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Nitro-functionalized analogues of 1,3-Butadiene: An overview of characteristic, synthesis, chemical transformations and biological activity

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A B S T R A C T

The nitrovinyl moiety is surely one of the most reactive fragments in organic chemistry, continuously employed to explore original pathways and reach new targets. One of the most important classes of chemicals containing this fragment are nitro-functionalised analogues of 1,3-butadiene. In this paper a comprehensive review study of these compounds is performed. The manuscript includes an analysis of physicochemical properties, spectral characteristic, synthesis, biological activity, and possible transformations of nitro substituted analogues of 1,3-butadiene. The analysis was divided into several parts, depending on the number of nitro groups included in the structure of a 1,3-butadiene analogue. In addition, the work includes information about hazards and safety principles when working with nitro compounds. Based on the analysis of the literature, it can be concluded that nitro-functionalised analogues of 1,3-butadiene exhibit diversified profile of properties, and an outstanding potential as valuable reagents in organic synthesis useful to obtain heterocycles that can be applied in medicine.

1. Introduction

Many aspects related to chemical properties of conjugated nitroalkenes (CNAs) are described in the literature. This topic is presented in many review articles and even books. The discussed subjects include the synthesis[1-2] and biological properties of CNAs,[3-4] as well as aspects of their chemical transformations, both of synthetic means[5-8] and based on quantum-chemistry.[9-13] CNAs are an attractive building block widely used in the modern organic chemistry for synthesis carbo- and heterocyclic compounds.[5-6] This is related to several facts. Firstly, the nitro group can be simply converted to other useful functional groups by means of oxidation as well as reduction (**Fig. 1**).[1] What is more, the presence of nitro group conjugated with ethylene moiety >C=C< additionally stimulates the biological activity of the compounds. In the effect, CNAs are characterised by antibacterial[3-4] and antifungal[14] properties.

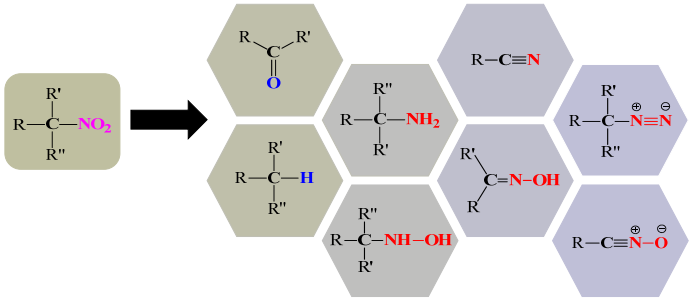

Fig. 1. Significant transformations of nitro group to others chemical compounds.

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A question arises, since CNAs can be useful building block for application in chemical synthesis, thanks to the presence of nitrovinyl moiety, what possibilities can be offered by a molecule containing a double bond conjugated with this nitrovinyl fragment? Nitro-functionalised analogues of 1,3-butadiene provide such an opportunity. The subject related with the chemistry of this class of organic compounds is interesting and attractive from several aspects. Firstly nitro-functionalised analogues of 1,3-butadiene are poorly known and described in the literature. Searching for "*nitrodiene*" in the SCOPUS database[15] returns 58 documents in total. The publication spectrum spans over 60 years, since 1962. It shows that the subject of this class of organic compounds is a relatively recent topic. It should be also noted that nitrodienes are a promising research direction due to an increasing number of recent publications about them (**Fig. 2**).

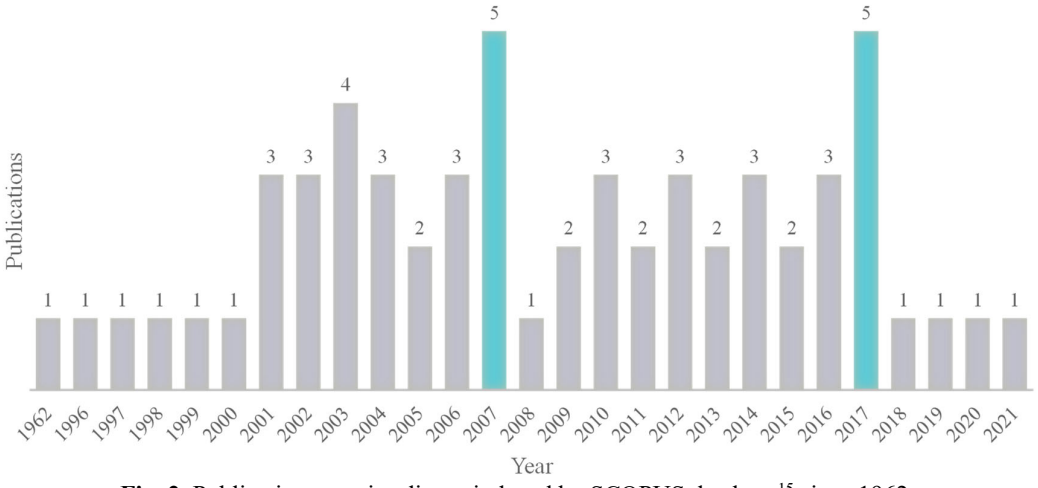


Fig. 2. Publications on nitrodienes indexed by SCOPUS database[15] since 1962.

