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Nitrobutadienes and their halogen derivatives: synthesis and reactions

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Contents

I.	Introduction	827
II.	Synthesis of nitrobutadienes and their halogen derivatives	827
III.	Addition reactions	832
IV.	Substitution reactions	834
V.	Other reactions	839

Abstract. The main methods of the synthesis of nitrobutadienes and their halogen derivatives, which are multipurpose electrophiles, are surveyed. The literature data on their chemical transformations are generalised, the possibilities for the preparation of new polyfunctional derivatives of different classes on the basis of nitro- and halo-nitrobutadienes that have been inaccessible earlier are demonstrated. The bibliography includes 112 references.

I. Introduction

The chemistry of nitro compounds has been intensively studied during the last 20 – 25 years. Since 1970, many scientific papers, monographs,[1–3] and reviews[4–18] on the synthesis and the properties of these compounds have been published.

The interest in nitro compounds is primarily due to the possibilities of their application as unique intermediate products for the synthesis of various organic compounds. It should be noted that at present most attention is attracted to aliphatic nitro compounds. Thus, a review[4] that first suggested the versatility and importance of aliphatic nitro compounds in organic synthesis appeared back in 1979. The results of subsequent studies in this direction (see for instance[5,6]) have confirmed the importance of new investigations in the chemistry of nitro compounds of the aliphatic series.

At present, much attention is paid to the synthesis and the properties of nitro-alkenes and -alkadienes. Studies along the first direction are rather diverse and mostly concern such specific questions as the synthesis of nitrogen-containing heterocycles involving O and N atoms of the alkene nitro group,[9] methods of synthesis and reactions of allylic nitro compounds and their derivatives,[15] and others.[12,16]

Recently interest increased in nitrobutadienes, and especially their halogen derivatives. These highly reactive substances were used to develop preparative methods for the synthesis of complex polyfunctional derivatives of different classes, that have been virtually inaccessible before. Thus an original method for the synthesis of a valuable amino acid, lysine, from 1-nitrobuta-1,3-diene has been proposed. A convenient route for building of isothiazole cycle from 2-nitropentachlorobuta-1,3-diene and sulfur has been developed. Halogen derivatives of nitrobutadienes are suitable model objects for elucidation of the features of nucleophilic vinylic substitution (S_NVin).

The publications that cover this subject, published before 1985, have been only partially discussed in monographs[1–3] and a review.[8] We have surveyed and systematised the results of investigations performed during the last two decades in the chemistry of nitrobutadienes and their halogen derivatives.

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II. Synthesis of nitrobutadienes and their halogen derivatives

Basically, two main methods for the synthesis of nitrobutadienes including their halogen derivatives are used: (1) the direct nitration of butadiene and its derivatives by different nitrating agents; (2) the synthesis from more complex aliphatic nitrocompounds by elimination of different molecules (hydrogen halides, acetic acid, *etc*.). In some cases the formation of different geometric isomers of the nitro-substituted butadienes is possible. However, the configuration and the ratio between *E*- and *Z*-isomers have not been determined for all the halogenonitrobutadienes synthesised, therefore, we specify the isomeric form only if it is given in the literature, cited.

1. Preparation of nitrobutadienes and their halogen derivatives by nitration of dienes

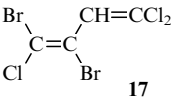
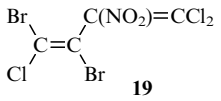
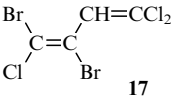
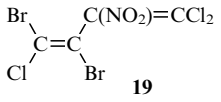
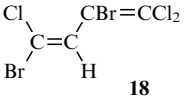
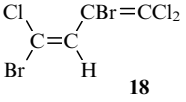
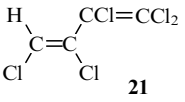
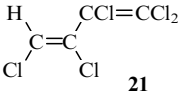
a. Synthesis of mononitrobutadienes

The direct nitration of butadiene (**1**) by nitric acid results in 1-nitrobutadiene (**2**).[19,20]

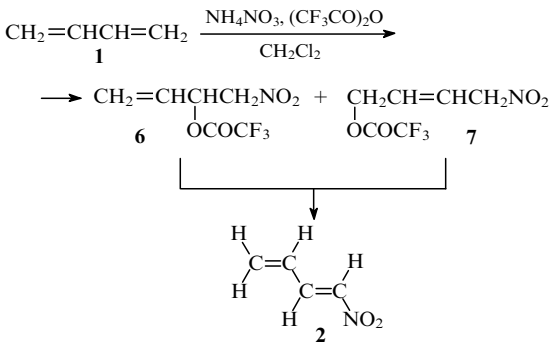
$$\underset{\mathbf{1}}{CH_2{=}CHCH{=}CH_2} \xrightarrow{HNO_3} \underset{\mathbf{2}}{CH_2{=}CHCH{=}CHNO_2}.$$

The conditions of this and other nitration reactions are summarised in Table 1. Dinitrogen tetroxide, dinitrogen pentoxide, and N_2O_4 in an oxygen flow can be used as the nitration agents in reaction with butadiene.[8,21,22] However, the formation of nitrobutadienes was not observed in these cases, the reactions lead to the products of addition of NO_2 and ONO_2 to the diene **1**: 1,4-dinitrobut-2-ene (**3**), 4-nitrobut-2-enylnitrate (**4**) or 1-nitrobut-3-enyl-2-nitrate (**5**). The latter were used for the synthesis of nitrobutadiene **2** (see Section II.2).

Table 1. Synthesis of nitrobutadienes and their halogen derivatives by nitration of the butadienes.

Starting diene	Nitrating reagent	T /°C	Nitrobutadiene	Yield (%)	Ref.
$CH_2{=}CHCH{=}CH_2$ **1**	Fuming HNO_3	–	$CH_2{=}CHCH{=}CHNO_2$ **2**	–	19, 20
$CH_2{=}CHCH{=}CH_2$ **1**	CF_3COONO_2	–	$CH_2{=}CHCH{=}CHNO_2$ **2**	89	23, 24
$Cl_2C{=}CClCH{=}CCl_2$ **8**	HNO_3 (conc.)	80 – 85	$CCl_2{=}CClC(NO_2){=}CCl_2$ **9**	40	25
$Cl_2C{=}CClCH{=}CCl_2$ **8**	$HNO_3 - H_3PO_4$ (10 : 1)	–	$CCl_2{=}CClC(NO_2){=}CCl_2$ **9**	60	26
$Cl_2C{=}CClCH{=}CCl_2$ **8**	$HNO_3 - H_2SO_4$ (10 : 1)	–	$CCl_2{=}CClC(NO_2){=}CCl_2$ **9**	55	26
$CBrCl{=}C(Cl)CH{=}CCl_2$ **14**	HNO_3 (conc.)	80 – 85	$CBrCl{=}CClC(NO_2){=}CCl_2$ **15**	40	27
$CBrCl{=}C(Cl)CH{=}CCl_2$ **14**	$HNO_3 - H_3PO_4$ (10 : 1)	95 – 100	$CBrCl{=}CClC(NO_2){=}CCl_2$ **15**	58	28
 **17**	HNO_3 (conc.)	80 – 85	 **19**	40	29
 **17**	$HNO_3 - H_3PO_4$ (10 : 1)	90 – 95	 **19**	48 – 50	29
 **18**	HNO_3 (conc.)	80 – 85	$CBrCl{=}CCBr{=}CCl_2$ (NO$_2$ at C^2) **20**	35	29
 **18**	$HNO_3 - H_3PO_4$ (10 : 1)	90 – 95	$CBrCl{=}CCBr{=}CCl_2$ (NO$_2$ at C^2) **20**	50	29
 **21**	HNO_3 (conc.)	70 – 75	$CCl_2{=}CClCCl{=}CCl$ (NO$_2$ at C^4) **22**	49	31
 **21**	$HNO_3 - H_3PO_4$ (10 : 1)	90 – 95	$CCl_2{=}CClCCl{=}CCl$ (NO$_2$ at C^4) **22**	56	31
$CHCl{=}CHCH{=}CHCl$ **25**	HNO_3 (conc.)	70	$CCl(NO_2){=}CHCH{=}CCl(NO_2)$ **26**	7.7	33
$CHCl{=}CHCH{=}CHCl$ **25**	$AcONO_2$ in AcOH	20 – 25	$CH(NO_2){=}CHCH{=}CCl(NO_2)$ **27** + $CCl(NO_2){=}CHCH{=}CCl(NO_2)$ **26**	9.1 1.4	33
$CBrCl{=}CHCH{=}CCl_2$ **29**	HNO_3 (conc.)	80 – 85	$CCl(NO_2){=}CHC(NO_2){=}CCl_2$ **28**	10	30
$CBrCl{=}CHCH{=}CCl_2$ **29**	$HNO_3 - H_3PO_4$ (10 : 1)	90 – 95	$CCl(NO_2){=}CHC(NO_2){=}CCl_2$ **28**	18	36

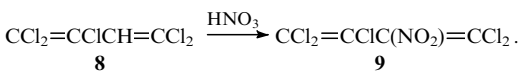
Recently, the nitration of butadiene by trifluoroacetyl nitrate has been proposed, the reagent being generated *in situ* from ammonium nitrate and trifluoroacetic anhydride. A mixture of 1,2- and 1,4-nitro-trifluoroacetates thus formed (**6** and **7**, respectively) was treated with potassium acetate in ether or by sodium hydride in THF to give one isomer of the nitrodiene **2** in 89% yield.[23,24] On the basis of IR-spectrum, *E*-configuration was assigned to the diene **2**. The nitrotrifluoroacetoxylation of butadiene may be represented by the following scheme:



b. Synthesis of halogenonitrobutadienes

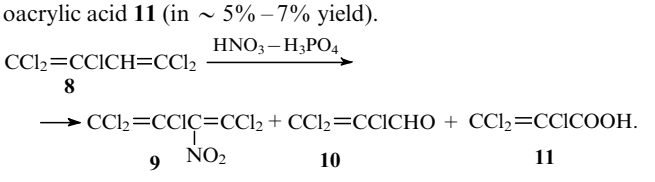
The direct nitration of the corresponding dienes is mostly used for the preparation of polyhalogenonitrobutadienes and products of their oxidative destruction.

The nitration of 1,1,2,4,4-pentachlorobutadiene (**8**) with concentrated HNO_3 occurs at the dichlorovinyl group by electrophilic substitution of the H atom by the nitro group with the formation of 2-nitropentachlorobuta-1,3-diene (**9**) in ~ 40% yield.[25]

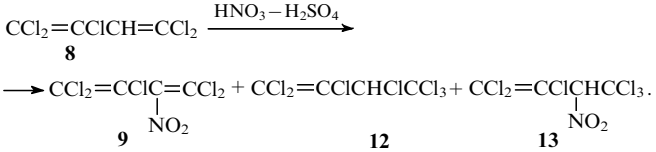


The same authors studied the interaction of the diene **8** with other nitration reagents.[26] It has been shown that the nitration of the diene **8** by a mixture of HNO_3 and H_3PO_4 (10 : 1) allowed one to increase the yield of the target product **9** up to 58%-60%, the duration of nitration was thus shortened three- to four-fold. Increase or decrease in the content of phosphoric acid in the reaction mixture increases the reaction time and decreases the yield of the nitrodiene.

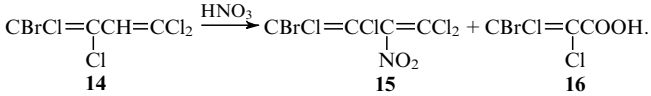
The nitration of the diene **8** by nitric acid and the 10 : 1 $HNO_3 - H_3PO_4$ mixture is accompanied by oxidative destruction, which leads to trichloroacrolein **10** (in ~ 12% yield) and trichloroacrylic acid **11** (in ~ 5% – 7% yield).



The nitrodiene **9** was synthesised in 54% – 55% yield by nitration of the diene **8** by a mixture of HNO_3 and H_2SO_4 (10 : 1). The higher content of H_2SO_4 in the mixture results in the activation of side reactions of chlorination and nitrochlorination of the starting diene **8**, which lead to 1,1,2,3,4,4,4-heptachlorobut-1-ene (**12**) and 3-nitro-1,1,2,4,4,4-hexachlorobut-1-ene (**13**).



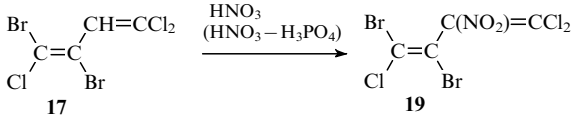
The nitration of mixed bromochlorobutadienes has been studied in detail using 1-bromo-1,2,4,4-tetrachlorobuta-1,3-diene (**14**) which contains a β,β-dichlorovinyl group, as an example. Its interaction with concentrated HNO_3 leads to 4-bromo-1,1,3,4-tetrachloro-2-nitrobuta-1,3-diene (**15**) (in 40% yield); bromodichloroacrylic acid (**16**) was found as a by-product.[27]



If an HNO_3(conc.) – H_3PO_4(conc.) nitration mixture is used, the yield of the target product **15** is considerably increased, and under the optimum conditions amounts to 52% – 53%.[28]

The nitration of a mixture of two geometric isomers of bromochlorobutadiene **14** (*Z*/*E* = 25 : 75) resulted in the nitrodiene **15** in the form of two isomers in practically the same ratio. The individual isomers were isolated by column chromatography on silica gel.

