U. D. C. 547.232/233

Progress in the Chemistry of Primary Aliphatic Nitroamines

A.L.Fridman, V.P.Ivshin, and S.S.Novikov

Methods of making primary aliphatic nitroamines are considered. In addition to the well-known traditional methods for the preparation of nitroamines, little known methods for making them are examined and prospects for their further development are discussed.
This review is the first attempt in the world's literature to systematise the wealth of published material on primary aliphatic nitroamines. The literature is covered up to the end of 1967 or beginning of 1968. There is a bibliography of 207 references.

CONTENTS

I. Introduction 640
II. Methods of making primary nitroamines 640
III. Physical properties and structure 644
IV. Chemical properties 646
V. Analytical determination 651
VI. Certain aspects of practical use 651

I. INTRODUCTION

The progress in the chemistry of aliphatic nitro-compounds has stimulated interest in the nitroamines. This is shown by the large number of journal papers and patents published in recent years. The interest in the chemistry of aliphatic primary nitroamines arose not only because of the most interesting conversions of these compounds[1-3], but also the wide range of practical applications[4-11].

Isolated facts about the methods of preparation and properties of the primary aliphatic nitroamines can be found in monographs and review papers devoted to the nitro-compounds[1,12-14]. However, many of these papers are out of date or do not give sufficiently complete information about primary aliphatic nitroamines. There is no previous review paper on nitroamines in the Russian literature.

The present review surveys the published information on aliphatic primary nitroamines up to the end of 1967. In doing this the classical studies of Franchimont and his students and also other work on nitroamines carried out at the end of the last century is cited only where necessary and for the purpose of completeness in the material given. The early studies on nitroamines were surveyed more completely in 1912 by Baker[1].

Historically, two main periods can be distinguished in the development of the chemistry of the primary aliphatic nitroamines. The first began in 1888, when Franchimont synthesised methyl nitroamine[15,16], and continued for 20–25 years. This period is characterised by the appearance of fundamental studies on the nitroamines by such investigators as Franchimont[16-28], Klobbie[16,17,21,26], van Erp[27,29,30], Romburgh[31,32], Hantzsch[33-37], Baker[1,38,39], and others[40-45]. After 1915 until the nineteen-forties there was little interest in the nitroamines. But in 1948–1952 a long series of papers by Lamberton and coworkers[2,46-55] appeared, as well as interesting papers by Wright and coworkers[56-60], the work of McKay[61-74], and others[75-80]. Interest in nitroamines was reawakened and has not diminished since.

II. METHODS OF MAKING PRIMARY NITROAMINES†

Most of the known methods of making nitroamines can be divided into four groups: (1) the nitration of amines with preliminary protection of the amino-group; (2) the nitration of *N*-dichloroamines (Smart and Wright's method); (3) synthesis of nitroamines from nitroguanidine; and (4) direct nitration of amines by certain nitrating agents. There are also a few methods which at present are not of a general nature.

1. Nitration of Amines with a Previously Protected Amino-Group

Primary nitroamines, with rare exceptions, are readily decomposed by concentrated acids and cannot be obtained by the nitration of corresponding amines with nitric acid or its mixture with sulphuric acid. For the successful nitration of an amino-group it must first be protected. There are four main stages in the preparation of primary nitroamines by this method: (1) introduction of a protective grouping into the amino-group; (2) nitration of the protected amine; (3) removal of the protective grouping; and (4) isolation of the nitroamine.

Acetyl, formyl, oxalyl, alkoxycarbonyl, carbonyl, picryl, tosyl, and cyanoethyl groups can be used as the protective groupings.

The simplest of the primary nitroamines—methylnitroamine—was synthesised by the introduction of the oxalyl group into methylamine[21]:

$$CH_3NH_2 + (COCl)_2 \rightarrow (CH_3NHCO)_2 \xrightarrow{HNO_3} \left(\begin{array}{c} NO_2 \\ | \\ CH_3NCO \end{array}\right)_2 \xrightarrow{NH_3,\ ether}$$

$$\rightarrow \begin{array}{c} NO_2 \\ | \\ CH_3NH \end{array} \cdot NH_3 \xrightarrow{HCl} \begin{array}{c} NO_2 \\ | \\ CH_3NH \end{array}.$$

† Here and subsequently primary aliphatic nitroamines are being discussed, therefore the term "aliphatic" is often omitted.

The protection of amines by the oxalyl group is general and is used for the synthesis of a series of primary nitroamines and also of ethylenebisnitroamine[21,43,81]. The symmetric dialkyloxamides are readily nitrated with nitric acid or nitrating mixture. An example is the nitration of polynitroalkyloxamides[82-84]:

$$\begin{matrix}OCOC_2H_5\\OCOC_2H_5\end{matrix} + 2H_2NCH_2CH_2C(NO_2)_3 \rightarrow \begin{matrix}OCNCHH_2CH_2C(NO_2)_3\\OCNHCH_2CH_2C(NO_2)_3\end{matrix} \rightarrow$$

$$\xrightarrow{HNO_3+H_2SO_4} \begin{matrix}OCN(NO_2)CH_2CH_2C(NO_2)_3\\OCN(NO_2)CH_2CH_2C(NO_2)_3\end{matrix}.$$

The removal of the oxalyl group proceeds smoothly under the action of ammonia or boiling water.

Franchimont and his students[16,85] used an alkoxycarbonyl group as well as oxalyl as a protecting group in the nitration of amines. The method of preparing primary nitroamines through alkylnitrourethanes was subsequently perfected and developed and is now very important.

N-Alkylcarbamates are usually obtained by the reaction of esters of chlorocarboxylic acids with alkylamines in the presence of alkali[86]. However, often *N*-alkylcarbamates can also be obtained by other methods and they are more accessible than amines. A method of obtaining *N*-alkyl-*N*-nitrourethanes by the alkylation of nitrourethane with diazo-compounds or alkyl halides is interesting in this connection[55,87]:

$$\left.\begin{matrix}RCHN_2 + HN(NO_2)COOC_2H_5\\RCH_2Hal + AgN(NO_2)COOC_2H_5\end{matrix}\right\} \rightarrow RCH_2NCOOC_2H_5.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad NO_2$$

The production of various polynitroalkyl carbamates by the decomposition of azides of polynitrocarboxylic acids in the presence of alcohols, the reaction of isocyanates with alcohols, etc., has been described[88-96]:

$$RC(NO_2)_2CH_2CH_2CH_3 \xrightarrow{R'OH} RC(NO_2)_2CH_2CH_2NHCOOR' \xrightarrow{HNO_3+Ac_2O}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad O$$

$$\rightarrow RC(NO_2)_2CH_2CH_2NCOOR'.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad NO_2$$

The nitration of *N*-alkylcarbamates is usually undertaken under the action of a sevenfold to fifteenfold excess of concentrated nitric acid[16,33,23,85,97]. Curry and Mason[98] proposed a mixture of acetic anhydride with nitric acid, which was more effective than nitric acid alone. This mixture nitrated many alkyl carbamates, including t-butyl carbamate, and also polynitroalkyl carbamates[89], whereas *N*-alkyl carbamates with branched alkyl residues are not nitrated by nitric acid[30]. An attempt to use tetranitromethane for the nitration of alkyl carbamates was unsuccessful[99].

The removal of an alkoxycarbonyl group is usually done under the action of ammonia in ethereal solution:

$$\begin{matrix}RNCOOC_2H_5\\NO_2\end{matrix} \xrightarrow{NH_3,\ ether} \begin{matrix}RNH\cdot NH_3\\NO_2\end{matrix} + C_2H_5OCONH_2.$$

Many alkylnitroamines and also ethylene-, trimethylene-, tetramethylene-, and pentamethylene-bisnitroamines were obtained by this method[16,85,100]. Hantzsch and Metcalf[33] obtained *N*-nitroglycine and some of its derivatives in a similar manner. Blomquist and Fiedorek[33] patented a method for making nitrates of nitroaminoalcohols of the type $C_2NOCH(R)CH(R')NHNO_2$.

It was subsequently shown that not only ammonia but also other amines are suitable for splitting *N*-alkyl-*N*-nitrourethanes and that the amination of *N*-alkyl-*N*-nitrourethanes is general and can be used to obtain the amine salts of primary nitroamines[99]. Hexamethylene-1,6-bisnitroamine was made in this way[99].

The hydrolysis of polynitroalkyl-*N*-nitrocarbamates has not been described. Such a study should give interesting information about the effect of electronegative groups on the ease of removal of alkoxycarbonyl groups.

Primary nitroamines are often obtained by the nitration of alkylureas. As long ago as 1888 Franchimont and Klobbie[17] nitrated imidazolid-2-one with nitrating mixture and then decomposed the 1,3-dinitroimidazolid-2-one with water to ethylenebisnitroamine:

$$\begin{matrix}H_2C-N\\|\\H_2C-N\end{matrix}\!\!>\!CO \xrightarrow{HNO_3+H_2SO_4} \begin{matrix}H_2C-N(NO_2)\\|\\H_2C-N(NO_2)\end{matrix}\!\!>\!CO \xrightarrow{H_2O} \begin{matrix}NO_2\\|\\HN-CH_2-CH_2-NH\end{matrix}\!\!<\begin{matrix}NO_2\\|\\.\end{matrix}$$

Imidazolid-2-one can also be nitrated with nitric acid[101].

In nitration, monoalkylureas are readily converted into *N*-alkyl-*N'*-nitroureas; nitration of the nitrogen atom connected with the alkyl group does not usually take place[81]. An exception is methylurea, which is converted rather smoothly into *N*-methyl-*N*-nitrourea. The latter can be hydrolysed to methylnitroamine[39].

An interesting paper was recently published on the preparation of the first representative of the *N*-dinitroamine series—methyl-*N*-dinitroamine, obtained by the nitration of methylurea nitrate by a mixture of acetic anhydride and nitric acid[102]:

$$CH_3NHCNH_2\cdot HNO_3 \xrightarrow{HNO_3+Ac_2O} CH_3N(NO_2)(NO_2).$$
$$\qquad\quad O$$

In nitration, *sym*-dimethylurea is smoothly converted into *NN'*-dinitro-*NN'*-dimethylurea[103]. We note that the nitration of substituted ureas and their derivatives has not yet been sufficiently studied and further investigations in this field can lead to both the development of simple methods for making primary nitroamines and also to the preparation of other interesting compounds. This is shown by the above study by Japanese scientists[102] and also by other investigations[104-106].

The acetyl group is important as a protective group for the nitration of amines. Thus, one of the methods of obtaining ethylenebisnitroamine is based on the introduction of acetyl groups into ethylenediamine followed by the nitration of ethylenebisacetamide with a mixture of nitric acid and acetic anhydride[81]. The acetyl group is readily detached with water, alkali, or ammonia. Methylenebisnitroamine was obtained from methylenediamine in a similar fashion[47]. The synthesis of polynitroalkyl-*N*-nitroamines by the hydrolysis of polynitroalkyl-*N*-nitroacetamides is described in the patent literature[107-109].

Formyl groups are sometimes used instead of acetyl for the protection of amino-groups[110]:

$$H_2C(NHCHO)(NHCHO) \rightarrow H_2C(N(NO_2)CHO)(N(NO_2)CHO) \rightarrow H_2C(N(NO_2)H)(N(NO_2)H).$$

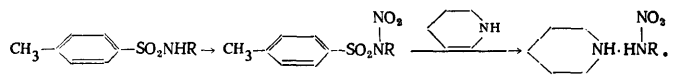
It is worth noting an extremely interesting method for obtaining *N*-alkylacetamides and *N*-alkylformamides, based on the condensation of the corresponding *N*-(hydroxymethyl)amides with nitroalkanes, for example, nitroform:

$$RCONHCH_2OH + HC(NO_2)_3 \rightarrow RCONHCH_2C(NO_2)_3 + H_2O.$$

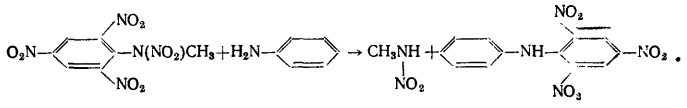
Unfortunately, the nitration of the trinitroethylacetamide and trinitroethylformamide thus obtained has not been described.

