{|}{C}}(NO_2){-}CH_2OCH_2Cl,$$

where R = H or CH_3 and R' = CH_3 or C_2H_5. In the presence of sodium methoxide nitromethane adds to esters of $\alpha\beta$-unsaturated fluoro-substituted acids with formation of fluoronitro-compounds containing other functional groups [65]:

$$RCH{=}CHCOOC_2H_5 + CH_3NO_2 \xrightarrow{CH_3ONa} RCH(CH_2NO_2)CH_2COOC_2H_5,$$

where R = CF_3 or C_3F_7. Bromonitropentanone has been obtained by the addition of bromonitroform to methyl vinyl ketone [162].

Boyd and Hansen [163] obtained 1-iodo-2-methyl-2-nitropropane by refluxing 2-methyl-2-nitropropyl esters of arenesulphonic acids with sodium iodide in acetone:

$$RSO_3CH_2\overset{\displaystyle NO_2}{\overset{|}{C}}(CH_3)_2 + NaI \rightarrow (CH_3)_2\overset{\displaystyle NO_2}{\overset{|}{C}}{-}CH_2I.$$

Under the action of nitrogen tetroxide in ether, the oxime of chloroacetone is converted into 1-chloro-2-nitro-2-nitrosopropane, which is oxidised by chromic acid to the *gem*-dinitro-compound [164]:

$$ClCH_2\overset{\displaystyle NOH}{\overset{\|}{C}}CH_3 \xrightarrow{N_2O_4} ClCH_2\overset{\displaystyle NO_2}{\overset{|}{\underset{\displaystyle NO}{\underset{|}{C}}}}CH_3 \xrightarrow{[O]} ClCH_2\overset{\displaystyle NO_2}{\overset{|}{C}}CH_3.$$

Nitrosoperhalogeno-alkanes, obtained by the irradiation of a mixture of nitric oxide and a monoiodoperhalogeno-alkane with ultraviolet light, are converted into halogeno-nitro-compounds on oxidation with Cr_2O_3, PbO_2, or Mn_2O_7:[165]

$$RCF_2I + NO \rightarrow RCF_2NO \xrightarrow{O} RCF_2NO_2,$$

where R = Cl, CF_3, or C_2F_5.

Knunyants and coworkers [166] obtained esters of α-nitro-perfluoropropionic acid by the action of nitrogen tetroxide on esters of α-nitrosoperfluoropropionic acid:

$$CF_3\underset{\displaystyle NO}{\underset{|}{C}}FCOOR + N_2O_4 \rightarrow CF_3\underset{\displaystyle NO_2}{\underset{|}{C}}FCOOR + N_2O_3.$$

Nitro-alcohols react with trichloroacetonitrile in the presence of hydrogen chloride or bromide with formation of the hydrohalides of the corresponding trichloronitroalkyl-acetimidates. On decomposition, the latter yield halogeno-nitro-alkanes [167]:

$$CCl_3C{\equiv}N + HOCH_2CH_2NO_2 \rightarrow CCl_3\underset{\displaystyle NH\cdot HX}{\underset{\|}{C}}{-}OCH_2CH_2NO_2 \rightarrow CCl_3CONH_2 + XCH_2CH_2NO_2$$

By this method 1-chloro-2-nitroethane and 1-bromo-2-nitroethane have been obtained from nitroethanol and 1-chloro- and 1-bromo-2-nitropropane from 2-nitropropanol.

III. CHEMICAL PROPERTIES OF HALOGENONITRO-COMPOUNDS

1. REACTIONS WITH PARTICIPATION OF THE HALOGEN ATOM

a. Dehydrohalogenation

The dehydrohalogenation of halogenonitro-compounds to form nitro-olefins can be achieved either by pyrolysis or by treatment with basic reagents. Gold[168,169] pyrolysed β-chloronitro-compounds in the gas phase; it is best to carry out the process in the presence of catalysts [for example, $CaCl_2$, $CaCO_3$, $Ca_3(PO_4)_2$, $CaSO_4$, $Al(SO_4)_3$][168-170], which partially reduces the reaction temperature and increases the yields of nitro-olefins:

$$RCHCH_2NO_2 \rightarrow RCH{=}CHNO_2 \ .$$
$$\quad\ Cl$$

Spontaneous thermal dehydrohalogenation takes place when the products of the addition of nitryl chloride to styrene[3] or acrylic acid[12] are heated:

$$C_6H_5CH\,(Cl)\,CH_2NO_2 \rightarrow C_6H_5CH{=}CHNO_2 \ ,$$
$$NO_2CH_2CH\,(Cl)\,COOH \rightarrow NO_2CH{=}CHCOOH \ .$$

A convenient method for the dehydrohalogenation of β-halogenonitro-compounds consists in the treatment of the latter with basic reagents: alkalis[45,171], alkali metal acetates[8,12,45,172-175], and organic bases[10,12,45,176]. The dehydrohalogenation takes place more readily when the halogen (chlorine) atom is attached to a primary carbon atom, as, for example, in chloronitroethane. The dehydrohalogenation of 2-chloro-1-nitrobutane is slower. That of 2-chloro-3-methyl-1-nitrobutane is even more difficult[8]. Perekalin and Lerner[177] obtained 1,4-dinitrobutadiene by the dehydrochlorination of the corresponding dichloro-derivative with lead acetate:

$$O_2NCH_2CH\,(Cl)\,CH\,(Cl)\,CH_2NO_2 \rightarrow NO_2CH{=}CHCH{=}CHNO_2 \ .$$

2-Nitrobuta-1,3-diene has been obtained from 1-chloro-2-nitro-3-butanol and 1,3-dichloro-2-nitrobutane by the treatment of the mixture with potassium hydroxide[132].