Formally, nitrodienes offer the same synthetic properties as CNAs. From a practical point of view, nitro-functionalised analogues of 1,3-butadiene may constitute more useful and attractive building block in organic synthesis when compared to CNAs.[16,17] An application of nitrodienes as primary addents to a Diels-Alder reaction is obvious. Thanks to this, obtaining six membered rings is possible under mild reaction conditions (**Fig. 3**).[18] However, the presence of two conjugated >C=C< carbon-carbon double bonds, in the structure, makes participation of nitrodienes in other kinds of cycloaddition reactions possible (**Fig. 3**).[19,20] Especially synthesis of compounds containing two rings connected by a carbon-carbon single bond.[21] In addition to synthetic aspects, it should be underlined that nitro-functionalized analogues of 1,3-butadiene also exhibit various biological properties. These compounds have, among others, antifungal[22,23] activity. That makes nitrodienes themselves an important class of compounds for the constantly developing heterocyclic chemistry. It should also be remembered that nitrodienes take participation in other reactions such as substitution[24] or *Michael* addition.[25] What is more, some nitrodienes found use in industry, such as 4-(*4*-(N,N-dimethylamine)phenyl)-1-nitrobuta-1,3-diene can be applied in composition of a rewriteable optical materials.[26]

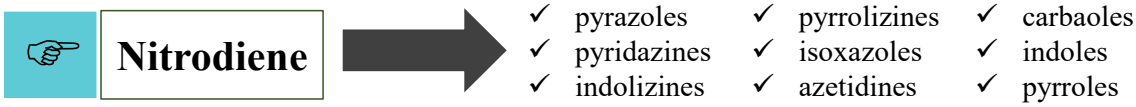


Fig. 3. Selected courses of transformation nitrodienes to obtain heterocycles ring.

In the scientific world systematic resources for analogues of dienes containing only nitro group(s) is not available. The topic is relatively new, hence the currently available review articles have many gaps. The first mentions of conjugated nitrodienes occurred in the beginning of the 60s. Thus, two independent Russian research groups, namely *Guseinov et al.*[27] and then *Petrzilka et al.*[28] wrote review articles on the chemistry of some 1-substituted alka-1,3-dienes as well as on the preparation and Diels-Alder reactions of heterosubstituted 1,3-dienes, respectively. In both cases, small sections with a few references on nitrodienes were included. *Perekalin et al.*[29] published a review book on the synthesis and reactivity of unsaturated nitrocompounds. The book contains large sections about mono- and dinitrodienes drawing from many of the Russian publications on the preparation and reactivity of these compounds, up until the early 90s. Afterwards, next extensive review was prepared by *Kaberdin et al.*[30] in the article the Authors described synthesis and reactivity of nitrobutadienes, with special consideration of their halogenated versions, covering the literature until 1996. In this review, methods for preparing these compounds are divided into two groups. The first is focused on the direct nitration of butadiene and some of its halogenated derivatives with different reagents, while the second describes elimination reactions from complex aliphatic nitro compounds. *Ballini et al.*[31] revised the literature on the synthesis and reactivity of nitrodienes that have appeared in the past two decades. In the manuscript the Authors presented information about compounds that include 1,3-butadiene moiety and one or two nitro groups and some that also contain aryl fragments or/and other heteroatoms. The latest review about chemistry of nitrodienes was presented by *Petrillo et al.*[32] In the manuscript the Authors focused only on the

exploitation of nitrosubstituted 1,3-dienes for the synthesis of heterocycles over the last twenty years, expanding review works of *Guseinov et al.*[27] and *Petrzilka et al.*[28] from several decades ago.

This review presents a comprehensive study of nitro-functionalised analogues of 1,3-butadiene. With a view to the last review articles in our manuscript we determined to include the latest literature reports about synthesis methods of nitrodienes and their application as building blocks in organic chemistry as well as collect, omitted in other publications, aspects such as physicochemical data of titled compounds, their spectral characteristic and biological activity (**Fig. 4**). In this manuscript we decided to describe analogues of 1,3-butadiene as the simplest representative of conjugated dienes. Also, we focused only on nitro-functionalised derivatives due to their possible potential routes of modification (**Fig. 1**).