Gillibrand and Lamberton used a tosyl group for the protection of the amino-group[55]. The tosyl group is removed under rather severe conditions but the yields of the

primary nitroamines are reasonably high[111]. Piperidine is a convenient reagent for removing the tosyl group[111]:

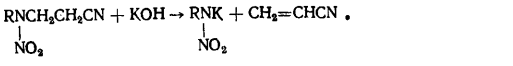


An example of the production of methylnitroamine by the removal of the picryl group from methylpicrylnitroamine under the action of aniline or *p*-toluidine has been described[1]:



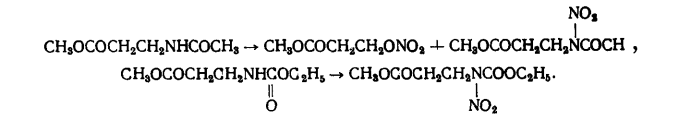
Since alkylpicrylnitroamines are readily obtained in the nitration of alkylanilines or dialkylanilines[12], the method of making primary nitroamines by using a protective picryl group opens up great possibilities.

Kissinger and Schwartz[112] observed the cleavage of 2-cyanoethylnitroamine in alkali into a salt of the nitroamine and acrylonitrile:

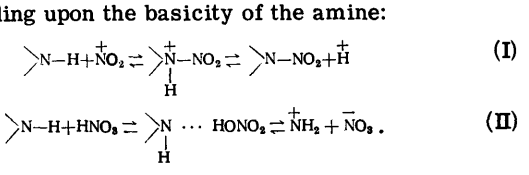


Although only one example of this reaction has been described, the readily accessible β-cyanoethylnitroamines, which are obtainable by the nitration of the corresponding aminonitriles[113,114], can probably serve as the initial compounds for obtaining primary nitroamines.

An analysis of the methods of preparation of primary nitroamines with protected amino-groups shows that the urethane method is the most universal, simplest, and most available at the present time. In every instance there are no indications in the literature of unsuccessful examples of the nitration of *N*-alkylcarbamates or of the removal of alkoxycarbonyl groups from *N*-alkyl-*N*-nitrocarbamates. In this connection it is interesting to compare the nitration of esters of glycine and β-alanine with the use of various protecting groups. Whereas nitration of the *N*-acetyl derivative of the methyl ester of β-alanine gives the *N*-nitroamide in insignificant yield the corresponding urethanes are nitrated quantitatively[115]:



The mechanism of the *N*-nitration of protected amines has not been discussed in the literature and there have not been systematic investigations in this field. A considerable drop in the basicity of the amine generally occurs on the introduction of the above protecting groups. It is well known that in the dialkylamine series strong bases without catalysts are not nitrated at the nitrogen atom, whereas amines of low basicity are nitrated rather readily[116]. Lamberton[2] considers that the reaction can proceed in two ways, depending upon the basicity of the amine:

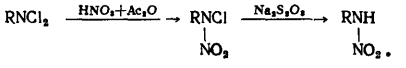


Strong bases react by scheme (II) and weak by scheme (I).

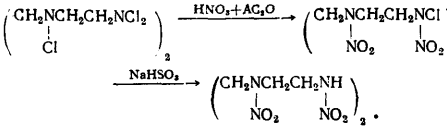
A protected amino-group is a weak base and its nitration can be described by scheme (I). The reversibility of the nitration is evidence for this scheme. It is known that *sym*-dinitrodimethyloxamide in sulphuric acid solution is a source of the nitronium cation and exhibits a nitrating action[117]. Similar examples have been given by Holstead and Lamberton[46].

2. Nitration of *N*-Dichloroamines (Smart and Wright's Method)

In 1948 Smart and Wright[56] proposed a new method for obtaining primary nitroamines. They found that on treatment of *N*-dichloroamines in an excess of acetic anhydride with concentrated nitric acid, chlorine is removed with the formation of *N*-chloro-*N*-nitroamines. In a reducing medium the latter lose a second chlorine atom and are converted into primary nitroamines:

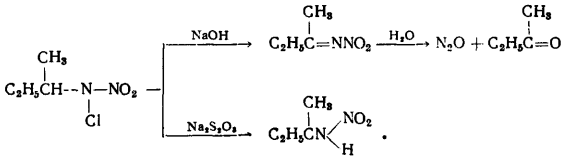


Butylnitroamine, isobutylnitroamine, n-octylnitroamine, ethylenebisnitroamine etc. have been obtained by Smart and Wright's method[56,57]. The example of *N*-hexachlorotriethylenetetramine has shown the possibility of the simultaneous substitution of nitro-groups for the chlorine atoms at primary and secondary nitrogen atoms[57]:

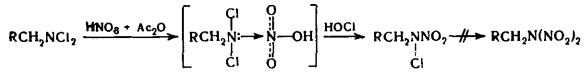


It is noteworthy that an intermediate *N*-chloro-*N*-nitroamine has been isolated in a pure form in only one instance, in small yield[56]. Nevertheless it is evident that *N*-chloro-*N*-nitroamines are more stable in acid than are primary nitroamines, which also ensures that the reaction will take place in the desired direction.

The replacement of a chlorine atom by hydrogen in *N*-chloro-*N*-nitroamines is effected under the action of aqueous solutions of alkalis, sodium hydrogen sulphite, or sodium thiosulphate[56,57]. When the product of the nitration of s-butyldichloroamine was treated with an aqueous solution of alkali the yield of s-butylnitroamine was only 10%, whereas sodium thiosulphate allowed the yield to be raised to 65%. It was thought[56] that depending upon the medium the intermediate *N*-chloro-*N*-nitroamine can be hydrolysed or can undergo intramolecular loss of hydrogen chloride[58]:



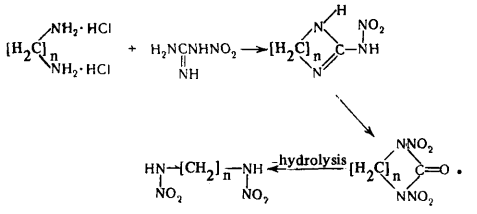
There has not been a thorough study of the mechanism of nitration of *N*-dichloroamines. In one of their papers[56] Smart and Wright suggested that nitric acid forms a complex with the *N*-dichloroamine, the nitrogen of the amino-group acting as a donor and the nitrogen of the nitric acid as an acceptor. The complex which is formed is unstable and readily loses hypochlorous acid to form an *N*-chloro-*N*-nitroamine. Because of the introduction of the nitro-group the *N*-chloro-*N*-nitroamine loses the donor properties and reaction cannot proceed further to form an *N*-dinitroamine:



3. Syntheses Based on Nitroguanidine

Nitroguanidine differs markedly from the primary nitroamines in its properties. Investigations in recent years [61] have shown that this compound should really be given a nitroimine structure. A review by McKay [14] dealt with the chemistry of nitroguanidine. The study of nitroguanidine derivatives has led to the discovery of new original methods of making primary nitroamines, which are also discussed in this section.

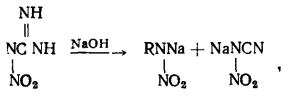
McKay and Manchester [62,63] developed a method for obtaining aliphatic bisnitroamines based on the nitration of the cyclic products of the interaction of diamines with nitroguanidine. The nitro-derivatives obtained are readily hydrolysed to the corresponding nitroamines:



1,2-Bisnitroaminopropane, 1,3-bisnitroaminobutane, and 1,3-bisnitroamino-2-nitroxypropane [62,63] were obtained in a similar manner.

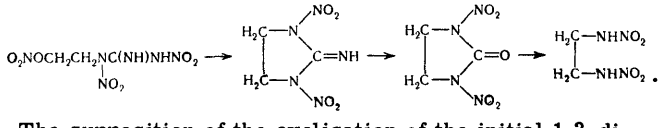
Primary nitroamines were obtained in many other instances. Thus in the cleavage of 2-amino-1-nitro-2-imidazoline a nitroamine salt is formed, the structure of which was proved by subsequent chemical transformations.

1-Alkyl-1,3-dinitroguanidines are split with alkali to salts of primary nitroamines and the extremely interesting, but little studied, cyanonitroamide [118]:



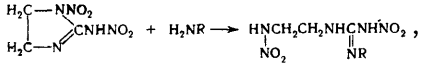
where R = CH_3 and n-C_4H_9.

The decomposition of 1,3-dinitro-1-(2-nitroxyethyl)-guanidine is extremely unusual. When this compound is boiled with water ethylenedinitroamine is isolated in 57% yield [118]:



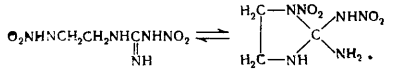
The supposition of the cyclisation of the initial 1,3-dinitro-1-(2-nitroxyethyl)guanidine is confirmed by the similar conversions of other *N*-(2-substituted ethyl)-*N'*-nitroguanidines [118].

In the interaction of 1-nitro-2-(nitroamino)imidazoline with ammonia or amines β-nitroaminoalkylnitroguanidines are formed [65,66,72,73]:



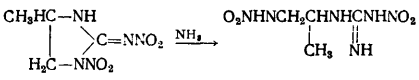
where R = H, CH_3, Ar.

Kirkwood and Wright [119] succeeded in showing that 1-nitro-2-(nitroamino)guanidine exists as two isomers. The position of the equilibrium is shifted to one side or the other depending upon the solvent:

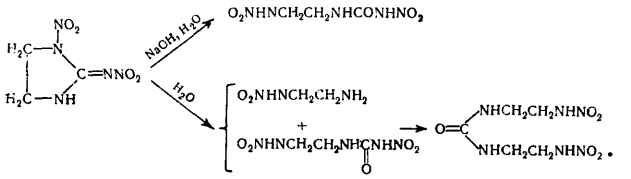


Later McKay [67] gave additional information in support of the existence of linear products.

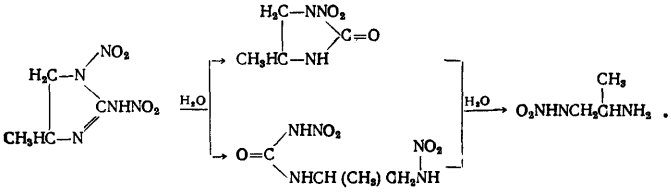
The difference in the opinions of these authors is evidently due to the ease of cyclisation and cleavage of the products of the addition of the amines to 1-nitro-2-nitriminoimidazolid-2-one. This circumstance makes difficult the hypothetical choice of any one structure. However, for certain compounds such a type of linear structure has been shown sufficiently clearly. For example, the product of the addition of ammonia to 4-methyl-1-nitro-2-nitriminoimidazolid-2-one is a linear primary nitroamine [68]:



When treated with alkali, 1-nitro-2-nitriminoimidazolid-2-ones are usually cleaved to primary nitroamines [69,70,120]. When 1-nitro-2-nitriminoimidazolid-2-one is hydrolysed with aqueous alkali, 3-nitro-1-(2-nitroaminoethyl)urea is obtained in good yield. The aqueous hydrolysis of this compound leads to bis-(2-nitroaminoethyl)urea as a result of the reaction of the primary decomposition products [121]:



Two products are also formed in the hydrolysis of 4-methyl-1-nitro-2-nitriminoimidazolid-2-one in water—*N*-2-(nitroamino)ethyl-1-methylnitrourea and 4-methyl-1-nitro-2-imidazoline, and on long boiling with water these are converted into 2-amino-3-nitroaminopropane [71]:



On dissolution in aqueous alkali, 1-nitro-2-propylamino-2-imidazoline is hydrolysed to *N*-2-nitroaminoethyl-*N'*-propylurea [120]. In an acid or alkali medium 1-nitro-2-*p*-acetamidophenylamino-1-nitro-2-imidazoline is hydrolysed to *N*-2-nitroaminoethyl-*N'*-pacetamidophenylurea [70].