Nitro-alkadienes are readily formed on dehydroiodination of the products of the addition of N_2O_4 and I_2 to diene hydrocarbons in the presence of a solution of lead acetate in glacial acetic acid[178]:

$$RCHI{-}CR'{=}CH{-}CH_2NO_2 \rightarrow R{-}CH{=}CR'{-}CH{=}CHNO_2 \ .$$

In the dehydrohalogenation of compounds in which the halogen and the nitro-group are further away than in β-halogenonitro-compounds, it is necessary to use strong bases, for example, sodium alkoxides[155]:

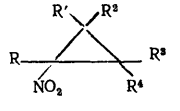
$$CH_3\overset{\displaystyle NO_2}{\overset{|}{C}}CH_2CH_2Br \xrightarrow{NaOCH_3} CH_3\overset{\displaystyle NO_2}{\overset{|}{C}}CH{=}CH_2 \ .$$
$$\qquad\quad NO_2 \qquad\qquad\qquad\quad NO_2$$

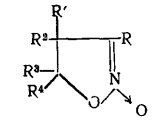
On elimination of hydrogen halides from γ-halogenonitroalkanes, nitrocyclopropanes have been obtained[179-185].

Koler and later Smith[179,180,184] showed that γ-bromonitro-compounds of the type

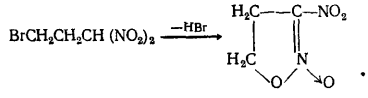
$$HC(R)(NO_2)-C(R')(R^2)-C(Br)(R^3)-R^4$$

where R = $R^{1,2,3}$ = H, alkyl, or aryl and $R^4 = \rangle C{=}O$ or –COAr, eliminate hydrogen bromide in an alkaline medium and form either the corresponding nitrocyclopropane derivatives or the isomeric isoxazoline *N*-oxides, depending on the structure of the starting material:





Intramolecular *O*-alkylation, which leads to the formation of 3-nitroisoxazoline-*N*-oxides under the action of alkaline reagents, is characteristic of γ-bromodinitro-compounds containing terminal *gem*-dinitro-groups[186]:



3-Nitro-2-isoxazoline has been obtained by treating 1-halogeno-3-nitropropanes with alkali metal nitrites[187]. Recently Bay[182,183] patented the synthesis of nitrocyclopropane by the dehydrohalogenation of 1-halogeno-3-nitropropanes under the action of sodamide in liquid ammonia or alkali metal carbonates and bicarbonates.

b. Reactions Involving the Substitution of the Halogen Atom

β-Halogenonitro-compounds readily react with aniline and its derivatives[3,7,8,53,188] forming *N*-nitroalkylanilines:

$$R{-}CHCl{-}CH_2NO_2 + C_6H_5NH_2 \rightarrow C_6H_5NH{-}CH\langle^{\displaystyle CH_2NO_2}_{\displaystyle R} + HCl \ .$$

In the case of dichloronitropropane both halogen atoms are substituted[8]:

$$CH_2Cl{-}CHCl{-}CH_2NO_2 + 2NH_2C_6H_5 \rightarrow C_6H_5NHCH_2{-}\underset{\displaystyle NHC_6H_5}{\underset{|}{CH}}{-}CH_2NO_2 \ .$$

When 2,3,3,3-tetrachloro-1-nitropropane reacts with ammonia, *p*-toluidine, and phenylhydrazine, the products are the corresponding 2-amino-derivatives[189]. The study of the hydrolysis of β-halogenonitroalkanes with aqueous solutions of alcohol and dioxan showed that the reaction takes place by an S_N2 nucleophilic mechanism[8,134,190-193] with formation of nitro-alcohols:

$$R\diagdown_{R'}\!\!>CCl{-}CH_2NO_2 + H_2O \longrightarrow R\diagdown_{R'}\!\!>\underset{\displaystyle OH}{\underset{|}{C}}{-}CH_2NO_2 + HCl \ ,$$

where R = H, C_2H_5, or iso-C_3H_7 and R′ = H or CH_3. The rate of hydrolysis depends on the nature of the carbon atoms to which the halogen is attached, decreasing on going from a primary to a tertiary carbon atom, as clearly illustrated by the following data[8]:

	Hydrolysis rate constant in 75% ethanol	Hydrolysis rate constant in 75% dioxan
$ClCH_2CH_2NO_2$	7.15×10^{-5}	5.27×10^{-5}
$H_3C\diagdown\ \diagup CH{-}CHClCH_2NO_2$ H_3C	2.27×10^{-5}	1.30×10^{-5}
$CH_3CH_2\diagdown\ \diagup CCl{-}CH_2NO_2$ H_3C	0.25×10^{-5}	0.21×10^{-5}

The halogen atom in the γ-position relative to the nitro-group is less mobile. Thus, whereas both chlorine atoms of 2,2-dichloro-1-nitroethane are readily substituted during hydrolysis, in 2,3-dichloro-1-nitropropane only the chlorine atom in the β-position is hydrolysed[8]:

$$O_2NCH_2—CHCl_2 \xrightarrow{2H_2O} O_2NCH_2CH(OH)_2 \xrightarrow{-H_2O} O_2NCH_2CHO,$$

$$O_2NCH_2—CHCl—CH_2Cl \xrightarrow{H_2O} O_2NCH_2\underset{\displaystyle OH}{\underset{|}{C}}H—CH_2Cl.$$

When acetate salts react with halogenonitro-alkanes, it is possible to obtain the acetates derived from the corresponding nitro-alcohols[8,156,194]:

$$\rangle CCl—CH_2NO_2 \xrightarrow[CH_3COOH]{CH_3COOK} \rangle \underset{\displaystyle OCOCH_3}{\underset{|}{C}}—CH_2NO_2,$$

$$BrCH_2CH_2—\underset{\displaystyle NO_2}{\underset{|}{\overset{\displaystyle NO_2}{\overset{|}{C}}}}—CH_2CH_2Br \xrightarrow[CH_3COOH]{CH_3COOAg} CH_3COOCH_2CH_2—\underset{\displaystyle NO_2}{\underset{|}{\overset{\displaystyle NO_2}{\overset{|}{C}}}}—CH_2CH_2OCOCH_3.$$