The nitration of mixed pentahalogenobutadienes containing two Br atoms in the molecule have been studied using 1,2-dibromo-1,4,4-trichlorobuta-1,3-diene (**17**) and 1,3-dibromo-1,4,4-trichlorobuta-1,3-diene (**18**) as examples. Reaction of the *E*-isomer of the diene **17** with concentrated HNO_3 gave (*E*)-3,4-dibromo-2-nitro-1,1,4-trichlorobuta-1,3-diene (**19**) in 40% yield. If the mixture of concentrated HNO_3 and H_3PO_4 (10 : 1) was used for the nitration of the diene **17**, the yield of the nitrodiene **19** increased by 8% – 10%.[29]

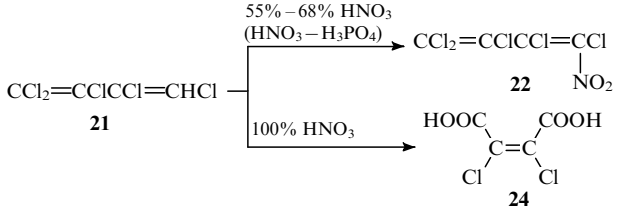


The dibromotrichlorodiene **18** behaves in nitration similarly to the diene **17**.[29] 1,3-Dibromo-2-nitro-1,4,4-trichlorobuta-1,3-diene (**20**) was obtained as one isomer (in 35% yield) by reaction of *E*-isomer of diene **18** with HNO_3. The nitration of the diene **18** by the mixture of $HNO_3 - H_3PO_4$ (10 : 1) allowed one to increase the yield of the target product **20** to 48% – 50%.

Thus, the nitration of all the above-discussed polyhalogenobutadienes containing the β,β-dichlorovinyl group † proceeds in the usual way with the substitution of the H atom by the nitro group.

The behaviour of halogenobutadienes containing α,β-dihalovinyl groups, in reaction with nitric acid has been studied only with the example of (*Z*)-1,1,2,3,4-pentachlorobuta-1,3-diene (**21**). The action of concentrated HNO_3 on the diene **21** results in the substitution of the only H atom by nitro group with the formation of 1,2,3,4,4-pentachloro-1-nitrobuta-1,3-diene (**22**) (in ~ 49% yield).[31] The use of a nitration mixture consisting of concentrated HNO_3 and H_3PO_4 allows one to obtain the target nitrodiene **22** in 55% – 56% yield.

Hexachlorobutadiene (**23**) (~ 6%), trichloroacrylic acid (**11**) (~ 8%), and dichloromaleic acid (**24**) (in ~ 4% yield) are the by-products of the reaction. The use of fuming HNO_3 directs the reaction towards the preponderant formation of the valuable acid **24** (60%).[32]

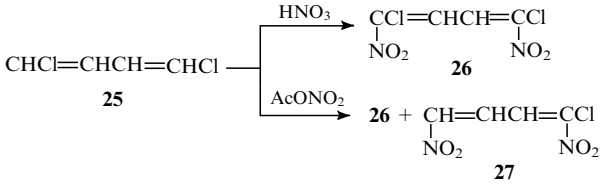


† It is interesting to note that 1,1,4,4-tetrachlorobuta-1,3-diene with two β,β-dichlorovinyl groups under the action of 58% – 60% HNO_3 gives the addition product — 1,1,4,4-tetrachloro-1,4-dinitrobut-2-ene. No products of the substitution of H atoms by the nitro group were registered.[30]

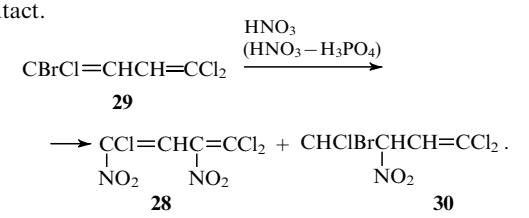
c. Synthesis of polynitrobutadienes

The introduction of two or more nitro groups into the butadiene molecule is a very difficult task, nevertheless methods of preparation of halogenodinitrobutadienes by direct nitration of halogen derivatives of butadiene have been described in a series of publications. Thus nitration of 1,4-dichlorobuta-1,3-diene (**25**) (a mixture of *E*,*E*-, *Z*,*Z*-, and *E*,*Z*-isomers) by nitric acid has been described.[33–35] The effect of the density of HNO_3, temperature, duration of the process, and the reagent ratio on the yield of the final product has been studied.[33] It was found that the maximum yield (7.7%) of 1,4-dichloro-1,4-dinitrobuta-1,3-diene (**26**) was achieved if the density of nitric acid was 1.36 g ml^{-1}, the HNO_3/diene ratio was 100 : 30 (by volume), and the reaction was performed at 70 °C for 10 min. Only *E*,*E*-form of the diene **25** is believed to undergo nitration, while other isomers were oxidised to gaseous products.

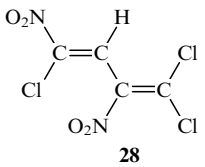
The treatment of a mixture of isomers of the diene **25** by acetyl nitrate in acetic acid resulted under these conditions in 1-chloro-1,4-dinitrobuta-1,3-diene **27** in 9% yield;[33] the yield of nitrobutadiene **26** did not exceed 1.4%.



Recently, the synthesis of 1,4,4-trichloro-1,3-dinitrobuta-1,3-diene (**28**) has been accomplished by nitration of 1-bromo-1,4,4-trichlorobuta-1,3-diene (**29**) by nitric acid and nitration mixtures.[30,36] 4-Bromo-1,1,4-trichloro-3-nitrobut-1-ene (**30**) was the other product of this reaction (~ 40%). It is interesting to note that the formation of the dinitrodiene **28** occurs as a result of the substitution of one H atom in the β,β-dichlorovinyl group and Br atom by nitro groups, the second H atom of the diene **29** remains intact.



The yield of dinitrodiene **28** under the optimum nitration conditions is 18% (Table 1). X-Ray structural analysis has shown that the nitrodiene **28** is a *Z*-isomer with a non-planar *s-trans*-conformation.[37]

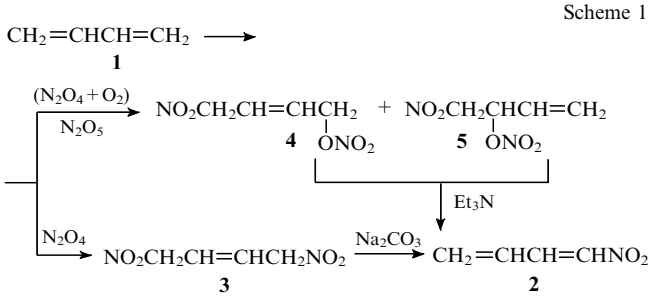


There are no data reporting the introduction of three or more nitro groups into the butadiene molecule by direct nitration.

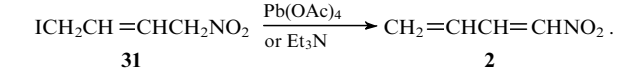
2. Preparation of nitrobutadienes and their derivatives by elimination reaction

The accessibility of certain nitrobutenes allowed one to develop reasonable methods for synthesis of a series of nitrobutadienes by elimination of different fragments (hydrogen halides, nitrous acid, *etc.*) from the starting compounds. Thus the nitrodiene **2** (the yield is not mentioned) was prepared by the treatment of 1,4-dinitrobut-2-ene **3** (the product of addition of dinitrogen tetroxide to butadiene **1**) with sodium carbonate in benzene.[21] Yet another method of the synthesis of the nitrodiene **2** is the reaction of a mixture of nitro-substituted butenes **4** and **5** (the products of the reaction of butadiene **1** with dinitrogen pentoxide or N_2O_4 in an oxygen flow) with triethylamine in an ethereal solution (Scheme 1).[22]

Scheme 1

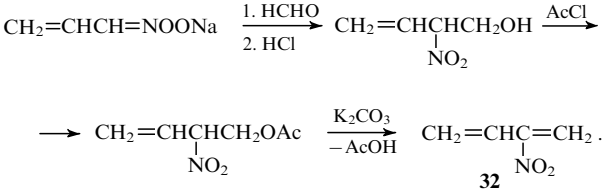


A method for the synthesis of the nitrodiene **2** (maximum yield 35%) by dehydroiodination of 4-iodo-1-nitrobut-2-ene (**31**) under the action of lead acetate in glacial acetic acid has earlier been suggested.[38] Dehydrohalogenation of butene **31** has also been done with triethylamine[22] in ether at −30 °C in the presence of hydroquinone as an additive to prevent polymerisation of the target product.

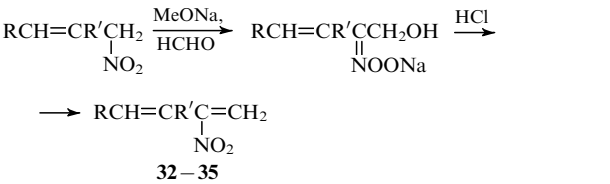


The use of alkalies as dehydrohalogenation agents resulted in complete resinification of the reaction mixture. The starting iodide **31** was synthesised by reaction of butadiene with dinitrogen tetroxide and iodine.

2-Nitrobuta-1,3-diene **32** was first synthesised (in 50% yield)[39] *via* the sodium derivative of 3-nitroprop-1-ene. Its condensation with formaldehyde gave 2-nitrobut-3-en-1-ol, which was further treated with acetyl chloride and deacetoxylated. In order to prevent polymerisation of the nitrodiene **32**, the reaction was performed in the presence of hydroquinone.

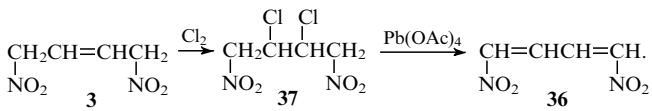


Later, a general method for the synthesis of 2-nitroalkadienes **32**–**35** by dehydration of salts of the corresponding nitroalcohols with mineral acids was developed.[40]

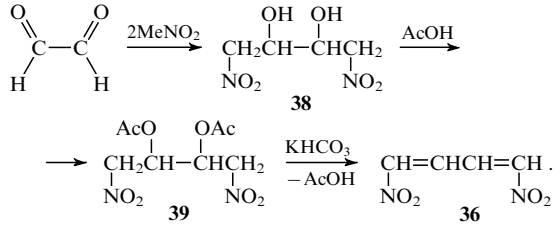


R = R′ = H (**32**); R = H, R′ = Me (**33**);
R = Me, R′ = H (**34**); R = R′ = Me (**35**).

The synthesis of 1,4-dinitrobuta-1,3-diene (**36**) has been described in detail by two groups of Russian chemists almost simultaneously. Perekalin and Lerner[41] have prepared the diene **36** by chlorination of 1,4-dinitrobut-2-ene (**3**) with subsequent dehydrochlorination of the formed 2,3-dichloro-1,4-dinitrobutane (**37**).



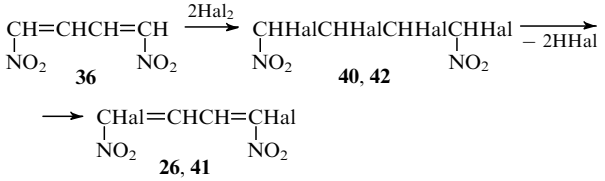
Novikov with coworkers [42] have synthesised the diene **36** from 1,4-dinitrobutane-2,3-diol (**38**), the product of condensation of glyoxal with nitromethane. Diol **38** was first converted into the diacetate and the ester was then deacetoxylated by the treatment with potassium hydrogencarbonate.



It has been shown [43] that the diol **38** was a mixture of D,L- and *meso*-isomers of 1,4-dinitrobutane-2,3-diol (in the ratio of 2.6 : 1.0). The nitrobutadiene **36** was synthesised in 70% – 85% yield by refluxing DL- or *meso*-2,3-diacetoxy-1,4-dinitrobutane (**39**) in chloroform with a catalytic amount of anhydrous $KHCO_3$.

Convenient methods for the synthesis of two dihalogenodinitro derivatives of butadiene from the nitrodiene **36** have been developed. Thus chlorination of diene **36** in acetic acid saturated with HCl gave 1,2,3,4-tetrachloro-1,4-dinitrobutane (**40**) in 98.5% yield. The latter was stirred with a suspension of florisil in benzene for 4 h, and the nitrodiene **26** was isolated in 99% yield.[44]

The diene **41** was synthesised by bromination of the diene **36** followed by dehydrobromination of 1,2,3,4-tetrabromo-1,4-dinitrobutane (**42**), its yield depended mostly on the nature of the dehydrobrominating agent.[44–50] It turned out that calcium and potassium carbonates and magnesium oxide could not be used for this purpose. When potassium acetate was used, the yield of the diene **41** was 67%. 2,6-Lutidine and 2-picoline were efficient dehydrobrominating agents, they allowed one to increase the yield of the diene **41** up to 85%.[46] It can also be readily prepared by the treatment of the butane **42** with aqueous methanol; in this case the yield of the target diene was 81%.[45]



Hal = Cl (**26**, **40**), Br (**41**, **42**).

In order to explore the possibility of the synthesis of 1,1,4,4-tetranitrobuta-1,3-diene (**43**) the behaviour of 1,1,4,4-tetranitrobutane-2,3-diol diacetate (**44**) in different media has been studied. It has been shown that in the presence of bases, the ester **44** can be easily deacetoxylated and tetranitrodiene **43** formed *in situ* gives bis-adducts (see Section III.1).[51]

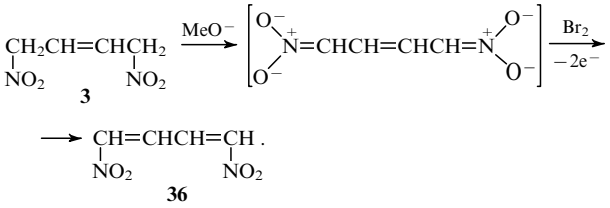
The conditions of the elimination reactions and the yields of the nitrodienes thus obtained are given in Table 2.