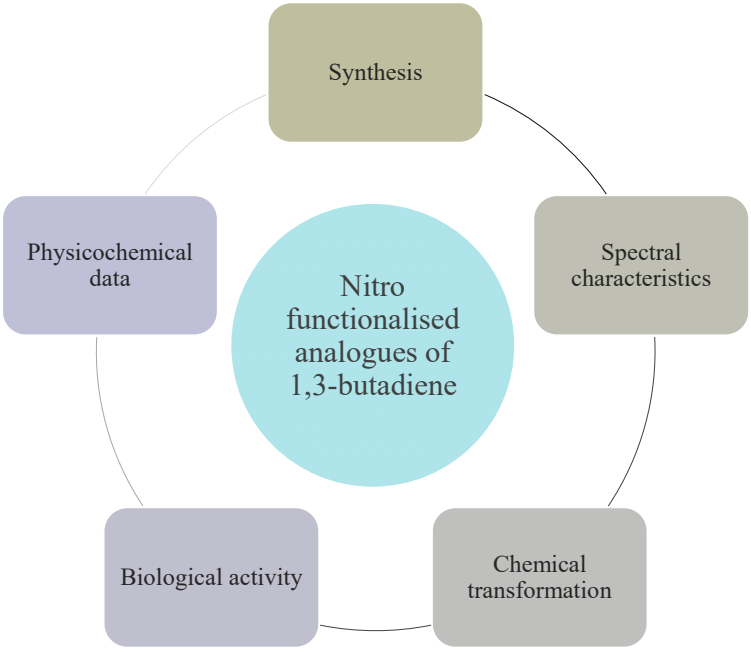


Fig. 4. Scope of the current review.

This work has the purpose of systematizationof current information on nitro-functionalised analogues of 1,3-butadiene aspromising build blocks for modern organic chemistry as well as of filling thegaps and indicating aspects omitted in other publications. We hope that thisreview will be helpful in planning both synthetic and quantum-chemical researchof the chemistry of those compounds.

2. The review and assessment methods

Firstly, all possibilities of the presence of nitro groups in 1,3-butadiene, their number and position in the molecule were investigated. For examples where the configurational isomerism is possible it was also considered. With this information, the search for a unique CAS number for all possible combinations of compounds began. The described procedure allowed for identification of **5** existing structures (**Fig. 5**, **red frame**).

Based on information about number of existing combinations of nitro substituted analogues of 1,3-butadiene full data for these compounds were found. For this purpose, the chemical databases such as *Reaxys*,[33] *ChemSpider*,[34] *PubChem*[35] and *Chemical Book*[36] were used. Additionally, in order to fully revise available literature, the searching process was also conducted using search function available in *Google Scholar*.[37] For the search of literature the word “nitrodiene" was chosen.

The literature search covered all publications about nitrobutadienes, from 1952 to 2017. To prepare this manuscript articles from Science Direct, Scopus, Springer, Web of Science and Wiley databases were used. A content-related check of the found literature was conducted (**Fig. 5**, **green frame**). The titles and abstracts of the literature were checked to identify relevant publications. For subjective analysis, publications describing physicochemical properties, spectral characteristic, synthesis, biological activity and possible transformation of nitro substituted analogues of 1,3-butadiene were selected. As a result, a total of 35 relevant and available publications were identified. Collected information for all compounds was extracted and sorted.

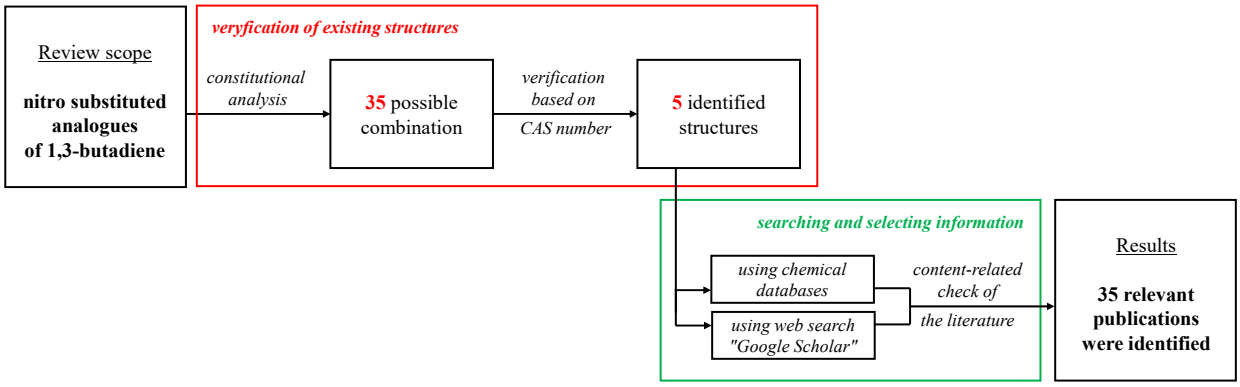


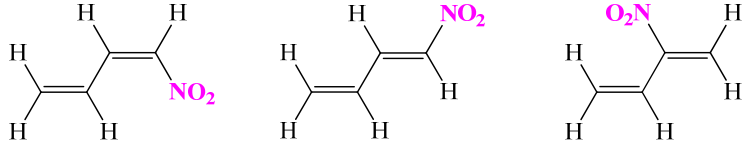
Fig. 5. Procedure of the applied literature analysis.