The reaction of β-chloronitro-compounds with mecarptans and their derivatives in the presence of sodium leads to the formation of sulphides[129,130]:

$$CH_3CHClCH_2NO_2 + HSCH_2CH(OC_2H_5)_2 \xrightarrow{Na} O_2NCH_2CH(CH_3)SCH_2CH(OC_2H_5)_2.$$

c. Dehalogenation

The dehalogenation of halogenonitro-alkanes has been little investigated. Only two reactions have been described in the literature: on heating above 120°C, 1,2-dibromo-1,2,2-trichloronitroethane decomposes with elimination of bromine[85]; on being refluxed with potassium cyanide, 1,2-dibromo-2-phenylnitroethane is converted into β-nitro-styrene[195]:

$$C_6H_5CHBr—CHBrNO_2 \rightarrow C_6H_5CH=CHNO_2.$$

2. REACTIONS WITH PARTICIPATION OF THE NITRO-GROUP

1. Reduction

Various methods may be used to convert halogenonitro-compounds into the corresponding aminohalogeno-derivatives. Konovalov[107] identified the nitro-derivatives which he obtained by reduction to the amines with zinc and hydrochloric acids. The reduction with iron and hydrochloric acid is also successful[139]:

$$NO_2C(CH_2Cl)_3 + Fe + HCl \rightarrow H_2NC(CH_2Cl)_3.$$

Another reagent used to convert halogenonitro-compounds into halogeno-amines is aluminium amalgam[133,188]. A number of investigators obtained aminohalogeno-compounds from the corresponding nitro-derivatives by reducing the latter with stannous chloride and hydrochloric acid[6,10,133,139,196].

Certain halogenonitro-compounds have been converted into halogeno-amines by catalytic hydrogenation over Raney nickel[8,55,65,67,197,198]. Hydroxylamines are then formed together with the amines. It has been mentioned that certain fluoronitro-compounds can be converted into amino-compounds with the aid of lithium aluminium hydride without affecting the C–F bond[57]. The electrolytic reduction of chloronitro-compounds to chloroalkylamines in aqueous alcohol in the presence of sulphuric acid has been reported[8].

When 6-chloro-5-nitrodec-5-ene is hydrogenated over PtO_2 in acetic acid in the presence of sodium acetate, simultaneous conversion of the nitro-group into NHOH and the replacement of the chlorine atom by hydrogen takes place[15]. Bromine atoms are replaced by hydrogen together with the reduction of the nitro-group in the hydrogenation of 1,2-dibromo-1-nitro-2-phenylethane over a palladium catalyst[148]:

$$C_6H_5CHBrCH(Br)NO_2 \xrightarrow{H_2} C_6H_5CH_2CH_2NH_2.$$

For the reduction of halogenonitro-compounds, see also the review of Novikov et al.[199]

b. The Effect of Mineral Acids

Under the action of mineral acids, halogenonitro-alkanes are converted into the corresponding halogeno-derivatives of carboxylic acids[19-22,105,200]. This reaction is so characteristic of fluoronitro-alkanes that it may serve as a convenient method for the synthesis of fluoro-carboxylic acids[200]:

$$—\underset{\displaystyle F}{\underset{|}{C}}—CH_2NO_2 \xrightarrow{H_2SO_4} —\underset{\displaystyle F}{\underset{|}{C}}—COOH.$$

When β-halogenonitro-alkanes are treated with aliphatic alcohols in the presence of strong acids (hydrochloric, sulphuric, and phosphoric), esters are produced[201]:

$$(CH_3)_2CClCH_2NO_2 + CH_3OH \xrightarrow{H_2SO_4} (CH_3)_2CClCOOCH_3.$$

When salts of the aci-forms of halogenonitro-alkanes are allowed to react with acids, halogeno-aldehydes are produced[109,121]:

$$NaOON=CHCH_2CH_2CHCl \xrightarrow[-15°]{H_2SO_4} CHClCH_2CH_2CHO.$$

3. OTHER REACTIONS

a. Reactions Involving a Mobile Hydrogen Atom

Reactions associated with the mobility of hydrogen atoms in the α-position relative to the nitro-group are characteristic of halogenonitro-alkanes as well as unsubstituted nitro-alkanes. Thus in the study of the condensation of trifluoro- and tetrafluoro-nitroethane with formaldehyde in the presence of alkalis, Knunyants et al.[198] obtained a good yield of fluoronitro-alcohols:

$$CF_3—CH_2NO_2 + 2CH_2O \xrightarrow{NaOH} CF_3—\underset{\displaystyle CH_2OH}{\overset{\displaystyle CH_2OH}{\overset{|}{\underset{|}{C}}}}—NO_2.$$

Chloronitro-alkanes enter into a similar condensation with formaldehyde in the presence of potassium carbonate[200]:

$$Cl_3CCHR'CH(NO_2)R + CH_2O \xrightarrow{K_2CO_3} Cl_3CCHR'\underset{\displaystyle CH_2OH}{\overset{\displaystyle R}{\overset{|}{\underset{|}{C}}}}NO_2,$$

where R = H or CH_3 and R' = OCH_3, OC_2H_5, C_2H_5, or C_4H_9. When the reaction is carried out in an alcoholic medium, the corresponding ethers are formed in both cases.

The "mobile" hydrogen atom is readily substituted by halogens[77]:

$$CF_3CHCH_2NO_2 \xrightarrow{Br_2} \underset{OH}{CF_3CH}-\underset{OH\ Br}{CHNO_2}.$$

When aryldiazonium salts react with acetates derived from halogenonitro-alcohols, diazotisation takes place[202]:

$$RCCl_2CH(OCOCH_3)CH_2NO_2 \xrightarrow{ArN_2^+} RCCl_2CH(OCOCH_3)C(NO_2)=NNHAr,$$

where R = Cl or CH_3CHCl.

b. Reactions with Formation of New C–C Bonds

Sayles and Degering[120] carried out the condensation of 4-chloro-1-nitrobutane with ethyl acetoacetate in the presence of sodium:

$$O_2N(CH_2)_4Cl + CH_3COCH_2COOC_2H_5 \xrightarrow{Na} O_2N(CH_2)_4CH(COCH_3)COOC_2H_5.$$

2-Chloro-1-nitropropane reacts with benzene in the presence of aluminium chloride[203]:

$$CH_3CHClCH_2NO_2 + C_6H_6 \xrightarrow{AlCl_3} C_6H_5-CH\begin{matrix}CH_3\\ \diagdown\\ CH_2NO_2\end{matrix}.$$

IV. APPLICATIONS OF HALOGENONITRO-COMPOUNDS

Compounds which contain both halogen atoms and nitro-groups are of definite interest because of their high physiological activity[200]. There have been a number of studies where it was shown that chloronitro-compounds can be used as insecticides[18,204-206], fungicides[57,71], bactericides[58,71,207], miticides[194], and herbicides[71].