Table 2. Synthesis of nitrobutadienes and their halogen derivatives by elimination reactions.

Starting compound	Eliminating reagent	Nitrobutadiene	Yield (%)	Ref.
$NO_2CH_2CH{=}CHCH_2NO_2$ **3**	Na_2CO_3	$CH_2{=}CHCH{=}CHNO_2$ **2**	–	21
$NO_2CH_2CH{=}CHCH_2$ (**4**) + $NO_2CH_2CH{=}CH_2$ (**5**)	Et_3N	$CH_2{=}CHCH{=}CHNO_2$ **2**	–	22
$ICH_2CH{=}CHCH_2NO_2$ **31**	$Pb(OAc)_4$	$CH_2{=}CHCH{=}CHNO_2$ **2**	35	38
$CH_2{=}CHCHCH_2OAc$ (NO_2)	K_2CO_3	$CH_2{=}CHC{=}CH_2$ (NO_2) **32**	50	39
$CH_2{=}CHCCH_2OH$ (NOONa)	HCl	$CH_2{=}CHC{=}CH_2$ (NO_2) **32**	–	40
$NO_2CH_2CHCHCH_2NO_2$ (Cl, Cl) **37**	$Pb(OAc)_4$	$NO_2CH{=}CHCH{=}CHNO_2$ **36**	40	41
$NO_2CH_2CH(OAc)CH(OAc)CH_2NO_2$ **39**	$KHCO_3$	$NO_2CH{=}CHCH{=}CHNO_2$ **36**	85	42, 44
$CHClCHClCHClCHCl$ (NO_2, NO_2) **40**	Suspension of florisil	$CCl{=}CHCH{=}CCl$ (NO_2, NO_2) **26**	99	44
$CHBrCHBrCHBrCHBr$ (NO_2, NO_2) **42**	2,6-Lutidine or 2-picoline	$CBr{=}CHCH{=}CBr$ (NO_2, NO_2) **41**	85	45, 46
$(NO_2)_2CH{-}CH(OAc){-}CH(OAc){-}CH(NO_2)_2$ **44**	Alkalies, NaOMe, aniline	$(NO_2)_2CH{=}CHCH{=}CH(NO_2)_2$ **43**	–	51

3. Other methods for the synthesis of nitrobutadienes

Among other methods for the synthesis of the nitro derivatives of butadiene, one should mention first of all the oxidation of the salts of 1,4-dinitrobut-2-ene into 1,4-dinitrobuta-1,3-diene **36**.[52–54] The addition of 1 mol of an oxidising agent (Br_2, I_2, $K_3Fe(CN)_6$, $AgNO_3$) to the suspension of **3** in ether gives dinitrobutadiene **36** in 50%–55% yield. Bromine, which has high oxidising potential, is the most universal oxidising agent.[53]

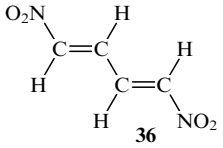


The treatment of the butene **3** with methanolic KOH and bromine in methanol at −10 °C gives diene **36** in 79% yield.[45]

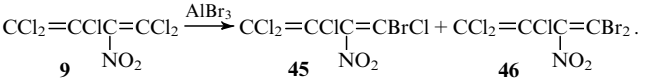
The redox titration has demonstrated that the transformations of the conjugated dianions proceeded as two-electron redox processes.[55]

It has been found [55] that the nitrodiene **36** can be prepared in 50% yield by reaction of butene **3** with butyllithium in a mixture of THF and hexametapol at −70 to −50 °C and subsequent bromination at this temperature. The nitrodiene **2** was also found in the reaction products in 5% yield. The compound **36** presumably resulted from the two-electron oxidation process.

On the basis of a combination of several spectral data [46, 54, 57] the *E*,*E*-structure was ascribed to the diene **36**.

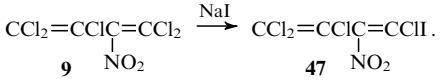


A series of mixed nitroperhalogenobutadienes was obtained by exchange of the halogen atoms. Thus in the reaction of the nitrodiene **9** with $AlBr_3$ substitution of one or two Cl atoms by Br in the nitrodichlorovinyl fragment occurs depending on the ratio of the reagents.[58] At the ratio of **9** : $AlBr_3$ = 1 : 1 in refluxing bromoethane, a mixture of mono- and di-substituted products, 1-bromo-1,3,4,4-tetrachloro-2-nitrobuta-1,3-diene (**45**) and 1,1-dibromo-3,4,4-trichloro-2-nitrobuta-1,3-diene (**46**) in the molar ratio of 1.0 : 5.3 (GLC) is formed in 71% total yield.

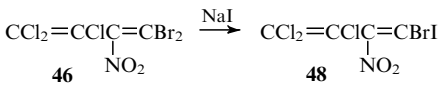


The use of an excess of $AlBr_3$ (**9** : $AlBr_3$ = 1.0 : 1.5) gives the diene **46** in 55% yield. The nitrobutadiene **46** was also prepared in 71% yield by the action of $AlBr_3$ on the diene **45**.

The reaction of the nitrodiene **9** with sodium iodide in acetone (the Finkelstein reaction) results in 1,3,4,4-tetrachloro-1-iodo-2-nitrobuta-1,3-diene (**47**) in 59% yield.[58]

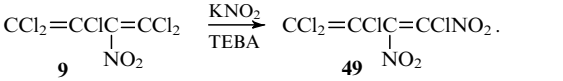


The butadiene **46** also exchanges only one Br atom for I in the nitrodibromovinyl fragment under analogous conditions, giving 1-bromo-3,4,4-trichloro-1-iodo-2-nitrobuta-1,3-diene (**48**) in 54% yield.[58]



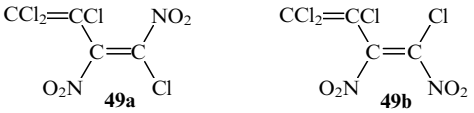
The substitution of halogen atoms by nitrite ion, which has been well studied in the alkyl halide series, is represented by only two examples in the synthesis of nitrobutadienes.

1,3,4,4-Tetrachloro-1,2-dinitrobutadiene (**49**) was synthesised by the reaction of 2-nitrodiene **9** with potassium nitrite in aqueous medium with triethylbenzyl ammonium chloride (TEBA) as a phase-transfer catalyst.[59]

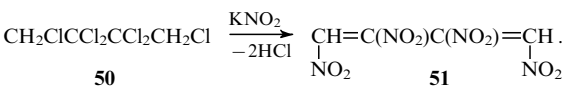


The study of the effect of temperature, the duration of reaction, the reagent ratio, and the KNO_2 concentration on the course of the reaction has shown that the optimum conditions are as follows: 5% TEBA and a twofold molar excess of the 30% KNO_2 solution. In all cases, the conversion of the nitrodiene **9** was not complete, the yield of **49** did not exceed 29% with respect to the diene **9** consumed. The use of other phase-transfer catalysts, *e.g.*, tetraethylammonium chloride, dibenzo-18-crown-6, and 18-crown-6 gave no advantages in comparison with TEBA.

The nitrobutadiene **49** was obtained as a 3 : 1 mixture of two isomers, which were separated by column chromatography on silica gel and characterised by spectroscopy. It was estimated that the main product was the *Z*-isomer **49a**, the other compound the *E*-isomer **49b**:



1,2,3,4-Tetranitrobuta-1,3-diene (**51**) was obtained by the reaction of 1,2,2,3,3,4-hexachlorobutane (**50**) with KNO_2 in methoxyethanol at 120 °C and isolated as salt in 91% yield.[60]

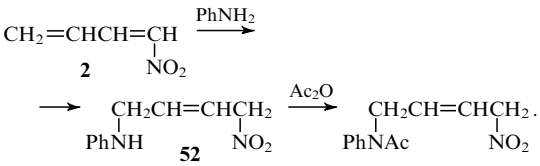


III. Addition reactions

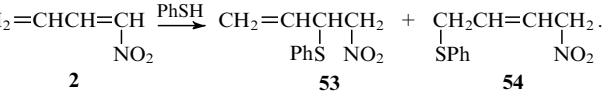
The development of methods for the synthesis of nitro- and nitrohalogen derivatives of butadiene paralleled their examination as the starting compounds for numerous chemical reactions.

1. Nucleophilic reactions

As a result of the electron-accepting effect of the nitro group, nitrobutadienes are able to participate in nucleophilic addition reactions. It has been shown, for example, that the simplest nitroalkadiene, 1-nitrobutadiene **2**, readily reacts with various nucleophilic reagents. The direction of these reactions depends on the nature of the nucleophile. They may occur both at the 1,2- and 1,4-positions of the diene system. Thus, the reaction of the nitrodiene **2** with aniline gives mostly 1-anilino-4-nitrobut-2-ene **52** (57%) characterised as the *N*-acetate.[24]

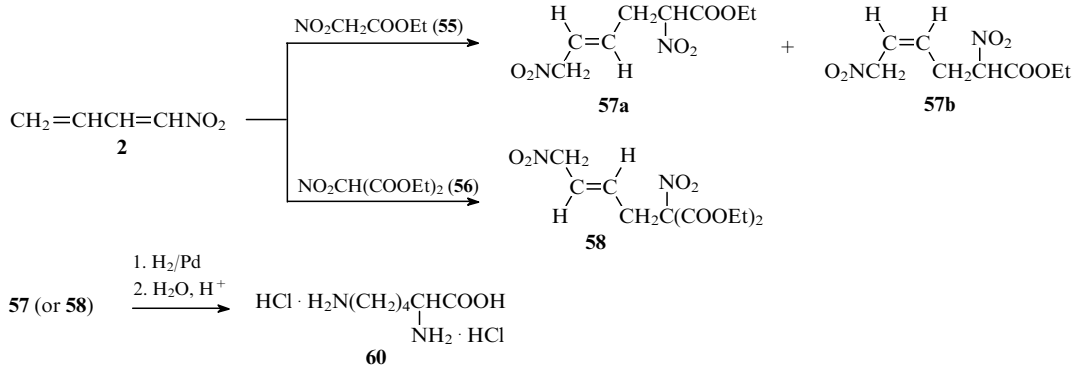


The reaction of the nitrodiene **2** with ethanethiol preferentially occurs at the nitrovinyl group.[61] The diene **2** reacts analogously with thiophenol to give the 1,2-adduct **53** in 54% and the 1,4-adduct in 13% yield: [24]



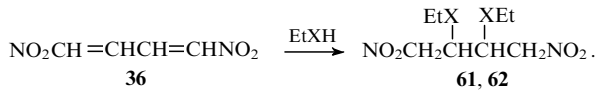
The addition of C-nucleophiles to nitrodienes has been studied using the reaction of the compound **2** with ethyl nitroacetate **55**

Scheme 2



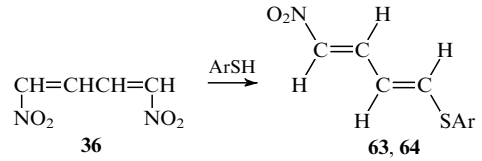
and nitromalonate **56** in the presence of triethylamine as examples.[22, 62, 63] This reaction occurs at the 1,4-position and results in ethyl 2,6-dinitrohex-4-enoate (**57**) and diethyl 1,5-dinitropent-3-ene-1,1-dicarboxylate (**58**) in 32% and 35% yields respectively. The ester **57** was obtained in the form of two isomers, (*E*)-**57a** and (*Z*)-**57b**; also in the second case the product of bis-addition, ethyl 1,5,9-trinitrononа-2,7-diene-5-carboxylate (**59**) was isolated (Scheme 2). Hydrogenation of the adducts **57** and **58** on a palladium catalyst in acidic ethanol resulted in the formation of ethyl 2,6-diaminohexanoate, its hydrolysis gave D,L-lysine hydrochloride **60** in 70% yield. This reaction is an original route for the preparation of a valuable amino acid, lysine.

In reactions with nucleophiles, dinitrobutadienes may give addition products of one or two molecules of the reagent as well as substitution products. The addition product of two molecules of ethanol, 2,3-diethoxy-1,4-dinitrobutane (**61**), has been isolated in 52% yield in the treatment of the nitrodiene **36** with ethanol at 25 °C.[64] The product of bis-addition **62** is also formed in the reaction of the diene **36** with ethanethiol.



X = O (**61**), S (**62**).

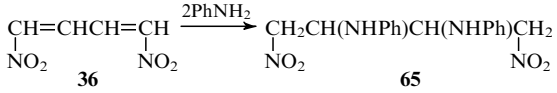
With more reactive arenethiols, the nitrodiene **36** gives the product of substitution of a nitro group, *e.g.* its reaction with thiophenol results in 4-nitro-1-phenylthiobuta-1,3-diene (**63**) in 42% yield.[65] The reaction of the nitrodiene **36** with *p*-toluenethiol in methanol proceeds analogously and gives 4-nitro-1-*p*-tolylthiobuta-1,3-diene (**64**) (28%).[66] In this case, presumably, the nucleophilic addition-elimination is realised. The direction of nucleophilic attack at the terminal C atom, which has never been observed earlier in reactions of aliphatic dinitrodienes with other nucleophiles, has been rationalised[66] as being due to the steric factors: the bulky reagent molecule and the stability of the conjugated system formed. On the basis of ^{1}H NMR spectra, an *E*,*E*-configuration was ascribed to compounds **63** and **64**.