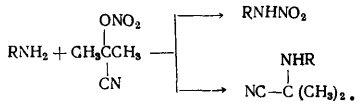
McKay and coworkers [74] described an interesting molecular rearrangement leading to the production of a primary nitroamine.

4. Direct Nitration of Amines

The relative complexity and multistage nature of the methods of synthesis of primary nitroamines are responsible for the search for new, simpler methods for their production. The most tempting was the direct nitration of primary amines.

From this point of view the method developed by Emmons and Freeman for the nitration of amines with acetone cyanohydrin nitrate 1-cyano-1-methylethyl nitrate is interesting [122]. Propyl, butyl, isobutyl, pentyl, and isopentyl nitroamines were obtained in 50–55% yield by this method. The reaction takes place under rather critical

conditions and is accompanied by the formation of aminonitriles:

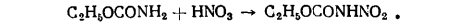


The method is suitable for the nitration of amines having bulky substituents at the α-carbon atom[122].

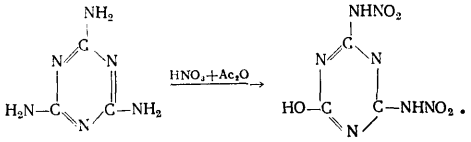
Another way of obtaining nitroamines was described recently in the patent literature. It is based on the reaction of nitryl fluoride with ammonia or amines in an inert solvent or in the vapour phase[123]. Information is available about the nitrating ability of nitrile chloride in relation to amines[124].

Primary nitroamines can also be obtained in the nitration of amines by acetyl nitrate in the presence of butyllithium[125]. The method is applicable only to compounds containing functional groups indifferent to butyl-lithium. Furthermore the complexity of the experimental conditions (low temperature, atmosphere of dry nitrogen) does not give this method a decisive advantage over the existing ones.

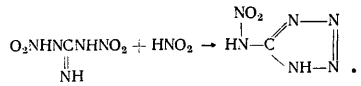
Although the methods of preparation and properties of nitroamides, which are similar in structure to the primary nitroamines, or those of aromatic and heterocyclic nitroamines are not discussed in the present review, we will note that some of these compounds can be obtained by the direct nitration of the corresponding amides and amines with nitric acid or nitrating mixture. Thus nitrourethanes are usually made by the nitration of urethane[47].



Benzosulphonitroamide and *p*-toluene sulphonitroamide are obtained in a similar fashion[126]. Aminopyridines are readily nitrated by nitrating mixture to the corresponding nitroaminopyridines[127]. The nitration of melamine with a mixture of acetic anhydride and nitric acid gives *NN'*-dinitroammeline[128]:



Triacetylmelamine gave nitroammelide. Under the action of nitrous acid, nitroaminoguanidine is converted into 5-nitroaminotetrazole[129,130]:

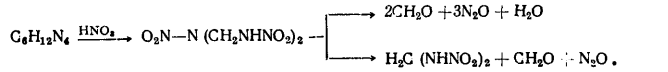


5. Other Methods of Preparation

The formation of nitroamines in the hydrolysis of linear products of the nitrolysis of tertiary amines has been described. Methylenebisnitroamine was first isolated as the barium salt from the pyrolysis products of hexamethylenetetramine[47].

2,4,6-Trinitro-2,4,6-triazaheptane-1,7-diol bistrifluoroacetate can be split by benzylamine to the corresponding amine salt of methylenebisnitroamine[131]. The hydrolysis of the linear products of the nitrolysis of Mannich bases also leads to the production of primary nitroamines[132].

The nitrolysis of hexamethylenetetramine is accompanied by the formation of a primary nitroamine as a side-product[133]. The latter is decomposed completely by hot water but under milder conditions it is hydrolysed to methylenebisnitroamine:

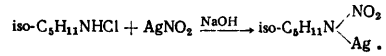


In reacting with nitric acid under mild conditions hexamethylenetetramine dinitrate forms 1,3-dinitro-1,3,5-triazapentane[134].

Freeman[135] obtained a series of nitroamines by the reduction of nitroimines with potassium tetrahydroborate or lithium tetrahydroaluminate. This work completed the discussion of the structure of nitroimines to which some investigators had ascribed the structure of pernitrosoketones.

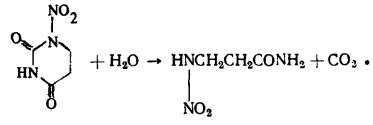
Examples are known of the production of primary nitroamines from the corresponding isodiazotates[136]. However, owing to the difficulty of obtaining the starting compounds this method is not widely used.

Finally, there is a single paper[137] on the production of a nitroamine in low yield by a reaction similar to the Wurtz reaction:



The preparation of primary nitroamines containing other functional groups in the alkyl residue is by the same methods as were given earlier. Naturally, the action of the functional group of the reagents employed for the preparation of the nitroamines must be considered. In particular, aminoalcohols are converted into the nitrates of the nitroaminoalcohols[19,138]. However, under certain conditions the nitrate group can be removed or its formation avoided completely[138,139].

Nitroaminoacetamide is obtained when nitrohydantoin is boiled in water for a long time[92]. Nitroaminopropionamide can be obtained from nitrohydrouracil[20]:



Free nitroaminocarboxylic acids are formed in the hydrolysis of amides with alkali. δ-Nitroaminovaleric and ϵ-nitroaminocapronic acids are obtained in the alkaline hydrolysis of the corresponding *N*-nitrolactams[140]. Propargylnitroamine is obtained by the usual scheme by the nitration of *N*-propargylurethane[141].

III. PHYSICAL PROPERTIES AND STRUCTURE

1. General Characteristics

Primary aliphatic nitroamines are liquids or readily melting crystalline compounds. The first member of the homologous series of monoalkylnitroamines—methylnitroamine—melts at 38°C,[16] ethylnitroamine at 6°C,[16] and the higher homologues are also low-melting or liquid substances. The bisnitroamines are solids whose melting points depend on the number and multiplicity of the methylene groups in the molecule.

Primary nitroamines are weak acids. Thus the pK_a of methylnitroamine is 6.0;[142] its homologues are even

weaker acids. When electronegative groups are introduced into the alkyl chain of the nitroamine the acidic properties increase. The dissociation constants of $\alpha\omega$-bisnitroamines have been determined[143]. A comparison of the pK values obtained with those for $\alpha\omega$-dicarboxylic acids shows that with increase in the number of methylene groups the difference between the first and second dissociation constants decreases in the bisnitroamine series more slowly than in the dicarboxylic acid series (Table 1).

Table 1. Dissociation constants of $\alpha\omega$-dinitroamines and $\alpha\omega$-dicarboxylic acids (20°C).

α,ω-Bisnitroamines	pK_1	pK_2	ΔpK	Acid	pK_1	pK_2	ΔpK
Methylene	5.0	6.6	1.6	Malonic	2.83	5.69	2.86
Ethylene	5.35	6.66	1.31	Succinic	4.22	5.67	1.45
Trimethylene	5.59	6.85	1.26	Glutaric	4.39	5.50	1.11
Tetramethylene	5.87	6.98	1.11	Adipic	4.43	5.49	0.95

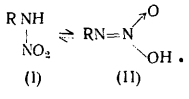
Baly and Desch studied the optical properties of the nitroamines[144]. They showed that the unsubstituted alkylnitroamines have normal molecular refraction.

The use of primary nitroamines as explosives stimulated the study for some of them of the thermochemical, stability and explosive characteristics. The information on these characteristics has been surveyed in Orlova's monograph[145]. Primary nitroamines are relatively stable thermally, the liquid compounds can be distilled under vacuum, and the thermal stability of the crystalline nitroamines is different. Methylenebisnitroamine is of low thermal stability, whereas ethylenebisnitroamine is distinguished by high stability, has good explosive characteristics, and diminished sensitivity to shock[146]. A differential thermal analysis of nitroamines was recently made[147]. Medard determined the heats of formation of ethylenebisnitroamine (25.65 kcal mole^{-1}) and nitroaminoethyl nitrate (45.8 kcal mole^{-1}).[148]

The physiological activity of the primary nitroamines has hardly been studied. There is information on the comparative physiological action on the human organism of nitromethane and methylnitroamine[149]. When the latter is introduced into the human organism it does not produce any changes in the composition and pressure of the blood, that is, unlike nitrates and nitroalkanes it is harmless for man. It was also noted that ethylenebisnitroamine has no harmful action on the human organism[12].

2. Structure and Spectra

The aliphatic nitroamines were first ascribed the structure of the true N-nitro-compounds (I). Later, Hantzsch[34-37] by starting from a formal analogy between the nitroalkanes and primary nitroamines, suggested that the latter exist in two tautomeric forms:



(I) (II)

By this scheme he explained the acidic properties of nitroamines and the formation of O-isomers in the alkylation of the salts of nitroamines. Hantzsch attempted to confirm this concept of tautomerism in a series of nitroamines by physicochemical methods. The evidence in support of tautomerism was that he observed an arrest (the time needed for the displacement of the equilibrium I⇌II) in the precipitation of the ammonium salt of the nitroamine on passing ammonia through a solution of the nitroamine in benzene. Furthermore, he observed a high temperature coefficient of electrical conductivity for salts of the nitroamine in aqueous solution. However, Euler showed[44] that these results cannot serve as proof of the tautomerism of the primary nitroamines.

Thorough physicochemical investigations made recently allowed the nature of the primary nitroamines to be more deeply understood. X-Ray structural analysis of ethylenebisnitroamine showed that the nitro-group in this compound exhibits normal properties, that is, the valence angles are similar to the angles of the nitro-group of p-dinitrobenzene, and the interatomic distances N–O (1.23 Å) in the nitroamine group are equal and comparable with the values for nitromethane[79]. Hence the conclusion that the structure of true N-nitro-compounds is more probable in the un-ionised form for the primary nitroamines. In addition there is a considerable shortening of the C–N and N–N bonds in comparison with the sum of the covalent radii (1.41 and 1.33 Å in comparison with 1.47 and 1.40 Å), and it is concluded that there is an electronic displacement from the nitrogen connected to the nitroamine group leading to the formation of a positive charge, which decreases the radius of the simple (N–C) bond of the nitrogen. The short N–N bond has 15% of the character of a double bond.

The X-ray structural method does not allow the location of the hydrogen atom in primary nitroamines to be determined. More reliable information on this aspect is obtained as a result of the spectroscopic analysis of nitroamines.

A study of the infrared spectra of a series of nitroamines showed that asymmetric vibrations in the range 1630–1550 cm^{-1} range and symmetric vibrations in the 1354–1262 cm^{-1} range are characteristic of the nitro-groups in these compounds. When there are electronegative substituents in the nitroamines the asymmetric vibrations are shifted to the side of higher frequencies[78,150,151]. The band in the 1000–948 cm^{-1} range is assigned to the vibrations of the N–N bond.