When products of the addition of alcohols to β-(trichloromethyl)nitroethylene are reduced, amines are formed, some of which can be used as antispasmodic agents[196].

2-Chloro-1-nitro-olefins have been patented as fumigants, selective extracting agents, cellulose solvents, and varnish components[94,135].

Krug and Elmer[207] took out a patent for the application of the compounds $Cl_3CCH(R)C(R^1)(R^2)NO_2$ (where R = H or acyl containing 2–3 carbon atoms and R^1 and R^2 = H, CH_3, or C_2H_5) as additives (in amounts of 0.05–15%) to greases for gas-turbine engines. The same compounds are used for the dilution and dispersion of oils[208]. The application of bromonitro-alkanes and bromonitro-alkenes as additives to motor fuel has been mentioned[209].

Halogenonitro-alkanes are used as solvents[24] and additives to resin adhesives[111].

The application of 3,3,3-trichloro-1-nitropropane as a solvent for the copolymers of acrylonitrile with vinyl acetate and vinylpyridine in the dyeing of the polymeric products by organic dyes has been described[197].

The chloro-derivatives of 2,2-dinitropropanol and 2,2-dinitropropanediol have been proposed as plasticisers, solvents, and explosive components[148].

REFERENCES

1. S.S.Novikov, A.A.Fainzil'berg, and V.V.Sevost'yanova, Uspekhi Khim., **31**, 1417 (1962) [Russ.Chem.Rev., 671 (1962)].
2. W.Steinkopf and M.Kühnel, Ber., **75**, 1323 (1942).
3. D.R.Goddard, J.Chem.Soc., 1955 (1958).
4. C.M.Himel, U.S.P. 2511915 (1950), Chem.Abs., **44**, 8360 (1950).
5. C.C.Price and C.A.Sears, J.Amer.Chem.Soc., **75**, 3275 (1953).
6. S.Bresadola, P.Canal, A.Nenz, and E.Gallinella, Chimica e Industria, **45**, 937 (1963); Chem.Abs., **59**, 9771e (1963).
7. J.Ville and G.Dupont, Bull.Soc.chim.(France), 804 (1956); Chem.Abs., **51**, 1024b (1957).
8. J.Ville, Mém.Poudres, **41A**, 1 (1959), Chem.Abs., **57**, 16370 (1962).
9. H.Petri, Z.anorg.Chem., **257**, 180 (1948).
10. L.I.Zakharkin, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1064 (1957).
11. H.Brintzinger and K.Pfanstiel, Z.anorg.Chem., **255**, 325 (1947); **256**, 324 (1948).
12. H.Shechter, F.Conrad, A.L.Daulton, and R.B.Kaplan, J.Amer.Chem.Soc., **74**, 3052 (1952).
13. S.S.Novikov, G.A.Shvekhgeimer, and N.S.Pyatakov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 914 (1961).
14. J.Freeman and W.Emmons, J.Amer.Chem.Soc., **79**, 1712 (1957).
15. H.H.Schlubach and A.Braun, Annalen, **627**, 28 (1959).
16. B.L.Dyatkin, E.P.Mochalina, and I.L.Knunyants, Uspekhi Khim., **35**, 979 (1966) [Russ.Chem.Rev., 417 (1966)].
17. A.M.Vil'davskaya, K.B.Rall', and A.A.Petrov, Zhur.Org.Khim., **2**, 561 (1966).
18. A.Ya.Yakubovich, V.A.Shpanskii, and A.L.Lemke, Dokl.Akad.Nauk SSSR, **96**, 773 (1954).
19. A.Ya.Yakubovich and A.L.Lemke, Zhur.Obshch.Khim., **19**, 649 (1949).
20. K.A.Ogloblin, Zhur.Obshch.Khim., **28**, 3245 (1958).
21. K.A.Ogloblin, Zhur.Obshch.Khim., **27**, 2541 (1957).
22. K.A.Ogloblin and A.A.Potekhin, Zhur.Obshch.Khim., **31**, 2438 (1961).
23. A.Ya.Yakubovich, V.A.Shpanskii, and A.L.Lemke, Zhur.Obshch.Khim., 24, 2257 (1954).
24. R.N.Haszeldine, B.P. 770618 (1957); Chem.Abs., **51**, 14790 (1957).
25. R.N.Haszeldine, J.Chem.Soc., 2075 (1953).
26. D.A.Barr and R.N.Haszeldine, J.Chem.Soc., 1151 (1960).
27. R.Perrot and R.Berger, Compt.rend., **235**, 185 (1952).
28. K.A.Ogloblin, Zhur.Obshch.Khim., **29**, 264 (1959).
29. K.A.Ogloblin, V.N.Kalikhevich, A.A.Potekhin, and A.P.Semenov, Zhur.Obshch.Khim., **34**, 170 (1964).
30. K.A.Ogloblin and M.A.Samartsev, Zhur.Obshch.Khim., **33**, 3257 (1963).
31. K.A.Ogloblin and M.A.Samartsev, Zhur.Obshch.Khim., **34**, 1530 (1964).
32. J.D.Park and An.P.Stefani, U.S.P. 3072705 (1960); Chem.Abs., **58**, 10771 (1963).
33. K.A.Ogloblin and V.P.Semenov, Zhur.Obshch.Khim., **34**, 1522 (1964).
34. K.A.Ogloblin and V.P.Semenov, Zhur.Org.Khim., **1**, 1356 (1965).
35. K.A.Ogloblin and V.P.Semenov, Zhur.Org.Khim., **1**, 1361 (1965).
36. K.A.Ogloblin and V.P.Semenov, Zhur.Org.Khim., **1**, 27 (1965).
37. J.D.Park, A.P.Stefani, and J.R.Lacher, J.Org.Chem., **26**, 4017 (1961).
38. S.N.Danilov and K.A.Ogloblin, Zhur.Obshch.Khim., **22**, 2113 (1952).
39. K.A.Ogloblin, Zhur.Obshch.Khim., **22**, 2121 (1952).
40. M.Tuot, Compt.rend., **204**, 647 (1937).
41. K.A.Ogloblin, Zhur.Obshch.Khim., **29**, 2006 (1959).
42. J.D.Park, A.P.Stefani, G.H.Crawford, and J.R.Lacher, J.Org.Chem., **26**, 3319 (1961).
43. I.L.Knunyants, E.G.Bykhovskaya, V.N.Fokin, and Ya.M.Kisel', Dokl.Akad.Nauk SSSR, **132**, 123 (1960).
44. S.Andreades, J.Org.Chem., **27**, 4163 (1962).