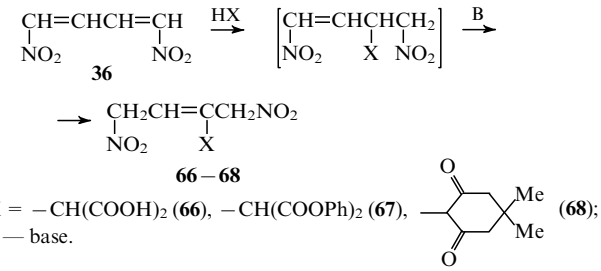
Ar = Ph (**63**); *p*-MeC_6H_4 (**64**).

The oxidation of the 1-arylthio-4-nitrobutadienes **63**, **64** was used for the preparation of hitherto unknown and inaccessible 4-nitro-1-sulfonylbutadienes.[67]

In the reaction of the dinitrodiene **36** with aniline, the C(2) and C(3) atoms are subjected to nucleophilic attack to give the product of bis-addition, 2,3-dianilino-1,4-dinitrobutane (**65**) isolated as a mixture of D,L- and *meso*-isomers in 65% overall yield.[68]

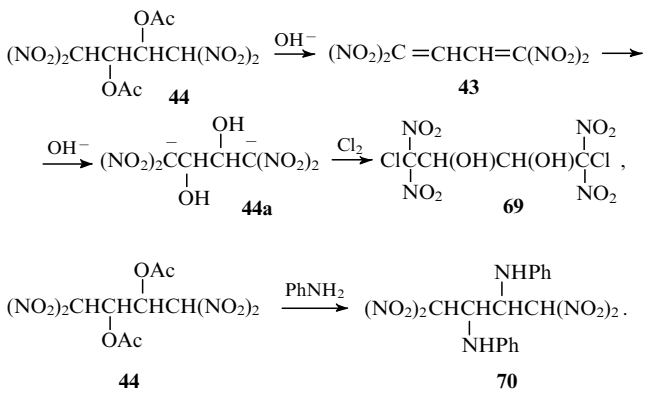


The nitrodiene **36** reacts with CH-acids to give the addition product at one of the nitrovinyl fragments; the other nitrovinyl fragment isomerises in the presence of a base into the nitroallyl system, which does not enter into addition reactions.[47, 51]



It has already been mentioned that tetranitrobutadiene **43** is unstable. However it was possible to accomplish some chemical transformations of this compound *in situ* without its isolation from the reaction mixture. Thus the reaction of 1,1,4,4-tetranitrobutane-2,3-diol diacetate (**44**) with an equivalent quantity of alkali in ether and subsequent chlorination of the formed tetranitrobutandiol salt **44a** results in 1,4-dichloro-1,1,4,4-tetranitrobutane-2,3-diol (**69**) (Scheme 3). The diacetate **44** is readily deacetoxylated even under the action of weak bases. Its treatment with aniline resulted in a quantitative yield of 2,3-dianilino-1,1,4,4-tetranitrobutane (**70**).[51]

Scheme 3



2. Electrophilic reactions

Nitrobutadienes are far less reactive in electrophilic substitution reactions in comparison with butadiene, as the nitro group imparts a pronounced electrophilic character to the diene system. Only the reactions of electrophilic halogenation of nitrobutadienes are known. It has been found[20] that the nitrobutadiene **2**

adds bromine at the vinyl group with the formation of the dibromide **71** (no yield is reported).

$$\underset{\mathbf{2}}{CH_2{=}CHCH{=}CHNO_2} \xrightarrow{Br_2} \underset{\mathbf{71}}{CH_2BrCHBrCH{=}CHNO_2}.$$

The bromination of the nitrobutadiene **32** in chloroform proceeds slowly, however in a more polar solvent, such as acetic acid, it quickly adds two Br_2 molecules to form the tetrabromide **72**.[69]

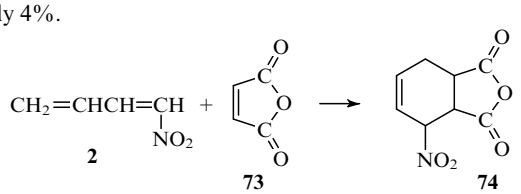
$$\underset{\mathbf{32}}{CH_2{=}CHC(NO_2){=}CH_2} \xrightarrow[AcOH]{Br_2} \underset{\mathbf{72}}{CH_2BrCHBrC(NO_2)BrCH_2Br}.$$

The bromination of the dinitrodiene **36** proceeds analogously, its product, tetrabromodinitrobutane **42**, is used in the synthesis of dibromodinitrodiene **41**.[44–50]

The chlorination of the nitrodiene **36**, which results in the formation of the tetrachlorodinitrobutane **40** has been discussed earlier [44] (see Section II.2).

3. Cycloaddition reactions

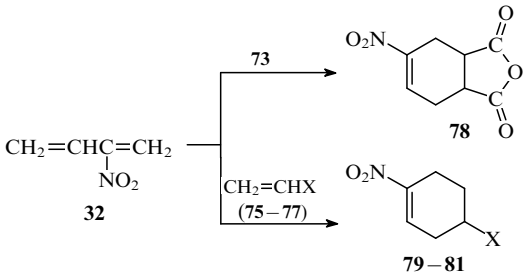
The Diels-Alder reaction involving nitrobutadienes has not been adequately explored. It is known [20] that the 1-nitrodiene **2** reacts with maleic anhydride **73**, however the yield of the adduct **74** is only 4%.



The nitrodiene **2** does not react with benzoquinone, α-naphthoquinone, acrylonitrile, acrolein, and dimethyl acetylenedicarboxylate even at 90–100 °C, at > 100 °C the reaction mixture resinifies.[20]

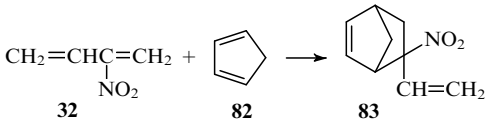
The 2-nitrodiene **32** has been shown to dimerise spontaneously in the process of its synthesis.[70] Dimerisation occurs as a [4 + 2]-cycloaddition reaction in which one nitrodiene molecule acts as a diene and the second one is a dienophile.

The nitrodiene **32** acts as a diene component in reactions with the maleic anhydride **73**, nitroethylene **75**, acrolein **76**, and acrylonitrile **77** and forms the corresponding adducts **78**–**81**.[69]

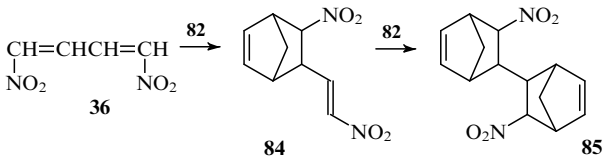


X = NO_2 (**75**, **79**), CHO (**76**, **80**), CN (**77**, **81**).

The nitrovinyl fragment in the molecules of 2-nitrodienes manifests dienophile properties. Thus the reaction of the nitrodiene **32** with cyclopentadiene **82** gives the adduct **83**.[69]

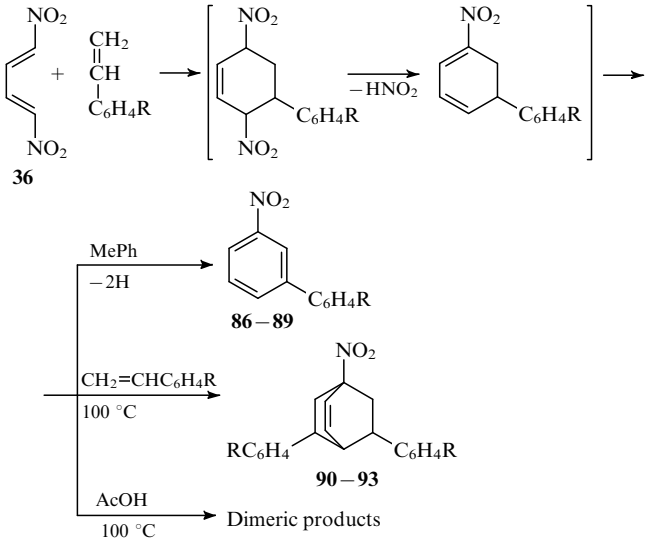


The behaviour of the diene **36** with pronounced electrophilic properties in the Diels–Alder reaction has been studied most extensively. Compound **36** has been shown to participate in reactions both as a diene and as a dienophile.[47, 70–72] It acts as a dienophile in the reaction with cyclopentadiene **82**. Thus at room temperature (48 h) 1 mol of diene **82** is added to the 1,2 position of the nitrodiene **36** to give 2-nitro-3-(2-nitroethenyl)bicyclo-[2.2.1]hept-5-ene (**84**) in a 57% yield. If compound **84** is refluxed with the diene **82** in benzene for 8 h, the addition of the second mole of diene at the exocyclic double bond occurs with the formation of 3,3′-dinitro-2,2′-bis(bicyclo[2.2.1]hept-5-enyl) (**85**) (in 60% yield).



The nitrodiene **36** does not react with the anhydride **73**, which is a typical dienophile, *i.e.* it is inactive in the classical Diels–Alder synthesis. It turned out, however, that **36** undergoes the reverse Diels–Alder synthesis with nucleophilic dienophiles. It acts as a diene-acceptor in reactions with styrene and its derivatives, and the second components act as dienophiles-donors. The reaction of nitrodiene **36** with equimolar quantities of styrene and its *p*-substituted derivatives results in 1,4-adducts (Scheme 4), which spontaneously eliminate HNO_2 and are converted, depending on the reaction conditions, into either the corresponding 3-nitrobiphenyls **86**–**89** (on refluxing in toluene), or the bicyclic nitrocompounds **90**–**93** (on heating with the excess of styrene), or dimers (on heating with acetic acid).[70–72]

Scheme 4



R = H (**86**, **90**), *p*-Cl (**87**, **91**), *p*-Br (**88**, **92**), *p*-Me (**89**, **93**).

IV. Substitution reactions

It is known that the occurrence of nucleophilic substitution reactions in the series of chlorine derivatives of butadiene depends to a considerable extent on the number of Cl atoms in the molecule and the nature of the terminal group and sometimes requires drastic conditions.[73]

The development of convenient methods for the synthesis of highly electrophilic halogenonitrobutadienes allowed one to study in detail their behaviour in nucleophilic vinyl substitution reactions. The necessity of the studies of these reactions has been proved by quantum-chemical calculations that have been performed for a few halogen-substituted nitrobutadienes.

1. Quantum-chemical calculations

The quantum-chemical calculations of spatial and electronic structures were performed by semi-empirical methods CNDO/2,

Table 3. Effective charges (q) on atoms in halogenonitrobutadiene molecules (quantum-chemical calculation).

Compound	Method of calculation	q						
		C(1)	C(2)	C(3)	C(4)	N_i	N_t	O
9	CNDO/2	+0.118	+0.066	+0.112	+0.085	+0.453	–	−0.293
9	MINDO/3	+0.471	−0.272	+0.111	+0.343	+1.120	–	−0.550
9	MNDO	+0.127	−0.029	−0.008	+0.104	+0.188	–	−0.070
E-**15**	MNDO	+0.134	−0.031	+0.005	+0.021	+0.362	–	−0.297
Z-**15**	MNDO	+0.134	−0.028	+0.005	+0.022	+0.361	–	−0.298
E-**22**	MNDO	+0.018	+0.083	−0.012	+0.078	–	+0.480	−0.290
Z-**22**	MNDO	+0.019	+0.085	−0.030	+0.079	–	+0.472	−0.293
E-**28**	MNDO	+0.026	+0.025	−0.070	+0.138	+0.475	+0.469	−0.293
Z-**28**	MNDO	+0.028	+0.017	−0.052	+0.119	+0.477	+0.468	−0.297

Note. N_i and N_t are internal and terminal N atoms respectively. The averaged charge values are given for O atoms.

MINDO/3, and MNDO [74–76] for the nitrobutadienes **9**, **15**, **22**, and **28**. It has been shown using diene **9** as an example that the results obtained by these methods are in satisfactory agreement with each other.[75]

The molecules of mononitrodienes **9**, **15**, and **22** were found to be nonplanar with vinyl groups located in the planes that are virtually mutually perpendicular and with a violated conjugation in the diene chain. The molecule of dinitrodiene **28** exists in a nonplanar *s-trans*-conformation with the torsion angle C=C−C=C of 142.8°. The main geometric parameters of the molecules, such as bond lengths and angles, are in agreement with the analogous values for related compounds.[2,77]

The lowest unoccupied molecular orbital (LUMO) is mostly (67%–85%) localised at the dihalogenonitrovinyl fragment of the molecule, mostly at the C atom adjacent to the $=C(NO_2)-$ group and with the maximum positive charge. Consequently, the position adjacent to $=C(NO_2)-$ is the most favourable for nucleophilic attack in the dihalogenonitrovinyl group. However, the exceptionally high positive charge at the N atom of the nitro group makes possible also the attack of hard nucleophiles at the $=C-NO_2$ fragment (Table 3).

The highest occupied molecular orbital (HOMO) is mostly ($\sim$ 70%) localised at the trihalogenovinyl group. In comparison with highly electrophilic dihalogenonitrovinyl groups, which represent hard electrophilic centres, the trihalogenovinyl fragments are soft electrophilic centres. The monochloronitrovinyl group in the nitrodiene **28** is less electrophilic than the dichlorovinyl group.

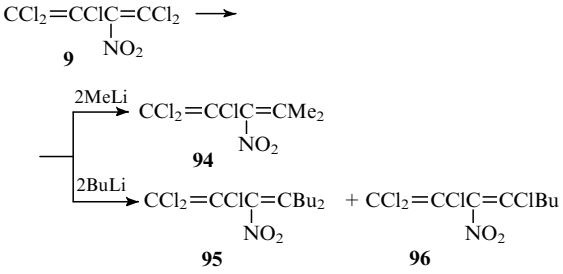
Thus, the quantum-chemical analysis shows that halogenonitrodienes must be active in processes of nucleophilic vinylic substitution (S_NVin).