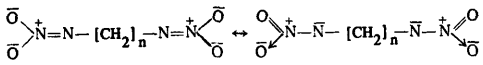
The complexity of the infrared spectra of the primary nitroamines in the 3600–3000 cm^{-1} range required additional confirmation that the bands in this region belong to the vibrations of the NH group. This information was obtained in a thorough study of the infrared spectra of crystalline ethylenebisnitroamine and tetramethylenebisnitroamine and their N-deuteriated analogues[152]. A comparison of the spectra of these nitroamine and their N-deuteriated derivatives allowed the 3240 and 3253 cm^{-1} bands observed in the spectra of ethylenebisnitroamine and tetramethylenebisnitroamine to be assigned to the stretching vibrations of the NH bond which participates in the formation of a hydrogen bond with the nitro-group of a neighbouring molecule in the crystal. In the spectra of the N-deuteriated nitroamines these bands are shifted into the 2400 cm^{-1} region. Bands characteristic for the asymmetric and symmetric stretching vibrations of the CH_2 group appear, which were masked earlier by the intense vibrations of the NH groups. In the spectra of the deuteriated analogues of the nitroamines studied there is also a displacement of the bands assigned to the asymmetric vibrations of the nitro-group, etc.

Hence the infrared spectra also confirm the true nitroamine structure of the primary nitroamines, at least in the un-ionised state.

The ultraviolet spectra of the primary nitroamines have been studied [78,153,155]. A maximum at 232 nm (235 nm in alkaline medium) is characteristic for methylenebisnitroamine in this range. In an alkaline medium there is a bathochromic shift of the maximum [78].

The Raman spectra of the primary nitroamines were studied by Kohlrausch and Wittek [156].

In discussing the structure of the primary nitroamines reference must again be made to the work on the determination of the dissociation constants of the $\alpha\omega$-bisnitroamines (Table 1). Since ΔpK decrease more slowly in the bisnitroamine series than in the dicarboxylic acid series, it was concluded that the effective distance between the charges of the double anions increases more slowly in the bisnitroamine series [143]. In this paper the ionised bisnitroamines are regarded as mesomeric anions. It is thought that the contribution of structure (III) is more characteristic for methylenebisnitroamine than for tetramethylenebisnitroamine.

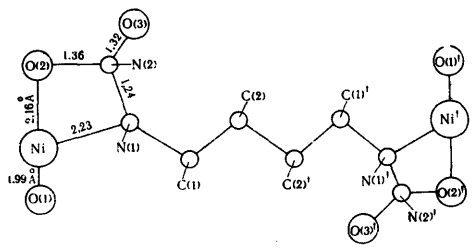


(IV)

It was recently suggested that the lower thermal stability of the primary nitroamines and their salts in comparison with secondary nitroamines is due to the conversion of the primary compounds into the aci-form on heating. Compounds in an aci-form are less stable and easily decompose [147]. However, experimental proof in support of this view has not been forthcoming.

Several studies deal with the explanation of the structure of salts of nitroamines by physicochemical methods. On the basis of an X-ray diffraction analysis of the disodium salt of ethylenebisnitroamine Alentoff and Wright maintain that the anionic centre in this compound is the oxygen atom and not the amine nitrogen [59]. However, the authors think it undesirable to attribute the structure found in a particular example to all the salts of the nitroamines with alkali metals, considering that the compound they investigated could be exceptional owing to the unique symmetry of the anion. Subsequent investigations showed that the salts of the nitroamines have a more complex structure.

In an X-ray diffraction study of the hydrate of the nickel salt of tetramethylenebisnitroamine it was found that in the crystalline state this compound exists in the form of polymeric chains. Each molecule of the ligand joins two nickel atoms with coordination of both nitroamine groups. The nitroamine group acts as a chelate ligand. The oxygen atom (Ni–O 2.16 Å) and the amine-nitrogen atom (Ni–N 2.23 Å) are coordinated so that a four-membered ring is formed with the nickel atom and the other nitrogen atom [157].



It is interesting that the study of the Raman spectra of the potassium salts of methyl- and ethylnitroamines showed that they have the structure of true *N*-nitrocompounds [156]. As already noted, on going from a free nitroamine to its salt there is a displacement of the maximum in the ultraviolet spectrum [78]. A difference was also noted in the infrared spectra of the primary nitroamines and their salts. This all suggests that the nitroamine anion should be regarded as a mesomeric anion with reaction centres at oxygen and nitrogen

IV. CHEMICAL PROPERTIES

The primary nitroamines exhibit high reactivity, which is in many respects similar to that for mono- and polynitroalkanes. Their activity is due to the presence of the labile hydrogen atom of the primary nitroamino-group and also to the nitroamino-group itself. Owing to the labile hydrogen the nitroamines form salts which undergo condensation with formalin‡, the Mannich reaction, add to activated double bonds, are alkylated, etc.

1. Reaction with Bases

Primary aliphatic nitroamines are weak acids and are capable of forming salts with bases. To obtain salts of nitroamines, bases, or metal oxides, carbonates, or alkoxides are used [1]. Potassium, barium, cobalt, zinc, copper, nickel, silver, mercury, lead, ammonium, and many other salts of primary nitroamines are known. In the preparation of salts of nitroamines in water, hydrates are often formed with various water contents in the molecule. Some metal salts of nitroamines are decomposed by boiling water. However, they are usually thermally more stable than the initial nitroamines but more sensitive to shock. In this respect the silver and mercury salts of the nitroamines are especially dangerous. Nitroamine salts are often used for the purification and analysis of nitroamines and also in certain chemical changes.

It is generally accepted that the primary nitroamines are stable in an alkaline medium. The anions of the aliphatic nitroamines do not react with a hot 20% solution of potassium hydroxide and only very concentrated alkali under severe conditions can bring about the decomposition of the primary nitroamines [29,30]. However, Hantzsch long ago observed [33] the decomposition of nitroaminoacetic acid and its derivatives by alkali under relatively mild conditions. These experiments were subsequently reproduced and analysed [51]. It was observed that some primary nitroamines, particularly those with electronegative substituents in the alkyl residue, are capable of decomposition by the scheme

$$RR'CHNHNO_2 \rightarrow RR'C{=}O + N_2 + H_2O$$

under the action of dilute alkali on heating.

Decomposition by this reaction is assisted by an increase in the hydroxide ion concentration, an increase in the concentration of sodium or potassium ions, and an increase in the electrical conductivity of the grouping in the alkyl residue. Furthermore, the presence of hydrogen at the α-carbon atom is important. Compounds without hydrogen in the α-position are stable to alkalis.

‡ Attempts to carry out condensation with other aldehydes were unsuccessful [24].

2. Reactions with Acids

Long ago Franchimont and coworkers[25,31,158] observed that primary nitroamines are decomposed by aqueous sulphuric acid with the formation of dinitrogen oxide and an alcohol:

$$RNHNO_2 \rightarrow ROH + N_2O.$$

Subsequent study of this reaction showed that it is more complex. During acid hydrolysis tetramethylenebisnitroamine forms butadiene and tetramethylene oxide in addition to dinitrogen oxide and butanediol. In the decomposition products of hexylnitroamine there are dinitrogen oxide, hexene, primary and secondary hexyl alcohols, and dihexyl ether[30]. Acetaldehyde was observed in the decomposition products of ethylenebisnitroamine[31].

On the basis of the results obtained in the acid decomposition of primary nitroamines and bisnitroamines it was suggested that the reaction proceeds through the intermediate formation of nitroamide and a carbonium ion[49]:

$$RNHNO_2 + H^+ \rightarrow R^+ + NH_2NO_2.$$

Nitroamide is the source of the dinitrogen oxide and water and the extremely active carbonium ion is stabilised with the formation of an alcohol (reaction with water), alkene (loss of a proton), or other decomposition products as a result of the reaction with nucleophilic reagents present in the reaction sphere.

The reaction of nitroamines with acids is regarded as an electrophilic substitution of the S_E2 type at the amine-nitrogen. The rate of reaction is directly proportional to the concentration of protons and of the primary nitroamine. The accumulation of electron-donating substituents at the nitrogen facilitates the decomposition of the nitroamines.

Further study of the acid decomposition of primary nitroamines was by the example of alkyl derivatives with a branched chain[50]. Such compounds decompose more rapidly than alkylnitroamines of linear structure and furthermore a definite difference in their behaviour in relation to sulphuric and hydrochloric acids is observed at the same pH. The decomposition of isopropyl nitroamine is catalysed by hydrogen sulphite ions.

In one study[50] the hypothesis about the formation of nitroamide at the first stage of acid hydrolysis has been doubted. Hence although there is a definite relation between the rate of decomposition of the primary nitroamines and the concentration of hydrogen ions the reaction is extremely complex and has still not been properly studied. The reaction of primary nitroamines with hydrochloric acid takes place rather smoothly with the formation of alkyl chlorides[49]:

$$RNHNO_2 + HCl \rightarrow RCl + N_2O + H_2O.$$

This is widely used for confirming the structure of the primary nitroamines[62,74,121,159]. The reaction of primary nitroamines with acetyl chloride and thionyl chloride proceeds similarly[14,58].

Primary nitroamines are extremely sensitive to nitric acid. Methyl nitroamine is decomposed by concentrated nitric acid even at 0°C with the formation of methyl nitrate and dinitrogen oxide[1]. Nitrous acid also readily decomposes methylnitroamines in aqueous solution to methanol, dimethylnitroamine and its *O*-isomer[23]. It was suggested that the decomposition proceeds through the intermediate formation of diazomethane[23]:

$$CH_3NHNO_2 + HNO_2 \rightarrow CH_3N{=}NOH + HNO_3,$$
$$CH_3N{=}NOH \rightarrow CH_2N_2 + H_2O,$$
$$CH_3NHNO_2 + CH_2N_2 \rightarrow (CH_3)_2NNO_2 + CH_3N{=}\overset{\overset{O}{\nearrow}}{N}{-}OCH_3.$$

3. Oxidation and Reduction

There has been almost no investigation of the reaction of primary aliphatic nitroamines with oxidants. There is only the statement that primary nitroamines are rather stable to oxidants[1].

The reduction of nitroamines has been studied in greater detail. When reduced with zinc in acetic acid methylnitroamine is converted into methanol, and when reduced with sodium amalgam methylamine is formed[18]; methylhydrazine is liberated by the action of zinc in nitric acid. An alkaline solution of aluminium converts methylnitroamine into methylisodiazotate[161]. In the reduction of ethylenebisnitroamine by zinc in hydrochloric acid a little ethylhydrazine is liberated[160]. It is suggested that the reduction of nitroamines proceeds through the intermediate formation of nitroso-derivatives which are readily isomerised into diazo-compounds. The latter can be isolated from alkaline solutions as diazotates.

4. Reaction with Formaldehyde

One of the characteristic reactions of primary nitroamines is their reaction with formaldehyde. Franchimont[24] first observed this reaction in the presence of bases. It was shown later that bisnitroamines readily form the corresponding nitroaminocarbinols on reaction with formaldehyde[75]:

$$[H_2C]_n(NHNO_2)_2 + CH_2O \xrightarrow{H_2O} [H_2C]_n(N(NO_2)CH_2OH)_2.$$

Only the monomethyl derivative could be isolated for ethylenebisnitroamine[75,81]:

$$O_2NHN{-}[CH_2]_2{-}NHNO_2 + CH_2O \xrightarrow{H_2O} HOCH_2\overset{\overset{NO_2}{|}}{N}{-}[CH_2]_n{-}\overset{\overset{NO_2}{|}}{N}H.$$

The mechanism of formation and the chemical nature of the hydroxymethyl derivatives was thoroughly studied with the aid of potentiometric titration and the analytical determination of formaldehyde[52]. It was shown that the hydroxymethylnitroamines dissociate readily in water with the loss of formaldehyde

$$RNCH_2OH \rightleftharpoons RNH + CH_2O.$$
$$\quad\;\; | \qquad\quad\; |$$
$$\quad NO_2 \qquad NO_2$$

The position of the equilibrium is displaced to the right. Aqueous solutions of the dicarbinol derivatives of ethylenebisnitroamines and trimethylenebisnitroamine can be accurately titrated with potassium hydroxide as free nitroamines; the combined formaldehyde is also readily determined by well known procedures[52].