3. Information overview about nitro-functionalised analogues of 1,3-butadiene

The performed analysis was divided into several parts. Respective subsections contain information about analogues of 1,3-butadiene depending on the number of nitro group included in their structure.

3.1. Analogues of 1,3-butadiene including one nitro group in the structure

For analogues of 1,3-butadiene containing one nitro group, due to its position in the structure, two isomers are possible. There are 1-nitro-1,3-butadiene (**Ia**) and 2-nitro-1,3-butadiene (**Ib**). In turn, due to geometric position of nitro group, for analogues **Ia** two isomers **Ia-*1-cis*** and **Ia-*1-trans*** are possible (**Fig. 6**).



	Ia-*1-cis*	**Ia-*1-trans***	**Ib**
CAS	29293-61-6	29293-60-5	19764-71-7

Fig. 6. Chemical structures for analogues of 1,3-butadiene with one nitro group described in literature, according to *Reaxys* database[33].

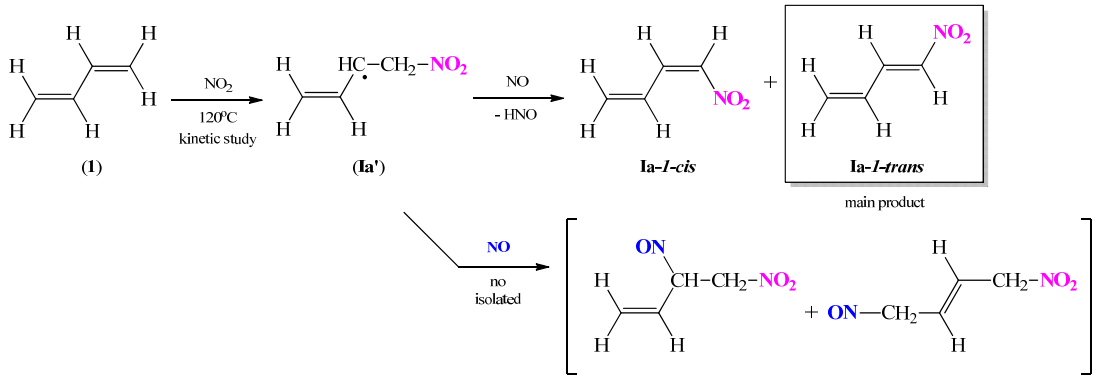
According to *Reaxys* database,[33] 56 references contain information about these compounds are available (among which 31 patents). However, most of sources do not contain any information about mono nitro substituted analogues 1,3-butadienes. Although, all of possible analogues are described in literature (**Fig. 6**), only **Ia-*1-trans*** has been fully characterized. Basic physicochemical data for **Ia-*1-trans*** is included in **Table 1**.

Table 1. Basic physicochemical and spectroscopic data for *1-trans*-1-nitro-1,3-butadiene **Ia-*1-trans***.

Ia-*1-trans*	**Physical form**	**Density [g·cm^{-1}]**	**Boiling point [°C]**	**Refractive index**	**^{1}H NMR δ [ppm]**	**^{13}C NMR δ [ppm]**	**IR υ [cm^{-1}]**	**UV-Vis λ [nm]**
	Yellow oil	1.0987 (20 °C)	40.0-43.0 (5 Tr)	1.5408 (20 °C)	7.60 (1H, –CH=CHNO$_2$) 7.20 (1H, –CH–NO$_2$) 6.54 (1H, –CH=CH$_2$) 5.82 (2H, =CH$_2$)	150 137 131 130	1640 1600 1550 1350	283 (MeOH)
Ref.	38	38	39	39	40	40	40	41