2. Interaction with C-nucleophiles

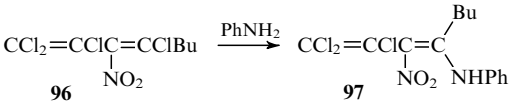
Reactions of halogenonitrobutadienes with organolithium compounds, which should described as soft nucleophiles, according to the hard and soft acid-base principle have been studied only for mononitrodienes **9** and **22**.

The reaction of the nitrodiene **9** with methyllithium (**9**:MeLi = 1:2, −75 to −70 °C) gives 1,1,2-trichloro-4-methyl-3-nitropenta-1,3-diene (**94**) (in 63% yield).[78,79]

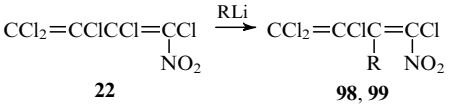
The reaction of the nitrodiene **9** with n-butyllithium under the same conditions results in a mixture of products of di- and monosubstitution, *viz*., 4-butyl-1,1,2-trichloro-3-nitroocta-1,3-diene (**95**) and 1,1,2,4-tetrachloro-3-nitroocta-1,3-diene (**96**), in the molar ratio of 1.5:1 in 58% overall yield. Increase in the amount of butyllithium practically does not change the ratio of the products formed, but decreases their overall yield. At the equimolar reagents ratio, the monosubstituted product **96** was isolated in 30% yield. It should be noted that the substitution is accompanied by considerable resinification.



The residual Cl atom of the nitrovinyl group of the monobutyl derivative **96** is readily substituted under the action of aniline, which results in the formation of 4-anilino-1,1,2-trichloro-3-nitroocta-1,3-diene (**97**).

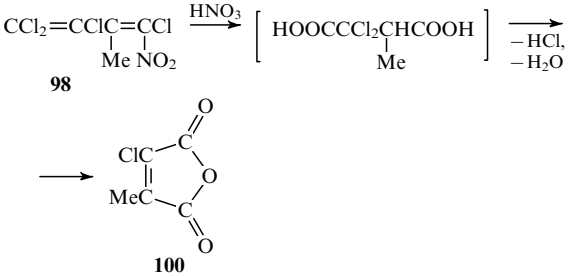


In contrast to the 2-nitrodiene **9**, the 1-nitrodiene **22** reacts with both methyl- and butyllithium with the substitution of only the Cl atom (at position 2) and the formation of the corresponding 2-alkyl-1,3,4,4-tetrachloro-1-nitrobuta-1,3-dienes (**98** and **99**).[80]



R = Me (**98**), Bu (**99**).

Under the optimum conditions (**22**:RLi = 1.0:1.2, −75 °C) the yield of the products is 36%–38%. The structure of the alkadienes **98** and **99** has been confirmed by spectral data and by a reaction of the butadiene **98** with fuming nitric acid leading to the formation of chlorocitraconic anhydride (**100**) and some other carbonyl compounds.



3. Interaction with thiols

The reactions of halogenonitrobutadienes with thiols, which, according to the Pearson' scale, are soft nucleophiles, have mostly been studied using pentahalogenodienes with terminal and inter-

nal nitro groups as examples. It has been shown [81–84] that the interaction of the 2-nitrodiene **9** with different thiols under mild conditions results in the substitution of only one geminal Cl atom in the nitrodichlorovinyl fragment of the molecule **9** by the thiol residue with the formation of 1-alkyl(aralkyl)-thio-1,3,4,4-tetrachloro-2-nitrobuta-1,3-dienes (**101**–**111**).

$$CCl_2{=}CClC(NO_2){=}CCl_2 \xrightarrow{RSH} CCl_2{=}CClC(NO_2){=}CCl{-}SR$$

9 **101**–**111**

R = Bu^n (**101**), C_8H_{17} (**102**), Ph (**103**), CH_2Ph (**104**),[81] Et (**105**), Bu^t (**106**), $C_{12}H_{25}$ (**107**), $C_{16}H_{33}$ (**108**), $C_{18}H_{37}$ (**109**),

 (**110**), 2,6-$Cl_2C_6H_3$ (**111**).[82]

Mixed bromochloronitrobutadienes behave in reactions with thiols analogously to the nitrodiene **9**. Thus under the action of octane- and α-toluene-thiols, the dibromonitrodiene **46** gives the corresponding alkyl(aralkyl)thiobromotrichloronitrobutadienes **112** and **113**, *i.e.* the substitution of only one Br atom in the dibromonitrovinyl group occurs.[58]

$$CCl_2{=}CClC(NO_2){=}CBr_2 \xrightarrow{RSH} CCl_2{=}CClC(NO_2){=}CBr{-}SR$$

46 **112**, **113**

R = C_8H_{17} (**112**), CH_2Ph (**113**).

4-Bromo-1,1,3,4-tetrachloro-2-nitrobuta-1,3-diene **15** also gives the products of monosubstitution **114**–**116** in reactions with thiols.

$$CBrCl{=}CClC(NO_2){=}CCl_2 \xrightarrow{RSH} CBrCl{=}CClC(NO_2){=}CCl{-}SR$$

15 **114**–**116**

R = Bu^n (**114**), Ph (**115**), CH_2Ph (**116**).

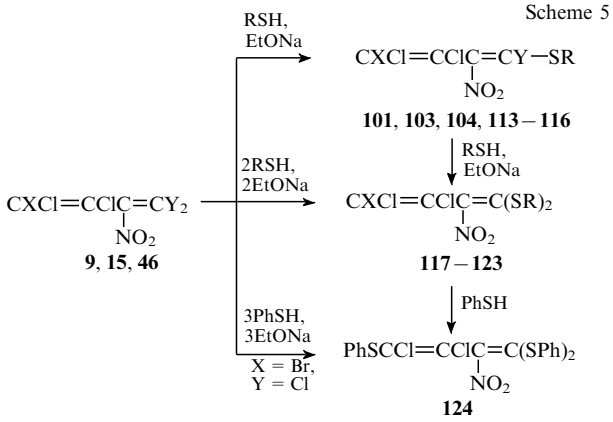
Compounds **101**–**116** have been isolated in high yields. It has been shown by ^1H NMR spectroscopy that the monothio derivatives of the nitrobutadienes **9**,**15**, and **46** are mixtures of *E*- and *Z*-isomers in a ~ 1 : 3 ratio.

In the presence of sodium ethoxide at the diene : thiol : sodium ethoxide ratio of 1 : 2 : 2, it was possible to substitute both halogen atoms in the dihalogenonitrovinyl fragment of the dienes **9**, **15**, and **46** to obtain the corresponding 1,1-dialkyl(aryl)thio-3,4,4-trihalogeno-2-nitrobutadienes (**117**–**123**) in 40%–73% yields (Scheme 5).[85] The process may be performed stepwise, as monosubstitution products are formed at the equimolar reagents ratio.

In the reaction of the nitrobutadiene **15** with thiophenol (diene : PhSH : EtONa = 1 : 3 : 3), alongside with di(phenylthio)-nitrodiene **122**, the products of substitution of two Cl atoms in the dichloronitrovinyl fragment and the Br atom in the bromodichlorovinyl group of the initial nitrodiene, *viz*., 3,4-dichloro-2-nitro-1,1,4-triphenylthiobuta-1,3-diene (**124**), is also formed in 27% yield. Compound **124** can be prepared in a higher yield by the treatment of a disubstituted derivative **122** with PhSH in the presence of an equimolar amount of sodium ethoxide.

The 1-nitrodiene **22** reacts with thiols only in the presence of sodium ethoxide to form exclusively monosubstituted products, 2-alkyl(aryl)thio-1,3,4,4-tetrachloro-1-nitrobuta-1,3-dienes (**125**–**128**) in 63%–81% yields.[85]

Scheme 5



Compound	X	Y	R
9	Cl	Cl	–
15	Br	Cl	–
46	Cl	Br	–
101, **117**	Cl	Cl	Bu^n
103, **118**	Cl	Cl	Ph
104, **119**	Cl	Cl	CH_2Ph
113, **120**	Cl	Br	CH_2Ph
114, **121**	Br	Cl	Bu^n
115, **122**	Br	Cl	Ph
116, **123**	Br	Cl	CH_2Ph

According to NMR spectroscopy data, compounds **125**–**128** are formed as mixtures of *E*- and *Z*-isomers in a 1 : 1 ratio.

$$CCl_2{=}CClCCl{=}CCl \xrightarrow[EtONa]{RSH,} CCl_2{=}CClC(SR){=}CCl$$

22 **125**–**128**

R = Me (**125**), Bu^n (**126**), Ph (**127**), CH_2Ph (**128**).

The reaction of dinitrosubstituted halogenobutadienes with thiols has been studied only in the example of trichlorodinitrodiene **28**. It turned out to proceed readily in the absence of a catalyst; however, depending on the diene : toluene ratio products of different composition and structure are formed.[36,86] In the case of an equimolar reagent ratio, the products of the substitution of one Cl atom in the dichloronitrovinyl fragment of the diene **28** by the thiol residue, *viz*., 4-alkyl(aryl)thio-1,4-dichloro-1,3-dinitrobuta-1,3-dienes (**129**–**131**), are formed at room temperature (ether as a solvent) in 51%–71% yields. The use of a twofold excess of thiol and conducting the reaction at elevated temperature (refluxing in ether for 5–6 h) results in the substitution of one Cl in the dichloronitrovinyl group, and the terminal nitro group in the dinitrodiene **28** by the thiol residues with formation of the corresponding disubstituted products, *viz*., 1,4-di[alkyl(aryl)thio]-1,4-dichloro-2-nitrobuta-1,3-dienes (**132**) and (**133**), in 46% and 66% yields respectively.

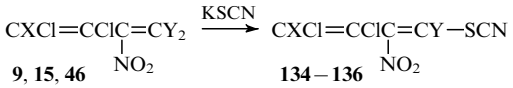
$$CCl(SR){=}CHC(NO_2){=}CCl \xleftarrow{RSH} CCl{=}CHC(NO_2){=}CCl_2 \xrightarrow{2RSH} CCl(SR){=}CHC(SR){=}CCl$$

129–**131** **28** **132**, **133**

R = Bu^n (**129**, **132**), Ph (**131**), CH_2Ph (**130**, **133**).

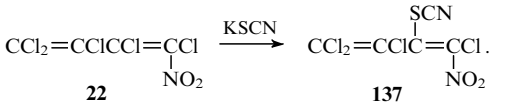
4. Synthesis of thiocyanate deivatives of halonitrobutadienes

The thiocyanate group was introduced into certain halogenonitrobutadienes by the reaction with potassium thiocyanate. Thus, the reaction of nitrodienes **9**, **15**, and **46** with KSCN (diene : KSCN = 1.0 : 1.3, EtOH, 20–25 °C) results in the substitution of one halogen atom in the β-position relative to the nitro group by the thiocyanate group with the formation of the corresponding 1,3,4,4-tetrahalogen-2-nitro-1-thiocyanatobutadienes (**134**–**136**) in 70%–75% yield.[59]



9, **134**: X = Y = Cl; **15**, **135**: X = Br, Y = Cl; **46**, **136**: X = Cl, Y = Br.

1,3,4,4-Tetrachloro-1-nitro-2-thiocyanatobuta-1,3-diene (**137**) was synthesised in 83% yield in a reaction of the nitrodiene **22** with potassium thiocyanate.[87]



It was impossible to synthesise disubstituted thiocyanate derivatives of nitrodienes by carrying out the reaction under more drastic conditions with a two- or threefold excess of KSCN; this resulted only in the increase in the amount of the resinous products.