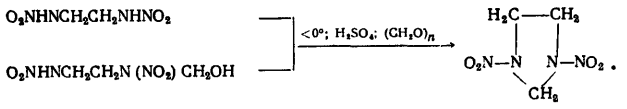
The hydroxymethylenebisnitroamines are more stable in acid solutions, since the electron-withdrawing properties of the nitroamino-group hinder the dissociation of the hydroxyl. Here the loss of a proton seems more hypothetical[52]:

$$RNCH_2OH \rightleftharpoons RNCH_2O^- + H^+.$$
$$\quad\;\; | \qquad\quad\; |$$
$$\quad NO_2 \qquad NO_2$$

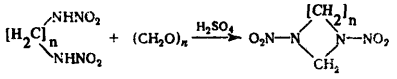
The interaction of nitroamines with paraformaldehyde in organic solvents also leads to the formation of nitroaminocarbinols. In sulphuric acid medium at low temperature methylenebisnitroamines are formed[162]:

$$RNH + [CH_2O]_n \xrightarrow{H_2SO_4} RNCH_2NR.$$
$$\quad\;\; | \qquad\qquad\qquad\quad\; | \quad\; |$$
$$\quad NO_2 \qquad\qquad\qquad NO_2 \;\; NO_2$$

Ethylenebisnitroamine and its hydroxy-derivative form 1,3-dinitro-1,3-diazacyclopentane under these conditions[162]:

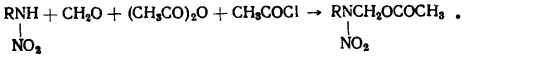


The higher homologues of ethylenebisnitroamine—trimethylenebisnitroamine and tetramethylenebisnitroamine—form 1,3-dinitro-1,3-diazacyclohexane and 1,3-dinitro-1,3-diazacycloheptane respectively in this reaction[80]:



where n = 3 or 4.

In research practice instead of the carbinol hydroxymethylnitroamines their derivatives are often used—acetates, nitrates, and chloromethylnitroamines[163]. The acetates of the nitroaminomethylols are obtained by the direct reaction of nitroamine, formalin, acetic anhydride, and acetyl chloride[163]:

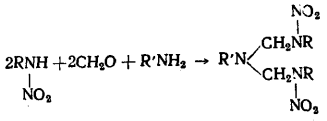


The nitrates of the hydroxymethylnitroamines, which exhibit an alkylating action, are usually of low stability and dangerous to use[164]. Important derivatives of the hydroxymethylnitroamines are the recently discovered *N*-(chloromethyl)-*N*-nitroamines, the chlorine atom of which has a reactivity reminiscent of the chlorine in chloromethyl ethers and is capable of replacement by various functional groups[164].

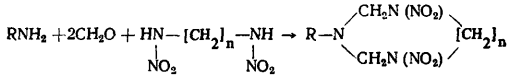
5. Aminomethylation of Primary Nitroamines

The possibility of using the primary nitroamines in a Mannich reaction was first demonstrated by the example of the reaction of methylnitroamine with *N*-hydroxymethylpiperidine[24]. Ammonia was investigated, as well as piperidine, as the amino-component, and methyl-, ethyl- and ethylenebis-nitroamines were also studied as the N–H acid component[25].

In the last 20 years there has been a thorough study of the Mannich reaction in a series of nitroamines. In 1949 Chapman and coworkers showed that for primary amines both of the hydrogen atoms of the latter take part in the condensation[165]:

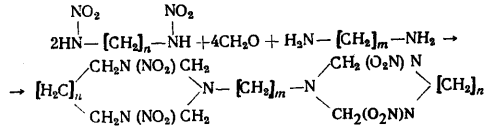


$\alpha\omega$-Bisnitroamines with not more than three methylene groups in a chain form cyclic condensation products[165]:



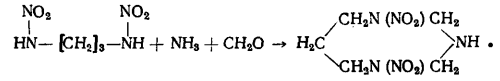
where $n = 1-3$.

Bicyclic compounds are isolated in the example of diamines[165]:

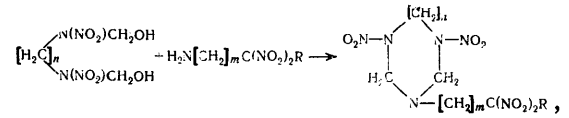


where $n = 1-3$, $m = 2$.

The formation of a bicyclic product was also observed in the condensation of ethylenebisnitroamine with ammonia and formalin ($n = 2$, $m = 1$)[166], but for trimethylenebisnitroamine a monocyclic product is formed as well as the bicyclic product ($n = 3$, $m = 1$)[80]:

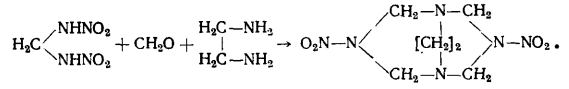


An interesting example of cyclisation was observed in the condensation of bisnitroaminodiols with polynitroalkylamines[167–170]:

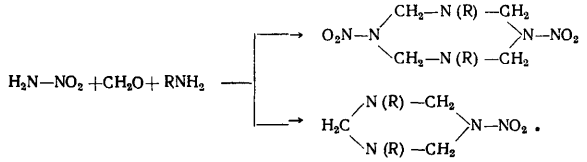


where $n = 1$ or 2, $m = 2-6$, R = NO_2 or CH_3.

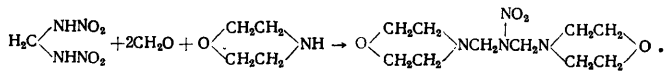
Quite recently[171–173] a new series of studies appeared on the condensation of dinitramines—$O_2NHN[CH_2]_nNHNO_2$, $n = 1-4$—with formaldehyde and diamines—$H_2N[CH_2]_nNH_2$, $n = 2, 3, 4, 6$—and also methyl-, ethyl-, butyl-, 2-hydroxyethyl-, hydroxypropyl-, trinitropropyl-, and benzylamines, aniline, phenylenediamine, 3,3-dinitropentamethylene-1,5-diamine, 3,6-dinitro-3,6-diazaoctamethylene-1,8-diamine, bis-2-aminoethyl ether. From a large amount of experimental material it was shown that the basicity of the amines and diamines in the aminomethylation of ethylenebisnitroamine has no effect on the nature of the reaction products. The more basic the amino-component introduced into the reaction the higher the pH of the medium at which formation of the cyclic products takes place. Special attention was paid to the behaviour of methylenebisnitroamine in the Mannich reaction. On reaction with ethylenediamine and formaldehyde at pH 4.6–5.6 it forms 3,7-dinitro-1,5-*endo*-ethylene-1,3,5,7-tetra-azacyclo-octane:



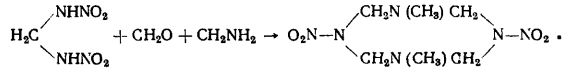
N-Nitroamide is the only nitro-derivative which contains two hydrogen atoms at the nitrogen carrying a nitro-group, therefore the aminomethylation of this compound can proceed in two directions:



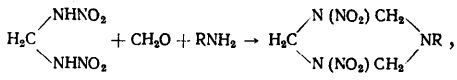
Methylenebisnitroamine is often used as a source of nitroamide, and depending on the conditions of carrying out the Mannich reaction it can function as a bisnitroamine or as a nitroamide[165]. The reaction of methylenebisnitroamine with morpholine and formaldehyde in water or ethyl acetate is:



The formation of derivatives of nitroamide was also observed in an anhydrous medium in the reaction with methyl-, benzyl-, and cyclohexylamines.

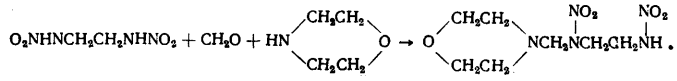


In aqueous medium products are obtained which contain the structural of methylenebisnitroaminemoiety[165].



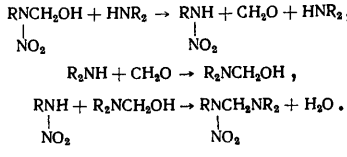
where R = CH_3, $C_6H_5CH_2$.

Linear Mannich bases are formed in the condensation of ethylenebisnitroamine with formaldehyde and morpholine[75]:



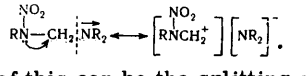
With two moles of formaldehyde and morpholine the reaction proceeds at two nitroamine groups[75].

The mechanism of the aminomethylation of the primary aliphatic nitroamines has been insufficiently studied. Lamberton and coworkers[52] proposed the following reaction scheme:

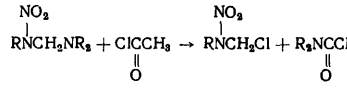


Under the action of alkalis Mannich bases are readily decomposed into nitroamine salts, amines, and formaldehyde; in an acid medium their stabilisation with the formation of the cation $RH(NO_2)CH_2N^+HR_2$ is possible[52].

It is interesting that the Mannich bases obtained from nitroalkanes (especially the mononitroalkanes) differ sharply in their chemical behaviour from the products of the aminomethylation of the primary nitroamines[52]. The former, as is well known, are insoluble in water, readily soluble in organic solvents; they cannot be titrated with alkali. The latter are readily titrated with alkali and soluble in water and other polar solvents. The reason for such a marked difference must, we think, be sought in the mutual influence of the nitroamine and amino-groupings at a single carbon atom. Like *N*-(chloromethyl)nitroamines, where the chlorine exhibits considerable lability on account of the $+M$ effect of the nitrogen atom and the I effect of the chlorine atom, the $+M$ effect of the amine-nitrogen of the nitroamino-group is evidently due to the stabilisation of the carbonium ion:



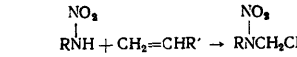
Confirmation of this can be the splitting of the Mannich bases by acetyl chloride[164]:



The polarisation of Mannich bases in neutral media is due to their preferential solubility in polar solvents and their ready cleavage by alkalis into their components.

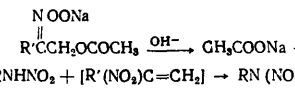
6. Addition at an Activated Double Bonds

Despite the fact that the addition of primary nitroamines to compounds which contain activated double bonds, found in the initial stages of the study, interesting results in this field were also obtained recently. This reaction was first found by Kissinger and Schwartz[112]. The alkenes studied were methyl acrylate, acrylonitrile, acrylamide, methyl vinyl ketone, and diethyl maleate; the nitroamines chosen were methyl-, ethyl-, and butyl-nitroamines and also ethylenebisnitroamines and *N*-methylethylenebisnitroamines. The reaction takes place only in the presence of an alkaline catalyst:

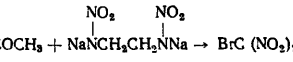


The addition of ethylnitroamine to 2,2-dinitropropanediol acrylate[174] takes place similarly.

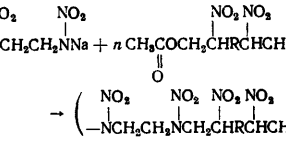
Nitroamines are capable of adding to a double bond of nitroalkenes and unsaturated ketones[175,176]. The reaction with nitroalkenes can also take place at the moment of their liberation from nitroalkyl acetates[177]:



An interesting example is the bromodinitroethylation of the alkali salts of nitroamines. In the first stage the reaction proceeds by the cleavage of bromodinitroethyl acetate into *gem*-dinitroethylene and sodium acetate. Subsequently the excess of the nitroamine salt adds to the dinitroethylene to form the corresponding salt of dinitroethylenetriamine. Under the action of a bromonium ion the latter is converted into the corresponding bromo-derivative[178].