45. T. E. Stevens and W. D. Emmons, J. Amer. Chem. Soc., **80**, 338 (1958).
46. A. A. Petrov and K. B. Rall', Zhur. Obshch. Khim., **34**, 3621 (1964).
47. G. B. Bachman, T. J. Logan, K. R. Hill, and N. W. Standish, J. Org. Chem., **25**, 1312 (1960).
48. G. B. Bachman and T. J. Logan, U. S. P. 2 933 535 (1960); Chem. Abs., **54**, 18 353c (1960).
49. M. Hauptschein, R. E. Oesterling, and M. Breid, J. Org. Chem., **28**, 1281 (1963).
50. M. Hauptschein and R. E. Oesterling, U. S. P. 3 118 004 (1962); Chem. Abs., **60**, 6745 (1962).
51. G. B. Bachman and T. J. Logan, J. Org. Chem., **21**, 1467 (1956).
52. G. B. Bachman and T. Hokama, J. Org. Chem., **25**, 178 (1960).
53. G. B. Bachman and J. P. Chupp, J. Org. Chem., **21**, 465 (1956).
54. L. Henry, Bull. Classe Sci., Acad. roy. Belg., [3], **34**, 547 (1898); Chem. Zentr., **1**, 192 (1898).
55. S. Malkiel and J. P. Mason, J. Amer. Chem. Soc., **64**, 2515 (1942).
56. E. D. Chattaway, J. G. N. Drewitt, and G. D. Parkes, J. Chem. Soc., 1294 (1936).
57. A. N. Bates, D. M. Spencer, and R. L. Wain, Ann. Appl. Biol., **51**, 153 (1963); Chem. Abs., **60**, 2269c (1964).
58. G. B. Bachman and N. W. Standish, U. S. P. 2 999 118 (1959); Chem. Abs., **56**, 2331d (1962).
59. French P. 804 589 (1936); Chem. Abs., **31**, 3505^3 (1937).
60. B. P. 473 143 (1937); Chem. Abs., **32**, 1712^7 (1938).
61. O. Nicodemus and O. Wulff, U. S. P. 2 123 556 (1938); Chem. Abs., **32**, 6667^3 (1938).
62. H. Shechter and F. Conrad, J. Amer. Chem. Soc., **76**, 2716 (1954).
63. F. D. Chattaway and J. G. Witherington, J. Chem. Soc., 1178 (1935).
64. A. Dornow and F. Boberg, Annalen, **578**, 113 (1952).
65. D. J. Cook, O. R. Pierce, and E. T. McBee, J. Amer. Chem. Soc., **76**, 83 (1954).
66. E. T. McBee, C. E. Hattaway, and C. W. Roberts, J. Amer. Chem. Soc., **78**, 4053 (1956).
67. M. Compton, H. Higgins, L. Makbeth, J. Osborn, and H. Burkett, J. Amer. Chem. Soc., **71**, 3229 (1949).
68. H. Shechter, D. E. Ley, and E. B. Robertson, J. Amer. Chem. Soc., **78**, 4984 (1956).
69. E. T. McBee, D. J. Cook, and O. R. Pierce, U. S. P. 2 997 505 (1961); Chem. Abs., **56**, 320e (1962).
70. Ch'en Ch'ing-Yun, N. N. Gambaryan, and I. L. Knunyants, Dokl. Akad. Nauk SSSR, **133**, 1113 (1960).
71. D. T. Mowry, U. S. P. 2 591 589 (1952); Chem. Abs., **48**, 11 485 (1954).
72. V. A. Tartakovskii, A. A. Onishchenko, I. E. Chlenov, and S. S. Novikov, Dokl. Akad. Nauk SSSR, **167**, 844 (1966).
73. F. Brower and H. Burkett, J. Amer. Chem. Soc., **75**, 1082 (1953).
74. E. R. Bissel, J. Org. Chem., **26**, 5100 (1961).
75. I. L. Knunyants, B. L. Dyatkin, A. V. Fokin, and V. A. Komarov, Izv. Akad. Nauk SSSR, Ser. Khim., 1425 (1964).
76. V. A. Komarov and N. N. Sorokin, USSR P. 166 664 (1963); Byul. Izobret., **23**, 18 (1964).
77. A. V. Fokin, V. A. Komarov, V. A. Komarov, I. N. Sorokin, and S. M. Davydova, Zhur. Vses. Khim. Obshch. im. Mendeleeva, **10**, 354 (1965).
78. I. L. Knunyants and A. V. Fokin, Dokl. Akad. Nauk SSSR, **111**, 1035 (1956).
79. I. L. Knunyants and A. V. Fokin, Dokl. Akad. Nauk SSSR, **112**, 67 (1957).
80. M. Hauptschein and R. E. Oesterling, J. Org. Chem., **28**, 1279 (1963).
81. I. L. Knunyants, A. V. Fokin, and V. A. Komarov, Zhur. Vses. Khim. Obshch. im. Mendeleeva, **7**, 709 (1962).
82. Yu. V. Baskov and V. V. Perekalin, Dokl. Akad. Nauk SSSR, **136**, 1075 (1961).
83. G. Kh. Kamai, A. D. Nikolaeva, V. S. Nikolaev, and R. Karimov, Trudy Kazan. Khim.-Tekh. Inst., **30**, 120 (1962).
84. E. C. Kooijman, E. Farenhorst, and E. G. Werner, Rec. Trav. chim., **70**, 689 (1961).
85. G. B. Bachman and C. Vogt, J. Amer. Chem. Soc., **80**, 2987 (1958).
86. A. V. Fokin, Yu. M. Kosyrev, I. N. Sorokin, and K. V. Frosina, Izv. Akad. Nauk SSSR, Ser. Khim., 1772 (1963).
87. H. Biltz and E. Kedesdy, Ber., **33**, 2190 (1900).
88. H. Biltz, Ber., **30**, 1200 (1897).
89. E. Ott and W. Bossaler, Ber., **76**, 88 (1943).
90. Yu. V. Baskov and V. V. Perekalin, Zhur. Org. Khim., **1**, 236 (1965).
91. W. Fogt and K. Gehrmann, German P. 1 103 917 (1961); Chem. Abs., **56**, 1345 (1962).
92. H. Biltz, Ber., **35**, 1533 (1902).
93. H. Johnston, U. S. P. 3 054 828 (1960); Chem. Abs., **58**, 3315e (1963).
94. E. C. Kooijman and J. Overhoff, U. S. P. 2 473 341 (1949); Chem. Abs., **43**, 6646 (1949).
95. B. P. 637 252 (1950); Chem. Abs., **44**, 8360 (1950).
96. Danish P. 679 261 (1951); Chem. Abs., **45**, 10 478 (1951).
97. A. D. Nikolaeva, E. V. Red'kina, and G. Kamai, Trudy Kazan. Khim.-Tekh. Inst., **23**, 243 (1957).
98. I. V. Martynov and Yu. L. Kruglyak, Zhur. Vses. Khim. Obshch. im. Mendeleeva, **8**, 237 (1963).
99. I. V. Martynov, Yu. L. Kruglyak, and S. N. Makarov, Zhur. Obshch. Khim., **33**, 3382 (1963).
100. I. V. Martynov, Yu. L. Kruglyak, and S. N. Makarov, Zhur. Obshch. Khim., **33**, 3384 (1963).
101. I. V. Martynov, Yu. L. Kruglyak, and S. N. Makarov, Zhur. Obshch. Khim., **33**, 3386 (1963).
102. I. V. Martynov, Yu. L. Kruglyak, S. N. Makarov, and V. G. Tkachev, Zhur. Obshch. Khim., **33**, 3388 (1963).
103. A. I. Titov, Dokl. Akad. Nauk SSSR, **149**, 330 (1963).
104. I. L. Knunyants, A. S. German, and I. N. Rozhkov, Izv. Akad. Nauk SSSR, Ser. Khim., 1946 (1963).
105. I. L. Knunyants, A. S. German, and I. N. Rozhkov, Izv. Akad. Nauk SSSR, Ser. Khim., 1950 (1963).
106. I. L. Knunyants, B. A. Dyatkin, L. S. German, I. N. Rozhkov, and V. A. Komarov, Zhur. Vses. Khim. Obshch. im. Mendeleeva, **8**, 709 (1963).
107. M. I. Konovalov, Zhur. Russ. Fiz.-Khim. Obshch., **36**, 220 (1904).
108. M. I. Konovalov, Zhur. Russ. Fiz.-Khim. Obshch., **38**, 607 (1906).
109. H. Shechter and F. Conrad, J. Amer. Chem. Soc., **72**, 3371 (1950).
110. E. T. McBee, H. B. Hass, and J. M. Robinson, J. Amer. Chem. Soc., **72**, 3579 (1950).
111. Sh. V. Aliev and R. N. Degtyarenko, Izv. Vys. Ucheb. Zaved., Neft' i Gaz, No. 5, 109 (1958).
112. H. Wieland and E. Sakellarios, Ber., **52**, 898 (1919).
113. H. B. Hass, A. G. Susic, and R. L. Heider, J. Org. Chem., **15**, 8 (1950).
114. V. T. Kataev, Soobshch. Nauch. Rabot. Vses. Khim. Obshch. im. Mendeleeva, No. 2, 49 (1955).
115. L. Clapp, J. Brown, and Z. Zeftel, J. Org. Chem., **15**, 1043 (1950).
116. H. Kondo, H. Katoaka, and V. Baba, Ann. Report ITSUU Lab., No. 4, 20 (1953); Chem. Abs., **50**, 11 982 (1956).
117. P. Askenasy and V. Meyer, Ber., **25**, 1701 (1892).
118. E. T. McBee and E. F. Riley, U. S. P. 2 337 912 (1943); Chem. Abs., **38**, 3295 (1944).
119. E. F. Riley and E. T. McBee, Abs. St. Louis Meeting, Amer. Chem. Soc., April 1941.