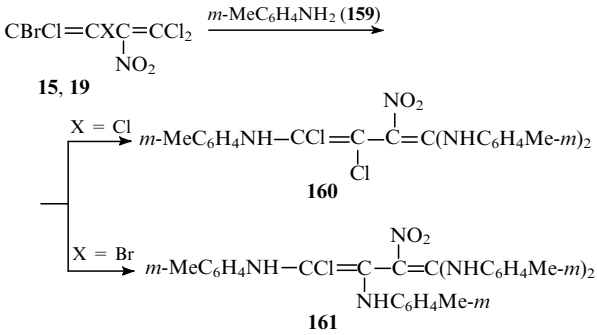
5. Interaction with N-nucleophiles

Pentahalogenonitrobutadienes readily react with various amines, which according to the Pearson's scale are hard nucleophiles. Thus reactions of primary and secondary amines with 2-nitrodienes **9**, **15**, and **19** occur under mild conditions (in ether, ethanol, or dichloromethane, −30 to 60 °C, the ratio nitrodiene : amine = 1 : 4) and lead to the substitution of both Cl atoms in dichloronitrovinyl group with the formation of the corresponding 1,1-diamino-3,4,4-trihalogeno-2-nitrobuta-1,3-dienes (**138**–**158**) in preparative yields.[28,29,36,88,89]



Compound	X	Y	R	R′
9	Cl	Cl	–	–
15	Br	Cl	–	–
19	Br	Br	–	–
138	Cl	Cl	H	Ph
139	Cl	Cl	H	*o*-ClC_6H_4
140	Cl	Cl	H	Pr
141	Cl	Cl	H	$CHMe_2$
142	Cl	Cl	H	$CH_2CH=CH_2$
143	Cl	Cl	H	cyclo-C_6H_{11}
144	Cl	Cl	Et	Et
145	Cl	Cl	Bu^n	Bu^n
146	Cl	Cl	$CH_2(CH_2)_3CH_2$	
147	Cl	Cl	$(CH_2)_2O(CH_2)_2$	
148	Br	Cl	H	Ph
149	Br	Cl	H	*m*-MeC_6H_4
150	Br	Cl	H	2,4-$Me_2C_6H_3$
151	Br	Cl	H	CH_2Ph
152	Br	Cl	H	CMe_3
153	Br	Cl	Et	Et
154	Br	Cl	$CH_2(CH_2)_3CH_2$	
155	Br	Cl	$(CH_2)_2O(CH_2)_2$	
156	Br	Br	H	*m*-MeC_6H_4
157	Br	Br	H	CH_2Ph
158	Br	Br	$(CH_2)_2O(CH_2)_2$	

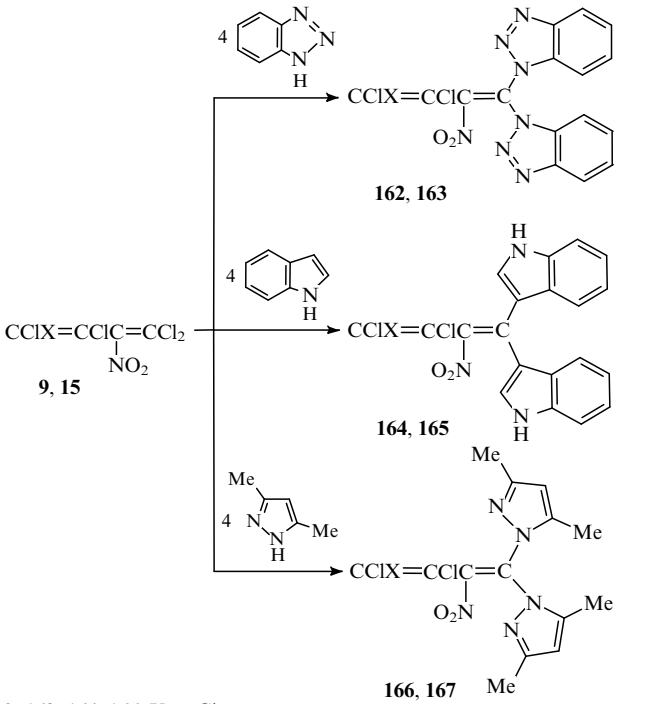
The reaction of *m*-toluidine **159** with the nitrodiene **15** (diene : amine = 1 : 6, 30 h, 20–25 °C) gives the trisubstitution product **160**.[28] Under the same conditions in reactions with the nitrodiene **19** (diene : amine = 1 : 8) the product of tetrasubstitution **161** was obtained in 22% yield.[29,36] The fact that the process involves the trihalogenovinyl fragment in the case of nitrodienes **15** and **19** is in agreement with the Pearson's 'symbiosis' principle: *m*-toluidine is the softest nucleophile among amines, while the Br atom is a softer leaving group than Cl atom.[90]



X = Cl (**15**), Br (**19**).

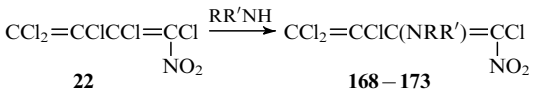
The reactions of amphoteric N-nucleophiles, such as benzotriazole, 3,5-dimethylpyrazole, and indol, with nitrodienes **9** and **15** take more time and lead to the formation of 1,1-disubstituted derivatives **162**–**167** in 47%–73% yields (Scheme 6).[91,92]

Scheme 6



9, **162**, **164**, **166**: X = Cl;
15, **163**, **165**, **167**: X = Br.

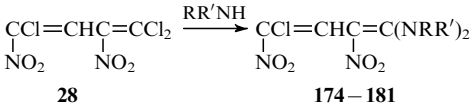
The interaction of 1-nitrodiene **22** with amines occurs with substitution of only the α-Cl atom in α,β-dichloro-β-nitrovinyl group to give 2-amino-1,3,4,4-tetrachloro-1-nitrobuta-1,3-dienes (**168**–**173**) in 57%–89% yields.[31,93] X-Ray structural analysis has shown that **168**–**173** have *E*-configurations.[94]



22 **168 – 173**

R = H: R′ = Ph (**168**), *m*-MeC_6H_4 (**169**), CH_2Ph (**170**), Bu^t (**171**);
RR′ = $CH_2(CH_2)_3CH_2$ (**172**), $(CH_2)_2O(CH_2)_2$ (**173**).

The reaction of the dinitrodiene **28**, the molecule of which has two types of chloronitrovinyl fragments, with primary and secondary amines leads to the substitution of two geminal Cl atoms in the β,β-dichloro-α-nitrovinyl group with the formation of the corresponding 4,4-diamino-1-chloro-1,3-dinitrobuta-1,3-dienes (**174 – 181**) in 55% – 75% yields.[95]

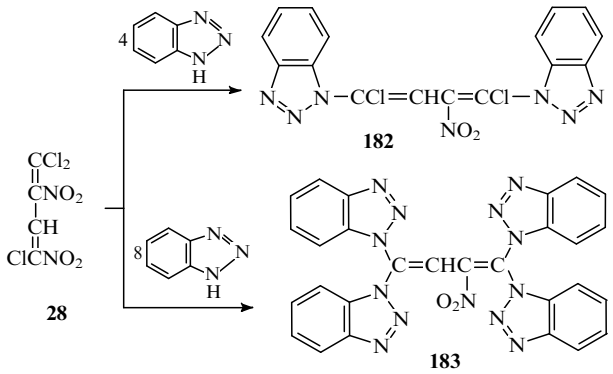


28 **174 – 181**

R = H: R′ = Ph (**174**), CH_2Ph (**175**), *m*-MeC_6H_4 (**176**), 2,4-$Me_2C_6H_3$ (**177**), Bu^t (**179**);
R = R′ = CH_2Ph (**178**);
R – R′ = $CH_2(CH_2)_3CH_2$ (**180**), $(CH_2)_2O(CH_2)_2$ (**181**).

The reaction of the dinitrobutadiene **28** with benzotriazole occurs with participation of both nitrovinyl groups.[36,91] When a 1 : 4 mixture of diene **28** and benzotriazole was refluxed in ether, the substitution of the NO_2 group in the chloronitrovinyl fragment and one of the geminal Cl atoms in dichloronitrovinyl group by the azole residues occur to form 1,4-di(1-benzotriazolyl)-1,4-dichloro-2-nitrobuta-1,3-diene (**182**) in 55% yield. With a larger excess of benzotriazole (eightfold), the substitution of all the remaining Cl atoms occurs to give 1,1,4,4-tetra(1-benzotriazolyl)-2-nitrobuta-1,3-diene (**183**) in 45% yield (Scheme 7).

Scheme 7

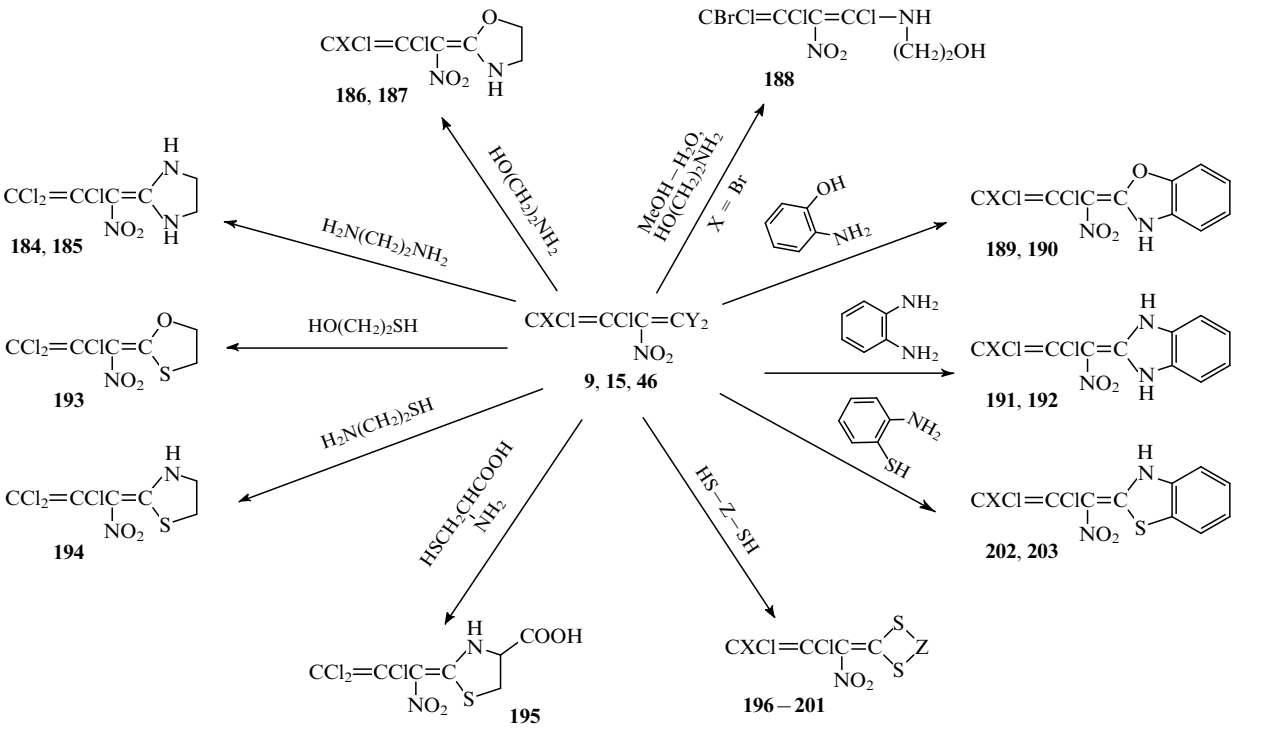


28 **182** **183**

6. Reactions with bifunctional nucleophilic reagents

Polyhalogenonitrobutadienes react readily with various bifunctional nucleophiles, which allows one to synthesise a series of heterocyclic systems. On the basis of nitrodienes **9**, **15**, and **46**, preparative methods for the synthesis of earlier inaccessible heterocyclic compounds, containing the trihalogeno-1-nitropropenylidene radical in the side chain have been developed.[85,96 – 99] In particular, the imidazolidine derivatives **184**, **185** were prepared by reaction of nitrodienes **9**, **15**, and **46** with ethylenediamine (Scheme 8), and reactions of the nitrodienes with monoethanolamine lead to the oxazolidine derivatives **186**, **187**. The nature of the solvent is very important for the reaction of the nitrodiene **15** with monoethanolamine. It turned out that the main reaction product in aqueous ethanol (5% H_2O) is the linear product **188**, *i.e.* monoethanolamine behaves as an N-nucleophile, which may

Scheme 8



9, **184**, **186**, **189**, **191**, **193 – 198**, **202**: X = Y = Cl;
15, **185**, **187**, **188**, **190**, **192**, **199 – 201**, **203**: X = Br, Y = Cl;
46, **184**, **186**, **189**, **191**, **193 – 198**, **202**: X = Cl, Y = Br.

Z = $(CH_2)_2$, $(CH_2)_3$, $(CH_2)_6$

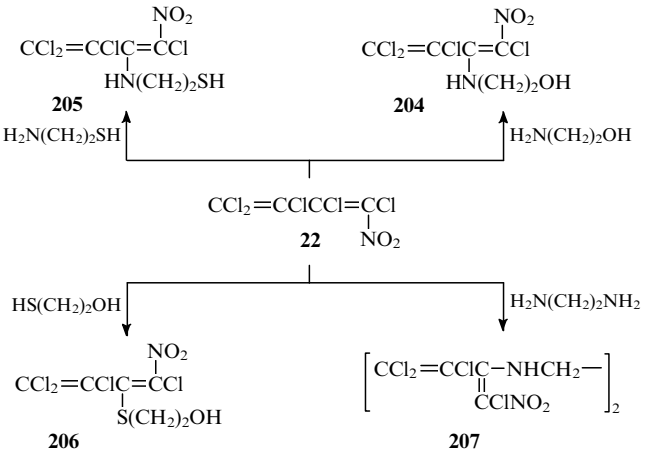
presumably be explained by solvation of the OH group of the aminoalcohol by molecules of water.

The benzoxazoline (**189**, **190**) and benzimidazoline (**191**, **192**) derivatives have been obtained by reaction of nitrodienes **9**, **15**, and **46** with *o*-aminophenol and *o*-phenylenediamine. Reactions of nitrodienes **9** and **46** with mercaptoethanol and cysteamine (and cysteine) result in the formation of the oxathiolane (**193**) and thiazolidine (**194**, **195**) derivatives respectively (Scheme 8).

The derivatives of 1,3-dithiocyclanes (**196**–**201**) were obtained by reaction of nitrodienes **9** and **15** with dithiols of HS–Z–SH [Z = $(CH_2)_2$, $(CH_2)_3$, $(CH_2)_6$] type. Nitrodienes **9** and **15** form the corresponding 2-(2,3-dichloro-1-nitro-3X-prop-2-enylidene)benzothiazolidines, where X = Cl (**202**), Br (**203**) in reactions with *o*-aminothiophenol (see Scheme 8).[98,99] The yields of **184**–**203** are 43%–80%.

The reaction of 1-nitrodiene **22** with bifunctional reagents occurs with the substitution of only one Cl atom in the α-position of the α,β-dichlorovinyl group to give the corresponding 2-monosubstituted products in preparative yields.[31] The diene **22** reacts with monoethanolamine and cysteamine at the N-nucleophilic centre only in the presence of sodium ethoxide to form 1,3,4,4-tetrachloro-2-(2-hydroxyethylamino)-1-nitrobuta-1,3-diene (**204**) and 1,3,4,4-tetrachloro-2-(2-mercaptoethylamino)-1-nitrobuta-1,3-diene (**205**), respectively (Scheme 9).