The addition of $\alpha\omega$-dinitroamines to the decomposition products of acetates of nitrodiols leads to the formation of polymeric products[179]:



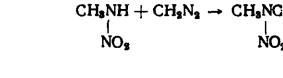
Polymers of high molecular weight are formed on carrying out the reaction in solvents indifferent to an activated double bond. When water, alcohols, or nitro-compounds are used as solvent the chain is broken owing to the addition of solvent molecules at the double bond.

7. Alkylation and Acylation

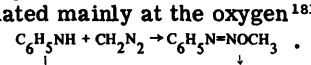
The alkylation of primary nitroamines is important for finding the structure of nitroamines and their salts and also for the synthesis of secondary nitroamines. In studying these reactions even the first investigators found that in alkylation often a mixture of isomers is formed, the quantitative composition of which depends on the nature of the alkylating agent, the metal cation, and the medium in which the reaction is carried out.

Alkylation of diazoalkanes. The reaction of primary nitroamines with diazoalkanes is of interest from the standpoint of finding the structure of nitroamines by chemical means.

In the treatment of nitroamide with diazomethane the main reaction product is dimethylnitroamine[180]. The latter is also obtained in quantitative yield in the alkylation of methylnitroamine[181]:



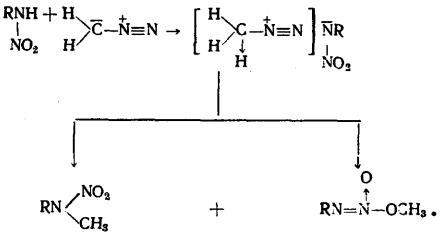
It is interesting to note that the more acid phenylnitroamines are alkylated mainly at the oxygen[181]:



In the alkylation of primary nitroamines with diazoethane ethyl derivatives are formed[57].

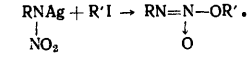
In the examples described above the investigators usually either did not note the formation of isomeric products of *O*-alkylation, or they were not investigated closely. More detailed study of the reaction of diazomethane with the isopropylnitroamine suggested the formation of a secondary nitroamine and the isomeric *O*-ester in the ratio 7 : 3.[48,53]

The reaction with diazomethane is usually carried out in non-polar solvents; we think that it can be described by the scheme:



After the release of nitrogen from the intermediate "diazonium" cation the nitroaminium ion can complete the octet of the carbon atom either by the electron pair of the amine nitrogen (when the nitroamine-nitrogen is not solvated), or owing to the electron pair of the oxygen of the nitro-group (when there is partial polarisation of the nitroammonium anion), which also leads to the products of *N*- and *O*-alkylation, or to their mixtures.

Alkylation by alkyl halides and dimethyl sulphate. The alkylation of the salts of nitroamines with alkyl halides has been studied in greater detail than the alkylation of primary nitroamines with diazoalkanes. The direction of the reaction here depends significantly on the nature of the cation. The silver salts of nitroamines usually form *O*-alkylacylnitroamines[30]:



Whereas sodium or potassium salts form *N*-alkylation products preferentially[24,27,182]. Thus the sodium salt of isopropylnitroamine with methyl iodide gives 60% isopropylmethylnitroamine and 9% *N*-isopropyl-*O*-methyl acinitroamine; the silver salt of the same nitroamine forms a mixture of the secondary nitroamine and its *O*-isomer in the ratio 1 : 10. On the basis of the sodium salts isopropyl-, butyl-, and octyl-nitroamines with the corresponding alkyl iodides, di-isopropylnitroamines, dibutylnitroamines, and dioctylnitroamines were obtained in yields of 14, 12, and 32%; the yields of the *O*-isomers were respectively 26, 24, and 30%. It was noted that the sodium salt of cyclohexylnitroamine is not alkylated by cyclohexyl iodide[56].

In the primary dinitroamine series the alkylation of the monopotassium salt of ethylenebisnitroamine with methyl iodide and dimethyl sulphate was studied. In both instances *N*-methyl-*NN'*-dinitroethylenediamine is isolated. In the alkylation of the dipotassium salt of ethylenebisnitroamine with dimethyl sulphate, *NN'*-dinitro-*NN'*-dimethylethylenediamine is formed[38]. The potassium salt of isopropylnitroamine gives equal proportions of the *N*- and *O*-isomers with dimethyl sulphate[183].

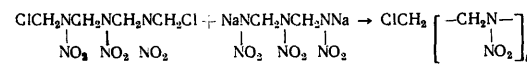
Hence the alkylation of salts of nitroamines with alkyl iodides or dimethyl sulphate often cannot serve as a convenient method for obtaining the secondary nitroamines, but it is completely suitable for the synthesis of *O*-alkylacinitroamines, which are studied as models of the aci-form of the nitroamines[54].

An interesting and practically useful series of papers deals with the alkylation of salts of nitroamines by chloroderivatives containing an active chlorine atom. Picryl chloride and the potassium salt of methyl nitroamine form tetryl in good yield[32]. Ethyl-, propyl-, and butyl-picrylnitroamines can be obtained similarly[26]. *N*-(Chloromethyl)nitroamines and *N*-(nitroxymethyl(-nitroamines react with the sodium salts of nitroamines, the yields of the resulting alkylation products varying from 15 to 81%[184]:

In this reaction a series of $\alpha\omega$-dimethylpolymethylenenitroamines

$$RN(NO_2)[CH_2N(NO_2)]_nR;$$

is obtained; 2,4,7,9-tetranitro-2,4,7,9-tetra-azadecane, and nitroaminoalkyl derivatives of nitrourethane[184]. In the condensation of the disodium salts of dinitroamines with bis-*N*-(chloromethyl)nitroamines polymeric compounds with nitroaza-groupings in a chain are formed[185]:



Acylation of primary nitroamines. Until recently it was thought that acid anhydrides do not attack primary nitroamines[21,24,43]. However, recently Woodcock[75] succeeded in obtaining ethylenebisnitroacetamide in small yields by the action of acetic anhydride on ethylenebisnitroamine.

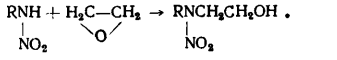
In studies at the end of the last century it was shown that the acid chlorides of organic acids either do not react with primary nitroamines or bring about complete decomposition. Acetyl chloride reacts with the silver salts of methylnitroamine and propylnitroamine with release of dinitrogen oxide[21]. Benzoyl chloride acts similarly on methyl- and isopropyl-nitroamines.

It was found recently that the potassium and silver salts of the esters of *N*-nitroglycine and *N*-nitroalanine are exceptions. They are smoothly acylated at the nitrogen by acetyl chloride, benzoyl chloride, and 3,5-dinitrobenzoyl chloride[115]. The formation of *O*-acylation products is almost not observed.

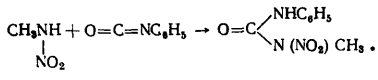
There have been reports of the reasons for such an unusual course of reaction in the failure of Kornblum's rule[186,187] for the alkylation of mesomeric anions. Starting from the fact that the alkali salts of nitroamines react with acylating agents at different rates, and silver salts do not react without catalytic additions of pyridine the investigators suggest that the salts have a chelate, not an ionic, structure. Sodium and potassium salts exist in solution in the form of associates in which the oxygen of the nitro-group is coordinated with metal ions. The silver salts are evidently chelates, therefore acylation is hindered both at nitrogen and at oxygen. The catalytic action of pyridine leads to the breakdown of the complex owing to the formation of a new donor–acceptor bond between the silver ion and the nitrogen atom of the pyridine, as a result of which the nitroamine group is capable of *N*- and *O*-acylation. This point of view satisfactorily explains the effect of the cation in the alkylation of various salts of nitroamines[115].

8. Other Reactions

Primary nitroamines are condensed with ethylene oxide to form the corresponding nitroaminoalcohols[188]:

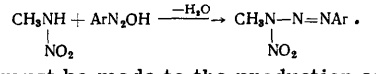


The reaction of methylnitroamine with phenyl isocyanate, leading to the formation of *N*-phenyl-*N'*-nitro-*N'*-methylurea has been described[45]:

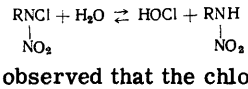


In the action of potassium isocyanate on methylnitroamine free isocyanic acid is released; the formation of the corresponding urea does not take place[45].

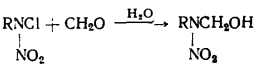
Methylnitroamine reacts with aromatic diazo-compounds. The reaction products in this instance are methylaryl-*N*-nitrotriazenes[189]:



Reference must be made to the production and the study of the properties of the little known *N*-halogeno-*N*-nitroamines. Franchimont and Klobbie[16] did not isolate any individual products from the reaction mixture in the bromination of salts of alkyl nitroamines. Much later Smart and Wright[56], in studying the conversion of alkyldichloroamines to nitroamines expressed the opinion that in aqueous solution there is the equilibrium involving *N*-chloro-*N*-nitroamines:

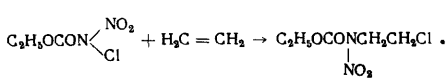


It was recently observed that the chlorine in *N*-chloro-*N*-nitroamines is smoothly converted into the hydroxymethyl group under the action of formaldehyde[190]:

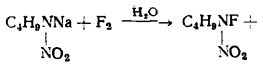


Detailed study of the properties of *N*-chloro-*N*-nitroamines has not been studied in detail nor has the chlorination of primary nitroamines been investigated. However, *N*-chloro-*N*-nitroamines should exhibit extremely interesting chemical properties owing to the strong polarisation of the chlorine atom under the influence of the nitroamino-group, which should lead, in turn, to great lability of the chlorine in reactions with nucleophilic compounds.

In this connection it is interesting to note that primary aromatic nitroamines are readily chlorinated by hypochlorous acid to the unstable *N*-chloro-*N*-nitroamines[191,192]. The production of *N*-chloro-*N*nitrourethane by the action of sodium hypochlorite on a solution of nitrourethane in sulphuric acid and its addition to ethylene and cyclohexene[193]:

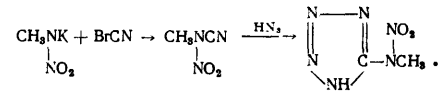


Elemental fluorine reacts readily with salts of nitroamines in an aqueous medium with the formation of *N*-fluoro-*N*-nitroamines. This reaction takes place, for example, with the isomeric butylnitroamines[194]. A thermochemical investigation of the compounds synthesised was also made[195,196].



N-Fluoro-*N*-nitroamines are low-boiling unstable liquids. *N*-Bromo- and *N*-iodonitroamines are unknown.

The reaction of the potassium salt of methylnitroamine with cyanogen bromide, taking place with the formation of *N*-cyanomethylnitroamine has also been described. Without isolating the latter in the pure state it was converted into 5-methyl-5-nitroaminotetrazole by treatment with hydrogen azide[197]:

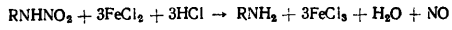


Methylnitroamine reacts vigorously with methylmagnesium iodide[1] with liberation of gaseous products. The products were not identified.

V. ANALYTICAL DETERMINATION

Four qualitative reactions for nitroamines are known: (1) the Franchimont reaction[23]; (2) Thiele and Lachman's reaction[87]; (3) Bamberger's reaction[198]; and (4) Lieberman's reaction[199]. All these reactions are discussed in sufficient detail in Houben–Weyl's monograph[200].