120. D.C.Sayles and E.F.Degering, J.Amer.Chem.Soc., **71**, 3161 (1949).
121. A.Erm, Chem.Listy, **50**, 668 (1956).
122. L.Henry, Bull.Classe Sci., Acad.roy.Belg., [3], **33**, 115 (1896); Chem.Zentr., **1**, 741 (1897).
123. L.Henry, Compt.rend., **120**, 1265 (1895); Chem.Zentr., **11**, 156 (1895).
124. L.Henry, Rec.Trav.chim., **17**, 1 (1898); Chem.Zentr., **1**, 926 (1898).
125. L.Henry, Bull.Classe Sci., Acad.roy.Belg., [3], **37**, 162 (1899); Chem.Zentr., **1**, 1154 (1899).
126. A.Shaw, Bull.Classe Sci., Acad.roy.Belg., [3], **34**, 1019 (1898); Chem.Zentr., **1**, 439 (1898).
127. J.Pauwels, Bull.Classe Sci., Acad.roy.Belg., [3], **34**, 645 (1898); Chem.Zentr., **1**, 193 (1898).
128. T.Moussett, Bull.Classe Sci., Acad.roy.Belg., 622 (1901); Chem.Zentr., **1**, 399 (1902).
129. C.A.Grob and H.von Sprecher, Helv.Chim.Acta, **35**, 902 (1952).
130. C.A.Grob, U.S.P. 2545433 (1951); Chem.Abs., **46**, 3085 (1952).
131. A.F.Childs, L.J.Golsworthy, G.F.Harding, S.G.P.Plant, and G.A.Weeks, J.Chem.Soc., 2320 (1948).
132. S.P.Lingo, U.S.P. 2397358 (1946).
133. H.Kleinfeller, Ber., **62**, 1582 (1929).
134. M.Simonetta and G.Favini, Atti Accad.naz.Lincei, Rend. Classe Sci.fis.mat.nat., **14**, 119 (1953); Chem.Abs., **48**, 2568 (1954).
135. O.Schick, German P. 856889; Chem.Abs., **52**, 9191 (1958).
136. J.P.Fourneau, Bull.Soc.chim.(France), **7**, 603 (1940); Chem.Abs., **3**, 2845 (1942).
137. P.Nikolinski, J.Mladenov, S.Dramov, and M.Tepelikyan, Godisnik Khim.-Tekhnol.Inst., **6**, 95 (1959); Chem.Abs., **56**, 3336c (1962).
138. T.Urbanski and R.Kolinski, Roczniki Chem., **30**, 201 (1956).
139. G.Fort and A.McLean, J.Chem.Soc., 1902 (1948).
140. S.S.Novikov, V.M.Belikov, and L.V.Epishina, Izv.Akad. Nauk SSSR, Otd.Khim.Nauk, 1111 (1962).
141. S.S.Novikov and G.A.Shvekhgeimer, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1026 (1960).
142. G.B.Bachman, U.S.P. 3169150 (1963); Chem.Abs., **62**, 14500d (1965).
143. G.B.Bachman and R.O.Downs, U.S.P. 3054829 (1961); Chem.Abs., **58**, 2370g (1963).
144. N.Ya.Dem'yanov, Zhur.Russ.Fiz.-Khim.Obshch., **30**, 898 (1898).
145. O.Piloty and O.Ruff, Ber., **30**, 2057 (1897).
146. Belg.P. 643786 (1963); Chem.Abs., **63**, 13077 (1965).
147. P.Nouble, W.Reed, and F.Borgardt, U.S.P. 3180899 (1962); Chem.Abs., **63**, 11359e (1965).
148. T.M.Benziger and R.R.Rohwer, U.S.P. 3207796 (1964); Chem.Abs., **63**, 14703a (1965).
149. L.Henry, Compt.rend., **123**, 311 (1896); Chem.Zentr., **11**, 629 (1896).
150. E.L.Pattison, W.J.Cott, W.C.Howell, and R.W.White, J.Amer.Chem.Soc., **78**, 3484 (1956).
151. T.S.Work, J.Chem.Soc., 194 (1946).
152. T.S.Work, J.Chem.Soc., 197 (1946).
153. R.Kh.Freidlina, V.N.Kost, and A.N.Nesmeyanov, Izv. Akad.Nauk SSSR, Otd.Khim.Nauk, 233 (1955).
154. H.Dreyfus, U.S.P. 2345701 (1944); Chem.Abs., **38**, 4620 (1944).
155. H.Schechter and L.Zeldin, J.Amer.Chem.Soc., **73**, 1276 (1951).
156. L.Herzog, K.Klager, and H.Gold, J.Org.Chem., **23**, 1809 (1958).
157. L.Herzog, U.S.P. 3000969 (1957); Chem.Abs., **56**, 4618 (1962).
158. R.M.Scribner, U.S.P. 3057931 (1959); Chem.Abs., **58**, 6694c (1963).
159. V.A.Tartakovskii, B.G.Gribov, and S.S.Novikov, Izv. Akad.Nauk SSSR, Ser.Khim., 1074 (1965).
160. E.B.Hodge, U.S.P. 2370540 (1945); Chem.Abs., **39**, 3549^3 (1945).
161. E.B.Hodge, J.Amer.Chem.Soc., **70**, 2006 (1948).
162. H.D.Anspon, U.S.P. 3041379 (1950); Chem.Abs., **57**, 13618b (1962).
163. R.N.Boyd and R.H.Hansen, J.Amer.Chem.Soc., **75**, 3737 (1953).
164. R.Scholl and G.Mattaiopouleus, Ber., **29**, 1550 (1896).
165. R.N.Haszeldine, B.P. 770619 (1957); Chem.Abs., **51**, 14790 (1957).
166. R.A.Bekker, B.L.Dyatkin, and I.L.Knunyants, Izv.Akad. Nauk SSSR, Ser.Khim., 194 (1966).
167. G.A.Shvekhgeimer and N.L.Shul'man, Zhur.Org.Khim., **2**, 560 (1966).
168. M.N.Gold, J.Amer.Chem.Soc., **68**, 2544 (1946).
169. M.N.Gold, U.S.P. 2414595 (1947); Chem.Abs., **41**, 4166g (1947).
170. B.P. 593109 (1947); Chem.Abs., **44**, 653e (1950).
171. P.Pfeiffer, Ber., **47**, 1755 (1914).
172. D.E.Worrall, J.Amer.Chem.Soc., **60**, 2841 (1938).
173. D.E.Worrall and J.Finkel, J.Amer.Chem.Soc., **61**, 2969 (1940).
174. D.E.Worrall and H.T.Wolosinski, J.Amer.Chem.Soc., **62**, 2449 (1940).
175. R.Scholl and M.Brenneisen, Ber., **31**, 642 (1898).
176. W.E.Parham and J.L.Bleasdale, J.Amer.Chem.Soc., **73**, 4664 (1951).
177. V.V.Perekalin and O.M.Lerner, Dokl.Akad.Nauk SSSR, **129**, 1303 (1959).
178. A.A.Petrov, K.B.Rall', and A.I.Vil'davskaya, Zhur.Org. Khim., **1**, 240 (1965).
179. L.S.Smith and V.A.Engehardt, J.Amer.Chem.Soc., **71**, 2671 (1949).
180. L.I.Smith and V.A.Engehardt, J.Amer.Chem.Soc., **71**, 2676 (1949).
181. L.I.Smith, Chem.Rev., **23**, 255 (1938).
182. P.G.Bay, U.S.P. 3100805 (1962); Chem.Abs., **60**, 421b (1964).
183. P.G.Bay, U.S.P. 3100806 (1962); Chem.Abs., **60**, 421c (1964).
184. L.I.Smith and R.M.Scribner, J.Amer.Chem.Soc., **78**, 3412 (1956).
185. A.S.Sokova, D.I.Yurchenko, and V.V.Perekalin, Zhur. Org.Khim., **1**, 1707 (1965).
186. V.A.Tartakovskii, B.G.Gribov, I.A.Sevast'yanova, and S.S.Novikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1624 (1965).
187. German P. 1188082 (1962); Chem.Abs., **62**, 13152 (1965).
188. A.P.Fourneau, Bull.Soc.chim.(France), **11**, 141 (1944); Chem.Abs., **40**, 24397 (1946).
189. H.Irving, J.Chem.Soc., 797 (1936).
190. M.Simonetta and G.Favini, Atti Accad.naz.Lincei, Rend. Classe Sci.fis.mat.nat., **14**, 268 (1953); Chem.Abs., **47**, 10974^c (1953).
191. M.Simonetta and G.Favini, Atti Accad.naz.Lincei, Rend. Classe Sci.fis.mat.nat., **17**, 375 (1954); Chem.Abs., **49**, 10832 (1955).
192. M.Simonetta and G.Favini, Atti.Accad.naz.Lincei, Rend. Classe Sci.fis.mat.nat., **18**, 636 (1955); Chem.Abs., **50**, 4600 (1956).
193. S.Carra and P.Beltrane, Gazzetta, **91**, 504 (1961); Chem.Abs., **56**, 15339d (1962).
194. L.Herzog, U.S.P. 3000933 (1957); Chem.Abs., **56**, 1346a (1962).