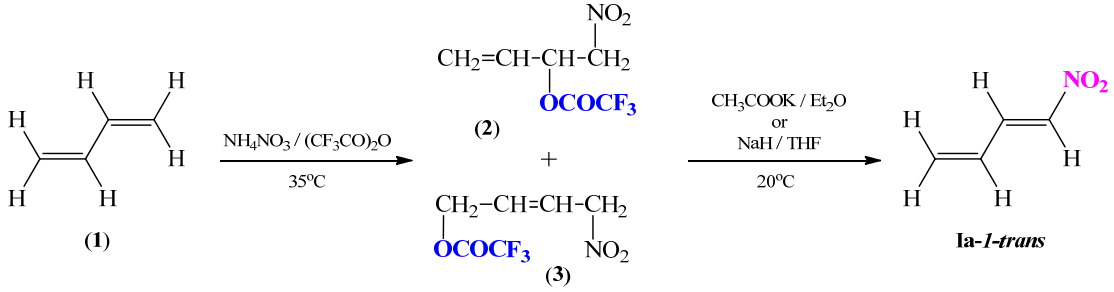
The preparation of *1-trans*-1-nitro-1,3-butadiene **Ia-*1-trans*** is well described. In the literature the synthesis of **Ia-*1-trans*** is presented in two ways. The first of them is direct nitration of 1,3-butadiene (**1**). In the role of nitrating agent a mixture of both nitrogen oxide and nitrogen dioxide is used (**Scheme 1**). The method was presented in 1996 by *Roth et al.*[42] in a gasphase kinetic study with negative activation energy. The Authors reported that in a first stage of reaction the radical structure **Ia'** is obtained. In the second stage the molecule of HNO is eliminated. Finally, during the reaction is possible to

obtain two isomers, namely *1-trans*-1-nitro-1,3-butadiene **Ia-*1-trans*** as a main product as well as the second isomer, namely *1-cis*-1-nitro-1,3-butadiene **Ia-*1-cis*** was also detected. The Authors reported also that during the reaction the creation of nitroso derivatives of 1-nitrobutadiene **Ia** is possible, but the Researcher underlined that structures are not possible to isolate.



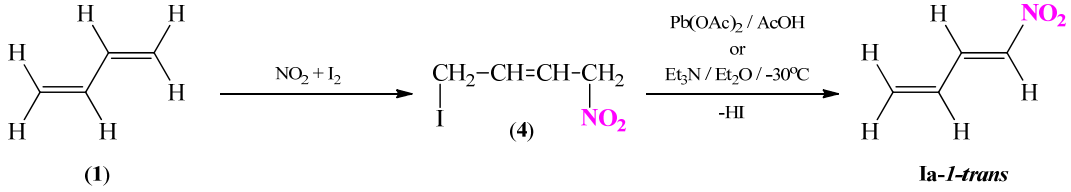
Scheme 1. Synthesis of nitrodiene **Ia-*1-cis*** and **Ia-*1-trans*** via direct nitration of 1,3-butadiene (**1**).

More popular synthesis method of *1-trans*-1-nitro-1,3-butadiene **Ia-*1-trans*** is a two-stepped process. One alternative includes a conversion of 1,3-butadiene (**1**) using ammonium nitrate and trifluoroacetic anhydride. As a result, 1,2- and 1,4-nitro-trifluoroacetates are obtained (**2** and **3** respectively). The reaction releases in situ in dichloromethane as a solvent. The second stage constitutes a pyrolysis of esters **2** and **3**, in the presence of potassium acetate in diethyl ether, or sodium hydride in tetrahydrofurane. It should be underlined that the elimination process is realised according to the E1cB mechanism. Generally, both steps occur within 18 hours. The **Ia-*1-trans*** isomer is obtained in 89.0 %. The presented method has been carried out twice by *Bloom et al.*[40,43] (**Scheme 2**).



Scheme 2. Synthesis of nitrodiene **Ia-*1-trans*** via multistep process with nitroester intermediate products **2** and **3**.

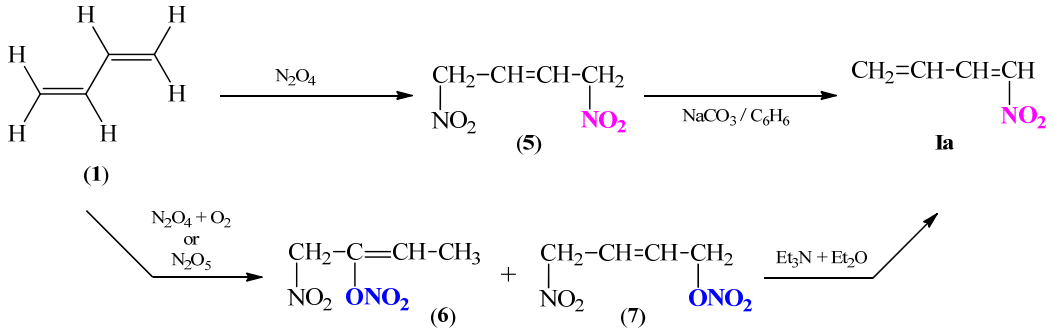
Another alternative two-stepped process was described by *Petrov et al.*[38,44] as well as *Sulimov et al.*[45] (**Scheme 3**). For this option, in a first stage 1,3-butadiene (**1**) is converted to 1-iodo-4-nitrobut-2-ene (**4**) using nitrogen dioxide and iodine. Next stage includes the dehydrohalogenation reaction of compound **4** with simultaneous reorganization of the molecule. The reaction can be carried under the action of lead acetate in glacial acetic acid[38,44] or, optionally, by using triethylamine in diethyl ether at -30 °C.[45] In order to prevent polymerisation of the nitrodiene **Ia-*1-trans*** hydroquinone was added to the reaction mixture. [45]



Scheme 3. Synthesis of nitrodiene **Ia-*1-trans*** via multistep process through a stadium of 1-iodo-4-nitrobut-2-ene (**4**).