Quantitative methods of analysis of nitroamines for dinitrogen oxygen liberated in the decomposition of nitroamines by hydrochloric acid and iron(II) chloride and also in a Lunge nitrometer[201]:



If the physicochemical methods of identification of primary nitroamines were developed rather intensively in recent years (see Section III), the chemical methods were perfected very poorly and there have been no significant approaches in this field recently. Mention must only be made of the method of identification of primary nitroamines in the form of *S*-benzylthiuronium salts[55]. The latter are formed in good yields on mixing aqueous solutions of *S*-benzylthiuronium hydrochloride with the sodium salts of primary nitroamines. The *S*-benzylthiuronium salts of the primary nitroamines crystallise well from 50% ethanol and have precise melting points. Thus the *S*-benzylthiuronium salt of methylnitroamine melts at 117°C, that of ethylenebisnitroamine at 125–129°C, and that of benzylnitroamine at 127°C.[55]

VI. CERTAIN ASPECTS OF PRACTICAL USE

Judging by the published information, some of the primary aliphatic nitroamines have definite practical value as explosives. The most important of these is ethylenebisnitroamine, which was manufactured in the U. S. A. on an industrial scale under the commercial name of "Haleite"[101]. Ethylenebisnitroamine was used as a high explosive[4]; it can also be used as a component of missile explosives[5] and as a main or reduced charge in percussion cap–detonators instead of tetryl[5].

Methylnitroamine is a low-melting explosive, more powerful than tetryl but weaker than hexogen[12]. It is recommended for use in explosive compositions mixed with T. E. N.[6]

Nitroaminoethanol nitrate and 1-nitroamino-2-nitroxypropane have been suggested as plasticisers for cellulose nitrate.

In recent years there have been patents on the possibility of using primary nitroamines in rocket technology.

Patents have been granted on the use of nitroamide and several primary alkylnitroamines as monopropellents [123,141]. Ethylenebisnitroamine and its hydrazinium salts are recommended as components of mixed rocket propellents [7,202]. The nitroaza-polymer

$$ClCH_2\left[N(NO_2)CH_2\right]_n CH_2Cl$$

obtained by condensation of a salt of a dinitroamine with a bis-*N*-(chloromethyl)-*N*-nitroamine has been recommended as a binder in solid rocket propellents [185].

Nitroamines have interesting and important prospects for use for other purposes. For example, a patent has been granted for the use of aliphatic nitroamines as weed-killers [203] and as effective plant growth stimulators [8,204,205]. Some of the nitroamines are recommended as additives for diesel fuel to increase the octane number [198], for removing the deposit in internal combustion engines [10], and also special additions in dyeing. [11]

REFERENCES

1. H. Backer, Samml. Chem. und Chem.-Techn. Vorträge, 18, (10/12), 350 (1912).
2. A. Lamberton, Quart. Rev., 5, 75 (1951).
3. "Methoden der organischen Chemie (Houben–Weyl)" (Edited by E. Müller), Thieme, Stuttgart, 1958, Vol. IX, Part 2, p. 99.
4. G. Hale, U. S. P. 2 742 105 (1949); Chem. Abs., 43, 6827 (1949).
5. G. Hale, U. S. P. 2 011 578 (1934); Chem. Zbl., II, 3738 (1935).
6. P. Naoum, German P. 499 403 (1928); Chem. Abs., 11, 2217 (1930).
7. C. Sauer and E. Kreide, U. S. P. 3 166 612 (1963); Chem. Abs., 62, 7579 (1965).
8. W. Lindsay and W. Mees, B. P. 935 671 (1963); Ref. Zhur. Khim., 23N483P (1964).
9. J. Hinkamp and R. Sugimoto, U. S. P. 2 595 789 (1952); Chem. Abs., 46, 8362e (1952).
10. A. Lacombe, U. S. P. 2 592 435 (1952); Chem. Abs., 46, 6374e (1952).
11. A. Schaffer and A. Carl, German P. 966 565 (1957); Chem. Abs., 53, 14533h (1959).
12. T. Urbanski, "Chemie und Technologie der Explosivstoffe", Leipzig, 1964, Vol. III.
13. A. V. Topchiev, "Nitrovanie Uglevodorodov i Drugikh Organicheskikh Soedinenii" (Nitration of Hydrocarbons and Other Organic Compounds), Izd. Akad. Nauk SSSR, Moscow, 1956, p. 320.
14. A. McKay, Chem. Rev., 51, 301 (1952).
15. A. Franchimont, Rec. trav. chim., 7, 258 (1888).
16. A. Franchimont and E. Klobbie, Rec. trav. chim., 7, 343 (1888).
17. A. Franchimont and E. Klobbie, Rec. trav. chim., 7, 236 (1888).
18. A. Franchimont, Rec. trav. chim., 13, 308 (1894).
19. A. Franchimont and I. Lublin, Rec. trav. chim., 21, 45 (1902).
20. A. Franchimont and H. Friedman, Rec. trav. chim., 26, 218 (1907).
21. A. Franchimont and E. Klobbie, Rec. trav. chim., 8, 283 (1907).
22. A. Franchimont, Rec. trav. chim., 4, 195 (1885).
23. A. Franchimont, Rec. trav. chim., 16, 226 (1897).
24. A. Franchimont, Rec. trav. chim., 29, 296 (1910).
25. A. Franchimont, Versl. Amst., 19, 501 (1910).
26. A. Franchimont and E. Klobbie, Rec. trav. chim., 29, 313 (1910).
27. A. Franchimont and H. van Erp, Rec. trav. chim., 14, 235 (1895).
28. A. Franchimont, Rec. trav. chim., 6, 213 (1887).
29. H. van Erp, Ber., 29, 474 (1896).
30. H. van Erp, Rec. trav. chim., 14, 1 (1895).
31. H. van Romburgh, Rec. trav. chim., 7, 226 (1888).
32. H. van Romburgh, Rec. trav. chim., 8, 215 (1889).
33. A. Hantzsch and W. Metcalf, Ber., 29, 1680 (1895).
34. A. Hantzsch, Ber., 32, 1728 (1899).
35. A. Hantzsch, Ber., 39, 2098 (1906).
36. A. Hantzsch, Ber., 39, 2703 (1906).
37. A. Hantzsch and F. Dollfus, Ber., 32, 1728 (1899).
38. H. Backer, Rec. trav. chim., 31, 142 (1912).
39. H. Backer, Rec. trav. chim., 34, 187 (1915).
40. J. Thiele and A. Lachman, Ber., 27, 1909 (1894).
41. H. Umbgrowe and A. Franchimont, Rec. trav. chim., 16, 385 (1897).
42. K. Swarts, Bull. acad. roy. Belg., 782 (1904).
43. S. Thomas, Rec. trav. chim., 9, 69 (1890).
44. H. Euler, Ber., 39, 1607 (1906).
45. R. Scholl and H. Holderman, Lieb. Ann., 345, 378 (1906).
46. C. Holstead and A. Lamberton, J. Chem. Soc., 1886 (1952).
47. R. Brian and A. Lamberton, J. Chem. Soc., 1633 (1949).
48. P. Bruck, J. Denton, and A. Lamberton, J. Chem. Soc., 921 (1956).
49. J. Barrot, J. Denton, and A. Lamberton, J. Chem. Soc., 1998 (1953).
50. J. Denton and A. Lamberton, J. Chem. Soc., 1655 (1955).
51. J. Barrot, M. Gillibrand, and A. Lamberton, J. Chem. Soc., 1282 (1951).
52. A. Lamberton, C. Lindley, P. Owston, and J. Speakman, 1641 (1949).
53. P. Bruck and A. Lamberton, J. Chem. Soc., 4198 (1957).
54. A. Lamberton and J. Newton, J. Chem. Soc., 1797 (1961).
55. T. M. Gillibrand and A. Lamberton, J. Chem. Soc., 1883 (1949).
56. G. Smart and G. Wright, Canad. J. Res., 26B, 284 (1948).
57. G. Smart and G. Wright, J. Amer. Chem. Soc., 70, 3142 (1948).
58. R. Hall and G. Wright, J. Amer. Chem. Soc., 73, 2213 (1951).
59. N. Alentoff and G. Wright, Acta Cryst., 6, 1 (1953).
60. C. Myers and G. Wright, Canad. J. Res., 27B, 489 (1949).
61. A. McKay, Chemistry in Canada, 3, 37 (1961).
62. A. McKay and G. Wright, J. Amer. Chem. Soc., 70, 3996 (1948).
63. A. McKay and D. Manchester, J. Amer. Chem. Soc., 71, 1970 (1949).
64. A. McKay and J. Milks, J. Amer. Chem. Soc., 72, 1616 (1950).
65. A. McKay, J. Picard, and P. Brunet, Canad. J. Chem., 29, 746 (1951).
66. A. McKay and C. Sandorfy, Canad. J. Chem., 31, 42 (1953).
67. A. McKay, J. Amer. Chem. Soc., 77, 1057 (1955).
68. R. Hall, A. McKay, and G. Wright, J. Amer. Chem. Soc., 73, 2205 (1951).
69. A. McKay, J. Org. Chem., 16, 1395 (1951).