195. H.Brintzinger and A.Scholz, Ber., **83**, 141 (1950).
196. J.Thompson, S.Louloudes, F.Fulmer, F.Evans, and H.Burkett, J.Amer.Chem.Soc., **75**, 5006 (1953).
197. H.Dewitt, B.P. 2732359 (1956).
198. I.L.Knunyants, L.S.German, and I.N.Rozhkov, Izv.Akad. Nauk SSSR, Ser.Khim., 1630 (1964).
199. S.S.Novikov, V.A.Tartakovskii, and S.L.Ioffe, Uspekhi Khim., **35**, 43 (1966) [Russ.Chem.Rev., 19 (1966)].
200. J.Colonge and G.Lartigau, Bull.Soc.chim.(France), 738 (1965).
201. C.M.Himel, U.S.P. 2525353 (1950); Chem.Abs., **45**, 2017e (1951).
202. F.D.Chattaway, J.G.Drewitt, and G.D.Parkes, J.Chem. Soc., 1693 (1936).
203. I.Romanova, Sbornik Stud.Rabot Sredneaz.Gos.Univ.im Lenina, No.8, 49 (1954).
204. H.B.Hass and A.C.Whitaker, U.S.P. 2447504 (1948); Chem.Abs., **43**, 3024i (1949).
205. V.Mark, U.S.P. 2771470 (1956); Chem.Abs., **51**, 6686 (1957).
206. F.Beran, V.Prey, and H.Böhm, Mitt.Chem.Forschungsinst., Wirtsch.Oesterr., **6**, 54 (1952); Chem.Abs., **46**, 9766e (1952).
207. T.Nishimura, Bull.Chem.Soc.Japan, **27**, 617 (1954).
208. R.N.Krug and O.C.Elmer, U.S.P. 2844538 (1958); Chem. Abs., 52, 19, 115d (1958).
209. J.C.Boad and H.R.Dittmar, U.S.P. 182252 (1958); Chem. Abs., **52**, 7680d (1958).