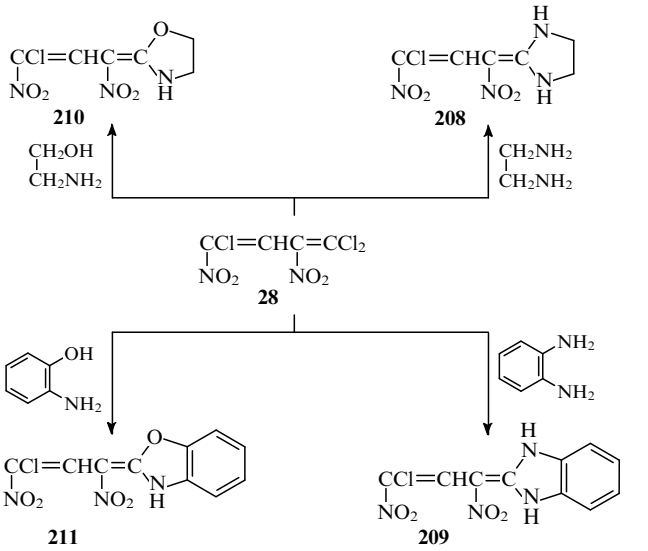
Scheme 9



The reaction of the diene **22** with mercaptoethanol occurs at the S-nucleophilic centre; as a result, 1,3,4,4-tetrachloro-2-(2-hydroxyethylthio)-1-nitrobuta-1,3-diene (**206**) is formed as a mixture of *E*- and *Z*-isomers in a 1:1 ratio. Ethylenediamine reacts with two molecules of the nitrodiene **22**, which results in the formation of *N*,*N*′-bis(1-chloronitromethylene-2,3,3-trichloroprop-3-enyl) ethylenediamine (**207**) (see Scheme 9).

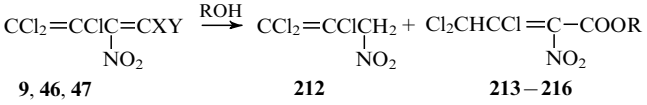
The dinitrodiene **28** reacts with N,N- and O,N-nucleophiles at the nitrodichlorovinyl group with the substitution of both Cl atoms, like 2-nitro-substituted perhalogenodienes, and the formation of heterocyclic compounds containing 3-chloro-1,3-dinitropropenylidene side chain.[100] Thus the reactions of the nitrodiene **28** with ethylenediamine and *o*-phenylendiamine give 2-(3-chloro-1,3-dinitroprop-2-enylidene)imidazolidine (**208**) and 2-(3-chloro-1,3-dinitroprop-2-enylidene)benzimidazoline (**209**), respectively (Scheme 10). The reaction of the diene **28** with monoethanolamine and *o*-aminophenol results in the formation of 2-(3-chloro-1,3-dinitroprop-2-enylidene)oxazolidine (**210**) and 2-(3-chloro-1,3-dinitroprop-2-enylidene)benzoxazoline (**211**), respectively (see Scheme 10).

Scheme 10



7. Interaction with O-nucleophiles

Reactions of polyhalogenonitrobutadienes with O-nucleophiles occur in an unusual way. Thus, the reaction of 2-nitropentahalogenobutadienes **9**, **46**, and **47** with methyl, ethyl, and isopropyl alcohols, *i.e.* with hard nucleophiles, leads to 1,1,2-trichloro-3-nitroprop-1-ene (**212**) and the corresponding esters of 3,4,4-trichloro-2-nitrocrotonic acid (**213**–**216**).[101,102]

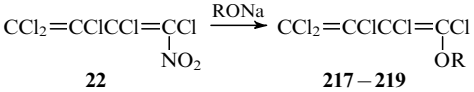


X = Y = Cl (**9**), Br (**46**); X = Cl, Y = I (**47**);
R = Me (**213**), Et (**214**), Pr^n (**215**), Pr^i (**216**).

By varying the conditions, one may direct the reaction towards preferential formation of either the propene **212** (in ~ 80% yield) or esters **213**–**216** (in ~ 50%–70% yields).

The formation of compound **212** occurs probably due to the cleavage of the C=C bond in dihalogenonitrovinyl groups of the nitrodienes studied. This is the first example of the heterolytic fragmentation of the double carbon-carbon bond under the action of alcohols.[103] It has been shown that C=C bond cleavage in the molecules of the dienes **9**, **46**, and **47** occurs also under the action of water in an alkaline medium, KF or CsF may be used instead of alkali.[102]

The 1-nitrodiene **22** does not react with aliphatic alcohols. The reaction takes place only under the action of sodium alkoxides as substitution of a nitro group rather than of the Cl atoms in the molecule of diene **22** and results in formation of 1-alkoxy-1,2,3,4,4-pentachlorobuta-1,3-dienes (**217**–**219**) in 45%–56% yields.[31] Compounds **217**–**219** are formed as mixtures of *E*- and *Z*-isomers in the 1:3 ratio.



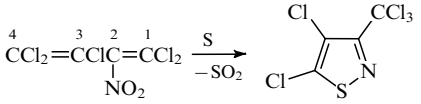
R = Me (**217**), Et (**218**), Pr^i (**219**).

1-Ethoxypentachlorobutadiene **218** is known [104] to be useful in the synthesis of a valuable squaric acid.

V. Other reactions

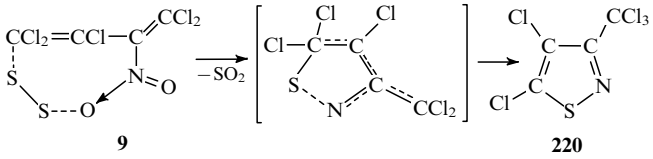
1. Synthesis of isothiazole derivatives

It is known that pentachlorobuta-1,3-dienes react with sulfur to form tetrachlorothiophenes.[105] Introduction of the nitro group into the polychlorodiene system considerably changes its reactivity. It has been recently shown [106–108] that the reaction of the 2-nitrodiene **9** with sulfur occurs in a different direction with the participation of the nitro group and results in the formation of 4,5-dichloro-3-trichloromethylisothiazole (**220**) in 52% yield. This new, previously unknown reaction opens a convenient way to the construction of the isothiazole ring.



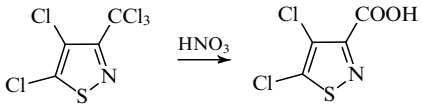
9 **220**

The unusual course of this reaction can be explained by the peculiarities of the electronic and molecular structure of the nitrodiene **9**. As has been shown by the quantum-chemical calculations,[75] C(4) and N atoms are closer to each other than C(4) and C(1) atoms, and the HOMO is mostly (about 70%) localised at the trichlorovinyl group, dominantly at the C(4) atom. Under the reaction conditions (180–200 °C), the sulfur molecules exist in the form of biradicals $^{\bullet}S_n^{\bullet}$, the direction of their attack is determined by the HOMO structure. Thus a possible scheme for the process may be presented as the attack of a sulfur atom at C(4), subsequent elimination of SO_2 and cyclisation accompanied by migration of Cl atom.



9 **220**

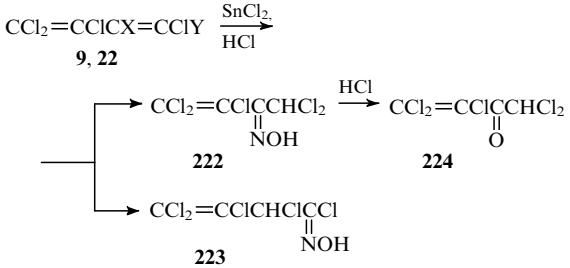
New methods for the preparation of previously inaccessible, valuable products, such as isothiazole derivatives have been developed. Thus starting from compound **220** a biologically important 4,5-dichlorothiazole-3-carboxylic acid (**221**) was obtained in 92% yield. [107, 109]



220 **221**

2. Reduction of nitro-substituted pentachlorobuta-1,3-dienes

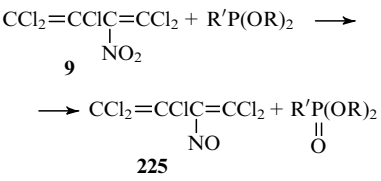
The reduction of 2-nitro- (**9**) and 1-nitropentachlorodienes (**22**) by tin dichloride in acidic medium proceeds in an unusual way and results in the formation of oximes of 1,1,3,4,4-pentachlorobut-3-en-2-one (**222**) (75%) and of 1,2,3,4,4-pentachlorobut-3-en-1-al (**223**) (59%), respectively.[110]



9: X = NO_2, Y = Cl;
22: X = Cl, Y = NO_2.

It has been found by spectral methods that oximes **222** and **223** are formed in one isomeric form: their configuration has been determined by measuring the Nuclear Overhauser Effect (NOE) according to the NOEDIFF technique. The OH and $CHCl_2$ groups in the molecule of the oxime **222** are in the *syn*-position relative to the C=N bond, while in the oxime **223** the groups OH and $CHClCCl=CCl_2$ are in *anti*-position. It is interesting to note that the compound **222** hydrolyses on prolonged refluxing with concentrated HCl to form 1,1,3,4,4-pentachlorobut-3-en-2-one (**224**), which is used in the synthesis of medicinals.[111]

Partial reduction of the nitrodiene **9** has been observed on its interaction with acyclic phosphites, 2-nitrosopentachlorobutadiene **225** (~ 10%) being one of the products.[112]



R = Me, $CH_2CF_2CHF_2$, $CH(CF_3)_2$; R′ = NCO, RO.

* * *

Thus, nitrobutadienes and their halogen derivatives are valuable intermediates that may be used for the synthesis of compounds of different classes; original synthetic procedures were developed on their basis.

Of numerous methods of preparation of nitrobutadienes, the most convenient are the reactions of nitration of the corresponding dienes; they are especially promising in the synthesis of chlorosubstituted nitrobutadienes and their mixed bromochloro-containing analogues. The main types of chemical transformations of nitrobutadienes are addition and substitution reactions. The former are characteristic of the nonsubstituted nitrodienes, while the latter are typical of their halogen derivatives.

Using halogenonitrobutadienes as examples, the formerly unknown peculiarities of the chemical behaviour of the nitro group in a polychlorodiene system have been elucidated. The possibility for the adequate interpretation of the regioselectivity of the nucleophilic vinylic substitution of the halogen atom and nitro group has been discussed in terms of the hard and soft acid-base principles.

It should, however, be noted that there are no data on fluorosubstituted nitrobutadienes. The development of the methods of their preparation and participation in chemical transformations is, to our mind, very interesting in both theoretical and practical aspects.

References

1. H Feuer (Ed.) *The Chemistry of the Nitro and Nitroso Groups* Part 2 (New York: Wiley, 1970)
2. V V Perekalin, A S Sopova, E S Lipina *Nepredel'nye Nitrosoedineniya* (Unsaturated Nitro-Compounds) (Leningrad: Khimiya, 1982)
3. S S Novikov, G A Shvekhgeimer, V V Sevost'yanova, V A Shlyapochnikov *Khimiya Alifaticheskikh i Alitsiklicheskikh Nitrosoedinenii* (The Chemistry of Aliphatic and Alicyclic Nitro Compounds) (Moscow: Khimiya, 1974)
4. D Seebach, E W Colvin, F Lehr, Th Weller *Chimia* **33** 1 (1979)
5. V A Tartakovskii *Izv. Akad. Nauk SSSR, Ser. Khim.* 165 (1984) [a]
6. A G M Barret, G G Grabowski *Chem. Rev.* **86** 751 (1986)
7. J Kochany *Wiad. Chem.* **32** 723 (1978)
8. V V Perekalin *Zh. Org. Khim.* **21** 1111 (1985) [b]
9. G A Shvekhgeimer, V I Zvolinskii, K I Kobrakov *Khim. Geterotsikl. Soedin.* 435 (1986) [c]
10. G Rosini, R Ballini *Synthesis* 833 (1988)
11. S G Zlotin, G N Varnaeva, O A Luk'yanov *Usp. Khim.* **58** 796 (1989) [*Russ. Chem. Rev.* **58** 470 (1989)]
12. A Baran'ski, V I Kelarov *Khim. Geterotsikl. Soedin.* 435 (1990) [c]