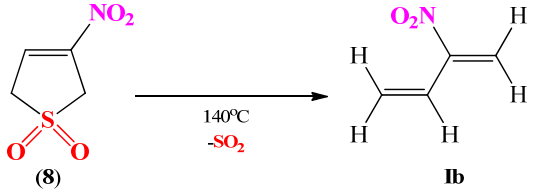
Also, a popular synthesis method of 1-nitro-1,3-butadienes **Ia** is dehydronitration of dinitro analogues of butane and their derivatives. The method was described by *Sulimov et al.*[45] and *Lipina et al.*[46-48] (**Scheme 4**). Unfortunately, both research groups did not give information on the regioisomericity of obtained connections. Firstly, 1,3-butadiene (**1**) is subjected to an additional reaction of the nitro group. In a role of nitrating agent, dinitrogen tetroxide with sodium carbonate in benzene was used. As an intermediate product a 1,4-dinitrobutene **5** is received. Optionally, the reaction may take place through a stadium of alkyl nitrates **6** and **7**. To the synthesis either dinitrogen tetroxide mixed with oxygen, or dinitrogen pentoxide, is used. In turn, triethylamine in diethyl ether solution is applied in the nitric acid elimination process. The mechanism of the nitrous acid extrusion from nitroalkyl moieties was very recently analysed in detail both under thermal

and catalytic conditions. According to the latest DFT study this kind of mechanism can be classified as extremely asynchronous.[49-51]



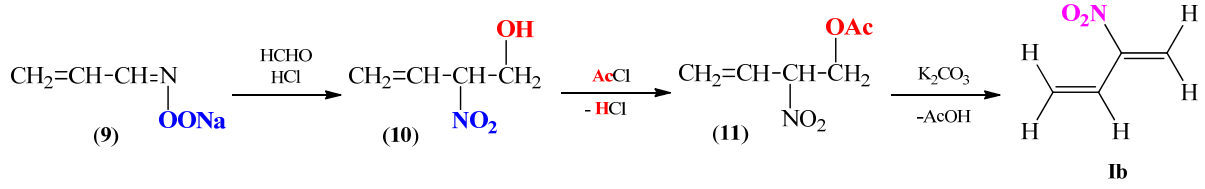
Scheme 4. Synthesis of nitrodiene **Ia-*1-trans*** via multistep process through the stadium of nitro and nitroso analogues of 2-butene.

In the literature, two main techniques for preparing the 2-nitro-1,3-butadiene (**Ib**) are described. The first was reported by *Berestovitskaya et al.*[52] in 1979. The method consists of heating a 3-nitro-3-sulfolene (**8**) at a temperature of 140 °C. During the thermal decomposition a molecule of SO_2 is eliminated with simultaneous formation of a second double bond (**Scheme 5**). In 2015 the mechanism of similar transformation to obtain analogues of 1,4-dinitro-1,3-butadiene via thermal decomposition a molecule of SO_2 was examined by *Jasiński and Dresler.*[53] According to the DFT calculation the desulfonylation process is realised as one-step nonpolar mechanism and can be equivalent to retro [4+1]-cycloaddition reaction in a formal point of view.



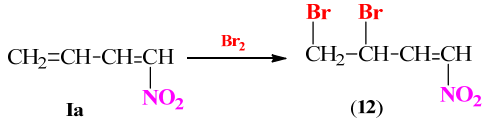
Scheme 5. Synthesis of nitrodiene **Ib** via reaction of thermal decomposition of sulfone **8**.

However, a three staged process of preparation of 2-nitro-1,3-butadiene (**Ib**) is more popular (**Scheme 6**). In the first stage, starting with the sodium derivative of 3-nitroprop-1-ene (**9**) a condensation reaction with formaldehyde was carried out. In effect 2-nitrobut-3-en-1-ol (**10**) was obtained. Next, during an acetylation reaction of the alcohol **10**, product **11** was obtained. For this process acetyl chloride was used. The last stage included a deacetoxylation of compound **11**. For this purpose potassium carbonate was applied. In order to prevent polymerisation of the nitrodiene **Ib**, the reaction was performed in the presence of hydroquinone. It should be underlined that the elimination process is released according to E1cB mechanism. The method was reported by *Nicolinski et al.*[54] in 1956.