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The Chemistry of Acyl and Sulphonyl Isocyanates, Isothiocyanates, and Isoselenocyanates

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The review presents the latest advances in the chemistry of acyl and sulphonyl isocyanates, isothiocyanates, and isoselenocyanates. All the methods for the preparation of these compounds are examined and treated systematically. Their reactions and their physical properties are described and the problems of their structure and isomerisation are discussed. In conclusion the available literature data on the practical importance and applications of acyl and sulphonyl isocyanates, isothiocyanates, and isoselenocyanates are presented.

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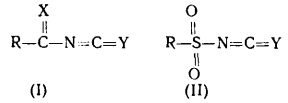
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I. INTRODUCTION

Organic isothiocyanates and isocyanates, first obtained towards the end of the last century, are assuming increasing importance at the present time. The enormous interest in this class of compounds is due to the fact that, by virtue of their reactivity, they have become important starting materials and intermediates for the synthesis of a wide variety of organic compounds, many of which have found practical applications. Organic isocyanates are essential for the synthesis of polymeric materials, synthetic fibres, medicinal preparations, insecticides, herbicides, fungicides, nematocides, photographic materials, and many other products.

In 1964 an International Symposium was held in Czechoslovakia on the chemistry of isocyanates [1]. Novel synthetic methods have been described in papers published recently[2-5] and new synthetic and practical applications have been found for organic isocyanates, isothiocyanates, and thiocyanates[6-7]. Reviews of the chemistry of isocyanates have been published[8-10].

The data on acyl isocyanates, isothiocyanates, and isoselenocyanates are scattered in many sources and information about them has not been compiled. The present review is an attempt to fill this gap. It deals with new data on the structure, methods of preparation, properties, and practical applications of acyl isocyanates, isothiocyanates, and isoselenocyanates, thioacyl isocyanates, sulphonyl isocyanates, and sulphonyl isothiocyanates with the general formulae (I) and (II):



(I) (II)

where X and Y can have the following significance: X = Y = O, X = Y = S, X = Y = Se, X = O and Y = S or Se, and X = S and Y = O or Se; R may be a halogen, alkyl, aryl, or an alkoxy- aryloxy-, or dialkylamino-group, etc.

The chemical properties of sulphonyl isocyanates [(II), Y = O] have been examined in Ulrich's review[10]. We shall deal only with those data on this class of compounds which were not included in Ulrich's review, but which are nevertheless of considerable interest.

Of the two types of acyl isocyanates and isothiocyanates examined here, the first has been known for a long time, but recently there has been an increase of interest in these compounds. The chemistry of thioacyl isocyanates of the type R–C(=S)–N=C=O began to be studied in the last 4–5 years, while thioacyl isothiocyanates R–C(=S)–N=C=S and thioacyl isoseleno-