13. T Rui, K Akio, O Noboru *Syhthesis* 423 (1991)
14. G M Baranov, V V Perekalin *Usp. Khim.* **61** 2215 (1992) [*Russ. Chem. Rev.* **61** 1220 (1992]
15. R Tamura *J. Synth. Org. Chem. (Jap.)* **50** 604 (1992)
16. R A Karakhanov, V I Kelarov, Yu N Polivin *Usp. Khim.* **62** 184 (1993) [*Russ. Chem. Rev.* **62** 169 (1993]
17. Y Liu, M Bei, H Zhy, Y Li *Huaxue Tongbao (Chemistry)* 6 (1993); *Ref. Zh. Khim.* 6 Zh 71 (1994)
18. G M Nazin, G B Manelis *Usp. Khim.* **63** 327 (1994) [*Russ. Chem. Rev.* **63** 313 (1994]
19. US P. 2 478 243; *Chem. Abstr.* **44** 1128 (1950)
20. E G Kataev *Soobshcheniya o Nauchnykh Rabotakh Chlenov Vses. Khim. O-va im. D I Mendeleeva* **49** 49 (1955)
21. E S Lipina, V V Perekalin, Ya S Bobovich *Zh. Obshch. Khim.* **34** 3640 (1964) [d]
22. T I Samoilovich, A S Polyanskaya, V V Perekalin *Dokl. Akad. Nauk SSSR* **217** 1335 (1974) e
23. A J Bloom, J M Mellor *Tetrahedron Lett.* **27** 873 (1986)
24. A J Bloom, J M Mellor *J. Chem. Soc., Perkin Trans. 1* 2737 (1987)
25. Yu A Ol'dekop, R V Kaberdin *Zh. Org. Khim.* **12** 2039 (1976) [b]
26. V I Potkin, V A Zapol'skii, R V Kaberdin *Dokl. Akad. Nauk Belarusi* **40** (1) 68 (1996)
27. Yu A Ol'dekop, R V Kaberdin, E E Buslovskaya *Zh. Org. Khim.* **15** 1321 (1979) [b]
28. V I Potkin, V I Gogolinskii, N I Nechai, V A Zapol'skii, R V Kaberdin *Zh. Org. Khim.* **31** 1816 (1995) [b]
29. V A Zapol'skii, V I Potkin, R V Kaberdin *Zh. Org. Khim.* **30** 1452 (1994) [b]
30. V A Zapol'skii, V I Potkin, R V Kaberdin *Izv Akad. Nauk Bel. SSR, Ser. Khim. Nauk* (3) 76 (1993)
31. V I Potkin, R V Kaberdin, Yu A Ol'dekop *Zh. Org. Khim.* **27** 56 (1991) [b]
32. V I Potkin, R V Kaberdin, E Yu Dubova, Yu A Ol'dekop *Zh. Org. Khim.* **26** 256 (1990) [b]
33. E H Braye *Bull. Soc. Chim. Belg.* **72** 699 (1963)
34. A Müller *Angew. Chem.* **62** 166 (1950)
35. R Criegee, W Horauf, W D Schellenberg *Chem. Ber.* **86** 126 (1953)
36. V A Zapol'skii, V I Potkin, R V Kaberdin *Zh. Org. Khim.* **30** 1368 (1994)
37. V I Potkin, A S Lyakhov, V A Zapol'skii, A A Govorova, R V Kaberdin *Dokl. Akad. Nauk Belarusi* **40** (4) 78 (1996)
38. A A Petrov, K B Ral', A I Vil'davskaya *Zh. Org. Khim.* **1** 240 (1965) [b]
39. P Nicolinski, G Spasov *Godishnik Khim.-Tekhnol. Inst.* **3** 94 (1956)
40. Bolg. P. 21 481; *Ref. Zh. Khim.* 23 N 64P (1980)
41. V V Perekalin, O M Lerner *Dokl. Akad. Nauk SSSR* **129** 1303 (1959) [e]
42. S S Novikov, I S Korsakova, K K Babievskii *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 944 (1960) [a]
43. F I Carrol *J. Org. Chem.* **31** 366 (1966)
44. F I Carrol, S C Kerrow, M E Wall *Canad. J. Chem.* **44** 2115 (1966)
45. G L Rowley, M B Frankel *J. Org. Chem.* **34** 1512 (1969)
46. J A Durden, D L Heywood, A A Sousa, H W Spurr *J. Agr. Food Chem.* **18** 50 (1970)
47. E S Lipina, V V Perekalin *Zh. Obshch. Khim.* **34** 3644 (1964) [d]
48. USSR P. 182 710; *Byull. Izobr.* (12) 34 (1966)
49. US P. 3 342 671; *Chem. Abstr.* **68** 12 468a (1968)
50. US P. 3 488 396; *Chem. Abstr.* **72** 78 379m (1970)
51. G V Nekrasova, E S Lipina, V P Pozdnyakov, V V Perekalin *Zh. Org. Khim.* **20** 2502 (1984) [b]
52. E S Lipina, V V Perekalin, Ya S Bobovich *Dokl. Akad. Nauk SSSR* **163** 894 (1965) [e]
53. E S Lipina, Z F Pavlova, L V Prikhod'ko, T Ya Paperno *Dokl. Akad. Nauk SSSR* **192** 810 (1970) [e]
54. E S Lipina, V V Perekalin *Acta Phys. Chem.* **19** 125 (1973)
55. E S Lipina, M D Stepanov, I L Bagal, R I Bodina, V V Perekalin *Zh. Org. Khim.* **16** 2404 (1980) [b]
56. G V Nekrasova, E S Lipina, E E Boldysh, V V Perekalin *Zh. Org. Khim.* **24** 1144 (1988) [b]
57. L M Elagin, V N Vasil'eva, E S Lipina, L A Chetkina, V V Perekalin *Dokl. Akad. Nauk SSSR* **201** 1356 (1971) [e]
58. V I Potkin, R V Kaberdin, Yu A Ol'dekop *Zh. Org. Khim.* **22** 1389 (1986) [b]
59. V I Potkin, R V Kaberdin, Yu A Ol'dekop *Izv. Akad. Nauk Bel. SSR, Ser. Khim. Nauk* (1) 114 (1987)
60. Jpn. P. 21 290; *Ref. Zh. Khim.* 15 N 107P (1971)
61. A I Vil'davskaya, K B Ral', A A Petrov *Zh. Org. Khim.* **3** 434 (1967) [b]
62. T I Samoilovich, A S Polyanskaya, V V Perekalin *Zh. Org. Khim.* **3** 1532 (1967) [b]
63. I G Sulimov, T I Samoilovich, V V Perekalin, A S Polyanskaya, N V Usik *Zh. Org. Khim.* **8** 1328 (1972) [b]
64. L V Mostyaeva *Nauch. Tr. Tyumensk. Univ.* **24** 84 (1975)
65. Z F Pavlova, Ya A Kasem, E S Lipina, G A Berkova, V V Perekalin *Zh. Org. Khim.* **21** 2300 (1985) [b]
66. E S Mukhina, G A Berkova, Z F Pavlova, E S Lipina, V V Perekalin *Zh. Org. Khim.* **26** 1447 (1990) [b]
67. E S Mukhina, Z F Pavlova, G A Berkova, E S Lipina, L V Mostyaeva, V V Perekalin, Ya A Kasem *Zh. Org. Khim.* **27** 910 (1991) [b]
68. E S Lipina, Z F Pavlova, T Ya Paperno, V V Perekalin, L V Prikhod'ko *Zh. Org. Khim.* **6** 1123 (1970) [b]
69. D I Aleksiev, I T Mladenov, V V Perekalin, E S Lipina *Dokl. Bolg. Akad. Nauk* **29** 1451 (1976)
70. L V Prikhod'ko, E S Lipina, V V Perekalin *Zh. Org. Khim.* **7** 622 (1971) [b]
71. N N Podgornova, E S Lipina, V V Perekalin *Zh. Org. Khim.* **10** 1985 (1974) [b]
72. N N Podgornova, E S Lipina, T Ya Paperno, V V Perekalin *Zh. Org. Khim.* **12** 25 (1976) [b]
73. R V Kaberdin, V I Potkin *Polikhlor-1,3-butadieny* (Polychlorobuta-1,3-dienes) (Minsk: Nauka i Tekhnika, 1991)
74. V N Kokorev, V I Potkin, R V Kaberdin, Yu A Ol'dekop *Izv. Akad. Nauk Bel. SSR, Ser. Khim. Nnauk* (2) 17 (1982)
75. V N Kokorev, V I Potkin, R V Kaberdin, Yu A Ol'dekop *Izv. Akad. Nauk Bel. SSR, Ser. Khim. Nauk* (3) 62 (1987)
76. V I Potkin, V M Zelenkovskii, V A Zapol'skii, I A Shingel', R V Kaberdin *Izv. Akad. Nauk Bel. SSR, Ser. Khim. Nnauk* (2) 71 (1995)
77. L V Vilkov, V S Mastryukov, N I Sadova *Opredelenie Geometricheskogo Stroeniya Svobodnykh Molekul* (Determination of the Geometric Structure of Free Molecules) (Leningrad: Khimiya, 1978)
78. V I Potkin, V A Knizhnikov, R V Kaberdin, Yu A Ol'dekop *Zh. Org. Khim.* **22** 86 (1986)
79. V I Potkin, R V Kaberdin, V A Knizhnikov, Yu A Ol'dekop, in *Tez. Dokl. IV Vsesoyuz. Konf. po Metalloorganicheskoi Khimii, Kazan', 1988* (Abstracts of Reports at the Fourth All-Union Conference on Organometallic Chemistry, Kazan, 1988) Part 2, p. 214
80. V I Potkin, R V Kaberdin, E Yu Dubova, Yu A Ol'dekop *Izv. Akad.'Nauk Bel. SSR, Ser. Khim. Nauk* (4) 113 (1991)
81. Yu A Ol'dekop, R V Kaberdin, V I Potkin *Zh. Org. Khim.* **16** 543 (1980) [b]
82. C Ibis, C Sayil *Phosphorus Sulfur Silicon Relat. Elem.* **92** 39 (1994)
83. V I Potkin, R V Kaberdin, V A Zapol'skii, N I Netchai, in *Abstracts of Reports of the 35th IUPAC Congress, Istanbul, Turkey, 1995* Vol. 1, p. 585
84. F S Göksel, C Ibis, in *Abstracts of Reports of the 35th IUPAC Congress, Istanbul, Turkey, 1995* Vol. 1, p. 683
85. V I Potkin, R V Kaberdin *Zh. Org. Khim.* **29** 56 (1993) [b]
86. V A Zapol'skii, V I Potkin, R V Kaberdin *Zh. Org. Khim.* **30** 193 (1994) [b]
87. V I Potkin, R V Kaberdin, M G Novikova *Izv. Akad. Nauk Bel., Ser. Khim. Nauk* (3) 116 (1995)
88. Yu A Ol'dekop, R V Kaberdin, V I Potkin, I A Shingel' *Zh. Org. Khim.* **15** 46 (1979) [b]
89. Yu A Ol'dekop, R V Kaberdin, V I Potkin *Zh. Org. Khim.* **15** 1099 (1979) [b]
90. B A Shainyan *Usp. Khim.* **55** 942 (1986) [*Russ. Chem. Rev.* **55** 511 (1986)
91. V A Zapol'skii, V I Potkin, N I Nechai, R V Kaberdin *Zh. Org. Khim.* **29** 885 (1993) [b]
92. V I Potkin, V A Zapol'skii, N I Nechai, R V Kaberdin *Dokl. Akad. Nauk Belarusi* **40** (3) 81 (1996)
93. V I Potkin, R V Kaberdin, Yu A Ol'dekop, in *Enaminy v Organicheskom Sinteze (Tez. Dokl.) Perm', 1991* [Enamines in Organic Synthesis (Abstracts of Report) Perm, 1991] p. 64

94. A I Verenich, A A Govorova, N M Galitskii, V I Potkin, R V Kaberdin *Zh. Strukt. Khim.* **33** (5) 150 (1992) [f]
95. V A Zapol'skii, V I Potkin, R V Kaberdin *Izv. Akad. Nauk Belarusi, Ser. Khim. Nauk* (3) 82 (1994)
96. Yu A Ol'dekop, R V Kaberdin, V I Potkin, I A Shingel' *Zh. Org. Khim.* **15** 276 (1979) [b]
97. V I Potkin *Izv. Akad. Nauk Bel., Ser. Khim. Nauk* (1) 65 (1991)
98. C Ibis, C Sayil *Synth. Commun.* **24** 2797 (1994)
99. C Ibis, C Sayil *Phosphorus Sulfur Silicon Relat. Elem.* **106** 29 (1995)
100. V I Potkin, V A Zapol'skii, R V Kaberdin *Zh. Org. Khim.* **29** 881 (1993) [b]
101. Yu A Ol'dekop, R V Kaberdin, V I Potkin *Zh. Org. Khim.* **14** 1594 (1978) [b]
102. V I Potkin, R V Kaberdin, Yu A Ol'dekop *Izv. Akad. Nauk Bel., Ser. Khim. Nauk* (5–6) 57 (1992)
103. V N Borisov, iIn *Sovremennye Problemy Organicheskoi Khimii* (Current Problems in Organic Chemistry) (Leningrad: Leningrad State University, 1975) No 4, p. 80
104. G. Maahs P.Hegenberg. *Angew. Chem.* **78** 927 (1966)
105. A M Akopyan, A M Saakyan, Z A Dzhauari *Arm. Khim. Zh.* **21** 414 (1968)
106. R V Kaberdin, V I Potkin, Yu A Ol'dekop *Dokl. Akad. Nauk SSSR* **300** 1133 (1988) [e]
107. R V Kaberdin, V I Potkin, Yu A Ol'dekop *Zh. Org. Khim.* **29** 1069 (1993) [b]
108. V I Potkin, N I Nechai, R V Kaberdin *Izv. Akad. Nauk Bel., Ser. Khim. Nauk* (4) 85 (1994)
109. A I Verenich, A A Govorova, N M Galitskii, V I Potkin, R V Kaberdin, Yu A Ol'dekop *Khim. Geterotsikl. Soedin.* 399 (1992) [c]
110. V I Potkin, R V Kaberdin, V P Suboch *Zh. Org. Khim.* **29** 1069 (1993) [b]
111. K Pilgram, K Hass *J. Med. Chem.* **18** 1204 (1975)
112. V F Mironov, L M Burnaeva, V I Potkin, E N Ofitserov, I V Konovalova *Zh. Obshch. Khim.* **63** 2237 (1993) [d]

[a] — *Russ. Chem. Bull. (Engl. Transl.)*
[b] — *Russ. J. Org. Chem. (Engl. Transl.)*
[c] — *Chem. Heterocycl. Compd. (Engl. Transl.)*
[d] — *Russ. J. Gen. Chem. (Engl. Transl.)*
[e] — *Dokl. Chem. Technol., Dokl. Chem. (Engl. Transl.)*
[f] — *J. Struct. Chem. (Engl. Transl.)*