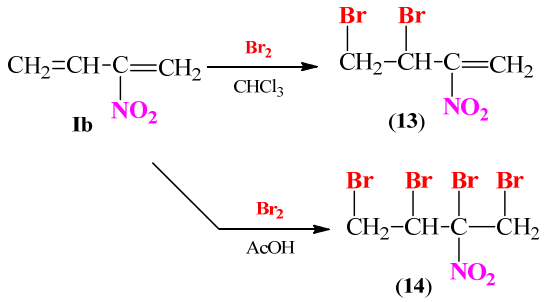
Scheme 6. A multistep synthesis of **Ib** including condensation, acetylation and further deacetylation stages.

There are many examples of the conversion of mono nitro substituted analogues of 1,3-butadiene. To the most popular reactions one can count nucleophilic and electrophilic additions as well as [4+2] cycloadditions.A historical reaction using mono nitro substituted analogues of 1,3-butadiene was presented by *Kataev*[55] in 1955. The author described two examples. The first of them included an electrophilic addition of bromine to 1-nitro-1,3-butadiene **Ia** (**Scheme 7**). In a course of the reaction 3,4-dibromo-1-nitro-1-butene (**12**) is formed as the only product. In the article the geometric isomerism of compound **Ia** is not defined.



Scheme 7. Electrophilic addition of bromine to 1-nitro-1,3-butadiene **Ia**.

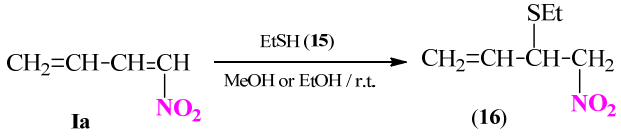
The electrophilic addition for 2-nitro-1,3-butadiene **Ib** was reported in 1976. *Aleksiev et al.*[56] carried out a reaction between nitrodiene **Ib** and bromine in different solvents (**Scheme 8**). The authors mentioned that the addition in chlororoform proceeds slowly and in effect the reaction leads to only one product which is 3,4-dibromo-2-nitro-1-butene (**13**). In turn, application of a more polar solvent such as acetic acid led to formation of 1,2,3,4-tetrabromo-2-nitro-1-butene (**14**).



Scheme 8. Electrophilic addition of bromine to 2-nitro-1,3-butadiene **Ib** in different solvents.

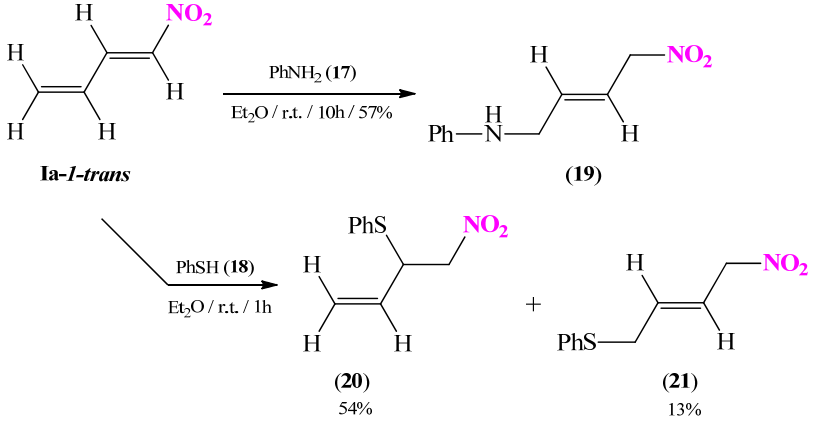
It should be underlined that nitrobutadienes are far less reactive in electrophilic substitution reactions in comparison with butadiene. This fact is connected with the presence of nitro group which imparts a pronounced electrophilic character to the diene system. Definitely an easier to realise type of chemical reactions involving nitrodienes are nucleophilic additions. The direction of these reactions depends on the nature of the nucleophile. They may occur both at the 1,2-position and 1,4-position of the nitrodiene.

Earliest described example of this class of reaction is addition of ethanethiol (**15**) to 1-nitro-1,3-butadiene **Ia** (**Scheme 9**) reported by *Vil'davskaya et al.*[57] in 1967. In the article the geometric isomerism of compound **Ia** is not defined. The reaction took place using sodium hydroxide and at room temperature. The authors reported that in the role of a solvent either methanol or ethanol can be used. During the reaction only one product of 1,2-addition (**16**) is obtained.



Scheme 9. Nucleophilic addition of ethanethiol (**15**) to 1-nitro-1,3-butadiene **Ia**.