70. A. McKay, J. Org. Chem., 16, 1848 (1951).
71. A. McKay and S. Viron, J. Amer. Chem. Soc., 72, 3965 (1950).
72. A. McKay and W. Hatton, J. Amer. Chem. Soc., 75, 963 (1953).
73. A. McKay, W. Hatton, and G. Taylor, J. Amer. Chem. Soc., 75, 1120 (1953).
74. A. McKay, W. Hatton, and R. Braun, J. Amer. Chem. Soc., 78, 6144 (1956).
75. D. Woodcock, J. Chem. Soc., 1635 (1949).
76. J. Bell and I. Dunstan, J. Chem. Soc. (C), 862 (1966).
77. H. Ficherolle, Mem. poudres, 37, 129 (1955).
78. M. Piskorz and T. Urbansky, Bull. Polon. sci., 11, 615 (1963).
79. F. Llewellyn and F. Whitmore, J. Chem. Soc., 1316 (1948).
80. J. Bell and I. Dunstan, J. Chem. Soc. (C), 870 (1966).
81. W. Bachman, W. Horton, E. Jenner, N. McNaughton, and E. Maxwell, J. Amer. Chem. Soc., 72, 3132 (1950).
82. M. Frankel, U. S. P. 3 000 945 (1961); Ref. Zhur. Khim., 3N422 (1963).
83. M. Frankel, U. S. P. 3 000 944 (1961); Ref. Zhur. Khim., 3N424 (1963).
84. M. Frankel, U. S. P. 3 000 942 (1961); Ref. Zhur. Khim., 3N423 (1963).
85. P. Dekkers, Res. trav. chim., 9, 92 (1890).
86. P. Adams and F. Baron, Chem. Rev., 65, 567 (1965).
87. J. Thiele and A. Lachman, Lieb. Ann., 288, 291 (1895).
88. H. Gold, M. Frankel, G. Linden, and K. Klager, J. Org. Chem., 27, 334 (1962).
89. M. Frankel, J. Chem. and Eng. Data, 7, 410 (1962).
90. K. Krager, U. S. P. 2 940 977 (1960); Ref. Zhur. Khim., 1L433 (1962).
91. M. Frankel, U. S. P. 2 978 491 (1961); Ref. Zhur. Khim., 10L449 (1962).
92. M. Frankel, U. S. P. 2 978 488 (1961); Ref. Zhur. Khim., 11L463 (1962).
93. M. Frankel, U. S. P. 2 978 492 (1961); Ref. Zhur. Khim., 12L395 (1962).
94. M. Frankel, U. S. P. 2 978 493 (1961); Ref. Zhur. Khim., 12L396 (1962).
95. M. Frankel, U. S. P. 2 978 486 (1961); Ref. Zhur. Khim., 12L397 (1962).
96. M. Frankel, U. S. P. 3 000 931 (1961); Ref. Zhur. Khim., 8N365 (1963).
97. A. Blomquist and F. Fiedorek, B. P. 2 485 855 (1949); Chem. Abs., 44, 3515 (1950).
98. H. Curry and J. Mason, J. Amer. Chem. Soc., 73, 5043 (1951).
99. H. Curry and J. Mason, J. Amer. Chem. Soc., 73, 5041 (1951).
100. R. Hardy, W. Lindsay, and C. Mees, B. P. 997 826 (1965); Chem. Abs., 63, 13075e (1965).
101. W. Bachman, Abst. warit. Res., 7, 314 (1948).
102. K. Shiino and S. Oinuma, J. Industr. Explos. Soc. Japan, 25, 283 (1964).
103. K. Shiino and S. Oinuma, J. Industr. Explos. Soc. Japan, 21, 351 (1960).
104. M. Frankel, U. S. P. 3 000 939 (1961); Chem. Abs., 56, 8574f (1962).
105. R. Schenk, Swedish P. 138 456 (1952); Chem. Abs., 48, 2759f (1954).
106. C. Parker, Tetrahedron, 17, 89 (1962).
107. M. Frankel and K. Klager, U. S. P. 2 978 504 (1961); Ref. Zhur. Khim., 11L460 (1962).
108. M. Frankel and K. Klager, U. S. P. 2 967 199 (1961); Ref. Zhur. Khim., 2L445 (1962).
109. M. Frankel and K. Klager, U. S. P. 2 967 198 (1961); Ref. Zhur. Khim., 2L446 (1962).
110. C. Sauer and R. Follett, J. Amer. Chem. Soc., 77, 2560 (1955).
111. Weygand-Hilgetag, "Org.-Chemische Experimentier kunst", Leipzig, p. 639.
112. L. Kissinger and M. Schwartz, J. Org. Chem., 23, 1342 (1958).
113. V. Kaderabek and J. Denkstein, Coll. Czech. Chem. Comm., 31, 2915 (1966).
114. I. S. Ivanova, G. F. Bogdanova, T. A. Alekseeva, and S. S. Novikov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2236 (1962).
115. E. White and R. Baumgarten, J. Org. Chem., 29, 3636 (1964).
116. G. Dunn, I. McKenzie, and G. Wright, Canad. J. Res., 26B, 104 (1948).
117. T. Urbanski and J. Zylowski, Bull. Acad. Polon. sci., 14, 7–9 (1957).
118. R. Meen and G. Wright, Bull. Acad. Polon. sci., 74, 2077 (1952).
119. M. Kirkwood and G. Wright, J. Org. Chem., 18, 629 (1953).
120. R. Hall and G. Wright, J. Amer. Chem. Soc., 73, 2208 (1951).
121. A. McKay, M. Weinberger, J. Picard, W. Hatton, M. Bedard, and H. Rowey, J. Amer. Chem. Soc., 76, 6371 (1954).
122. W. Emmons and I. Freeman, J. Amer. Chem. Soc., 77, 4387 (1955).
123. H. Mandel, U. S. P. 3 071 438 (1963); Chem. Abs., 59, 447 (1963).
124. E. Bamberger, Ber., 27, 668 (1894).
125. L. Winters, D. Learn, and S. Desay, J. Org. Chem., 30, 2471 (1965).
126. A. Hinsberg, Ber., 25, 1093 (1892).
127. M. Eerles and J. Jitba, "Chemie pyridinu", Praga, 1957.
128. E. Atkinson and F. Whitmore, J. Amer. Chem. Soc., 73, 4443 (1951).
129. T. O'Konnor, G. Fleming, and J. Neily, J. Soc. Chem. Ind., 68, 309 (1949).
130. E. Lieber, E. Scherman, R. Henry, and J. Cohen, J. Amer. Chem. Soc., 73, 2327 (1951).
131. R. Reed, J. Amer. Chem. Soc., 78, 801 (1956).
132. J. Bell and I. Dunstan, J. Chem. Soc. (C), 562 (1967).
133. L. A. di Cerrione, Ann. chimika Applic, 38, 5, 255 (1955).
134. K. Dunning and W. Dunning, J. Chem. Soc., 2920 (1950).
135. J. Freeman, J. Org. Chem., 26, 4190 (1961).
136. J. Thiele, Lieb. Ann., 376, 254 (1910).
137. A. Berg. Ann. chim. phys., [7], 3, 357 (1894).
138. J. Wayghan, J. Chem. Soc., 748 (1950).
139. J. Cason and F. Prout, J. Amer. Chem. Soc., 71, 1218 (1949).
140. J. Runge and W. Treibs, J. pract. chem., 15, 223 (1962).
141. M. Kohen, D. Perry, and P. Keenan, U. S. P. 3 120 566 (1964); Ref. Zhur. Khim., 14P1220 (1965).
142. J. Mathieu and A. Allais, "Principes de Synthèse Organique" (Translated into Russian), Inostr. Lit., Moscow, 1962.
143. C. Lindley and J. Speakman, J. Chem. Soc., 1657 (1949).
144. E. Baly and C. Desch, J. Chem. Soc., 93, 1752 (1908).
145. E. Yu. Orlova, "Khimiya i Tekhnologiya Brizantnykh Vzryvchatykh Veshchestv" (Chemistry and Technology of High Explosives), Oborongiz, 1960, p. 224.

146. J. Young, J. Heith, P. Stehe, W. Dzomback, and H. Hunt, Ind. Eng. Chem., 48, 1375 (1956).
147. Y. Carignan and D. Satriana, J. Org. Chem., 32, 285 (1967).
148. L. Medard and M. Thomas, Mem. poudres, 39, 195 (1957).
149. B. Spruyt, Chem. Zbl., 16, 185 (1892).
150. M. Davies and N. Jontan, Trans. Faraday Soc., 54, 469 (1958).
151. L. J. Bellamy, "The Infra-red Spectra of Complex Molecules" (Translated into Russian), Inostr. Lit., 1957.
152. V. G. Avakyan, G. N. Gosteva, and V. A. Chekrygin, Izv. Akad. Nauk SSSR, Ser. Khim., 432 (1968).
153. R. Jones and G. Thorn, Canad. J. Res., 27B, 828 (1949).
154. H. Curry and J. Mason, J. Amer. Chem. Soc., 73, 5449 (1951).
155. G. Kortum and B. Funk, Z. phys. Chem., 48B, 46 (1940).
156. K. Kholrausch and H. Wittek, Acta phys. Austriaca, 1, 292 (1948).
157. D. Liebig, J. Robertson, and M. Truter, J. Chem. Soc. (A), 879 (1966).
158. H. Umbgrowe and A. Franchimont, Rec. trav. chim., 17, 270 (1898).
159. A. McKay, W. Hatton, and M. Skulski, Canad. J. Chem., 33, 1197 (1955).
160. J. Thiele and K. Meyer, Ber., 29, 961 (1896).
161. J. Thiele, Lieb. Ann., 376, 254 (1910).
162. L. Goodman, J. Amer. Chem. Soc., 75, 3019 (1953).
163. J. Denkstein and V. Kaderabek, Coll. Czech. Chem. Comm., 25, 2334 (1960).
164. I. Majer and J. Denkstein, Coll. Czech. Chem. Comm., 31, 2547 (1966).
165. F. Chapman, P. Owston, and D. Woodcock, J. Chem. Soc., 1638, 1647 (1949).
166. W. Chute, A. McKay, R. Meen, C. Myers, and G. Wright, Canad. J. Res., 27B, 503 (1949).
167. M. Frankel, J. Org. Chem., 26, 4709 (1961).
168. E. Hamel, Tetrahedron, 19(1), 85 (1963).
169. M. Frankel, U. S. P. 3 228 929 (1966); Chem. Abs., 64, 9594 (1966).
170. M. Frankel, U. S. P. 3 228 929 (1966); Ref. Zhur. Khim., 12N241P (1967).
171. S. S. Novikov, A. A. Dudinskaya, N. V. Makarov, and L. I. Khmel'nitskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1833 (1967).
172. I. V. Makarov, A. A. Dudinskaya, S. S. Novikov, and L. I. Khmel'nitskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1837 (1967).
173. S. S. Novikov, A. A. Dudinskaya, I. V. Makarov, and L. I. Khmel'nitskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1839 (1967).
174. L. Kissinger, M. Schwartz, and W. McQuiston, J. Org. Chem., 26, 5203 (1961).
175. I. S. Ivanova, Yu. V. Konnova, and S. S. Novikov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 920 (1962).
176. I. S. Ivanova, N. I. Bulatova, and S. S. Novikov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1858 (1962).
177. H. Feuer and R. Miller, J. Org. Chem., 26, 1348 (1961).
178. J. Winters and W. McEwen, Tetrahedron, 19(1), 46 (1963).
179. H. Feuer and R. Miller, U. S. P. 3 040 099 (1962); Chem. Abs., 57, 12 778 (1962).
180. J. Heinke, Ber., 31, 1395 (1898).
181. O. Degner and H. Pechman, Ber., 30, 647 (1897).
182. H. Umbgrowe and A. Franchimont, Rec. trav. chim., 15, 195 (1896).
183. P. Bruck and A. Lamberton, J. Chem. Soc., 3997 (1955).
184. J. Denkstein and V. Kaderabek, Coll. Czech. Chem. Comm., 31, 2904 (1966).
185. G. Sammons, U. S. P. 3 151 165 (1964); Chem. Abs., 62, 2662 (1965).
186. N. Kornblum, R. Smily, R. Blackwood, and D. Iffand, J. Amer. Chem. Soc., 77, 6269 (1955).
187. N. Kornblum and A. Lurie, J. Amer. Chem. Soc., 81, 2705 (1959).
188. J. Johnson and A. Blomquist, U. S. P. 2 863 165 (1954); Chem. Abs., 49, 7590 (1955).
189. N. M. Baranchik, I. V. Grachev, and D. Z. Zavel'skii, Zhur. Obshch. Khim., 27, 117 (1957).
190. A. L. Fridman, V. P. Ivshin, and T. N. Ivshina, Zhur. Obshch. Khim., 3, 1529 (1967).
191. E. Bamberger, Ber., 27, 376 (1894).
192. K. Orton, J. Org. Chem. Soc., 81, 865 (1902).
193. G. Thomas, U. S. P. 2 772 306 (1956); Chem. Abs., 51, 6686 (1957).
194. M. Graff, C. Gotzmer, and W. McQuiston, J. Org. Chem., 32, 3827 (1967).
195. M. Zimmer, E. Baroody, D. Carpenter, and M. Graff, Paper presented at the Symposium on Organofluorine Compounds, Munich, Federal Republic of Germany, 1965.
196. M. Zimmer, E. Baroody, M. Graff, and D. Carpenter, J. Chem. and Eng. Data, 11, 579 (1966).
197. J. Garrison and R. Herbst, J. Org. Chem., 22, 278 (1957).
198. E. Bamberger, Ber., 30, 1248 (1897).
199. L. Gatterman, Ber., 18, 1482 (1885).
200. E. Müller (Editor), "Methoden der organischen Chemie, (Houben-Weyl)", Thieme, Stuttgart.
201. Lehmstedt and O. Zumstein, Ber., 58, 2024 (1925).
202. K. Baum, U. S. P. 3 258 483 (1966); Chem. Abs., 65, 6991 (1966).
203. H. Hageman and J. Riddel, French P. 1 377 695 (1963); Chem. Abs., 62, 11 087b (1965).
204. French P. 1 388 762 (1964); Chem. Abs., 62, 16 904d (1965).
205. R. Hardy, D. Spratt, and C. Mees, B. P. 1 005 860 (1965); Chem. Abs., 63, 71 911h (1965).

Zelinskii Institute of
Organic Chemistry,
Academy of Sciences of
the USSR, Moscow