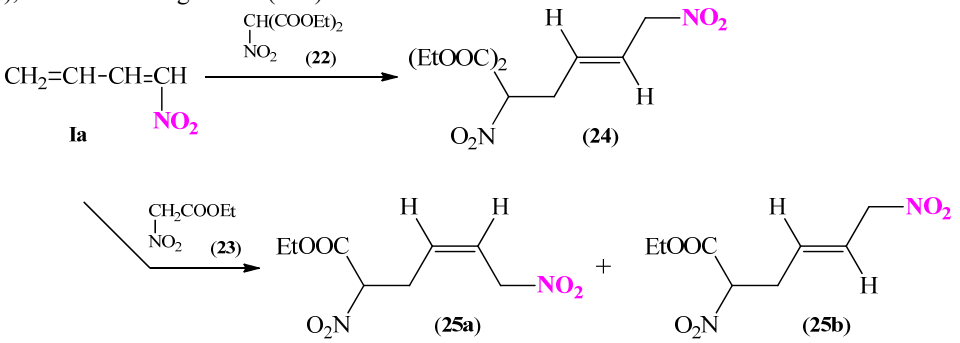
In 1987 *Bloom and Mellor*[40,43] conducted a study about addition of various nucleophilic agents, like aromatic amines and thiols to *1-trans*-1-nitro-1,3-butadiene **Ia-*1-trans***. An example of such reaction is addition of aniline (**17**) to nitrodiene **Ia-*1-trans*** (**Scheme 10**). The reaction is realised in diethyl ether as a solvent and at room temperature. In this condition the conversion of substrate took 10 hours. In effect the 1,4-adduct in *trans* configuration (**19**) as the only product was obtained with 57.0 % yield. On another way addition of thiophenole (**18**) to nitrodiene **Ia-*1-trans*** (**Scheme 10**) is realised. The reaction is realised in the same solvent and temperature conditions. Additionally, triethylamine is used. In this condition the conversion of substrate took 1 hour. Interestingly, for this case two reaction products of 1,2-addition (**20**) as well as 1,4-addition in *trans* configuration (**21**) were obtained (**20**:**21** 54%:13%).



Scheme 10. Nucleophilic addition of aniline (**17**) and thiophenol (**18**) to nitrodiene **Ia-*1-trans***.

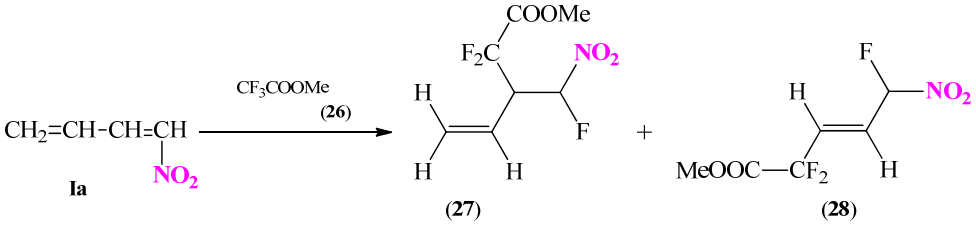
Another example of nucleophilic addition to 1-nitro-1,3-butadiene **Ia** include reactions using diethyl nitromalonate (**22**) and ethyl nitroacetate (**23**) (**Scheme 11**). The processes were reported in 1967 and 1969 by *Samoilovich research group*.[58,59]

In the article the geometric isomerism of compound **Ia** is not defined. In case of interaction between nitrodiene **Ia** and diethyl nitromalonate (**22**) reactions led to only one product of 1,4-addition in *trans* configuration (**24**). In turn, in the case of reaction between nitrodiene **Ia** and ethyl nitroacetate (**23**) two products of 1,4-addition were obtained, in both *cis* configuration (**25a**), and *trans* configuration (**25b**).



Scheme 11. Nucleophilic addition of diethyl nitromalonate (**22**) and ethyl nitroacetate (**23**) to 1-nitro-1,3-butadiene **Ia**.

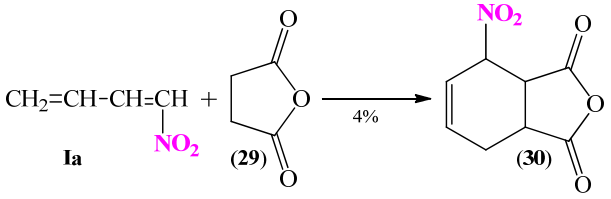
A very interesting example of nucleophilic addition is a reaction reported in *Startsev et al.*[60] in 1988. The authors presented a reaction of 1-nitro-1,3-butadiene **Ia** with methyl trifluoroacetate (**26**) (**Scheme 12**). In the article the geometric isomerism of compound **Ia** is not defined. In a course of reaction both products of 1,2-addition (**27**) as well as 1,4-addition in *trans* configuration (**28**) were obtained. According to the authors the products **27** and **28** were not separated from the mixture.



Scheme 12. Nucleophilic addition of methyl trifluoroacetate (**26**) to 1-nitro-1,3-butadiene **Ia**.

Due to their structure, mono-nitrodienes as well as other nitrodienes are an excellent reagent for use in Diels-Alder reactions. Despite this fact, Diels-Alder reactions involving nitrobutadienes has not been adequately explored. In literature only several examples of these reactions are found.

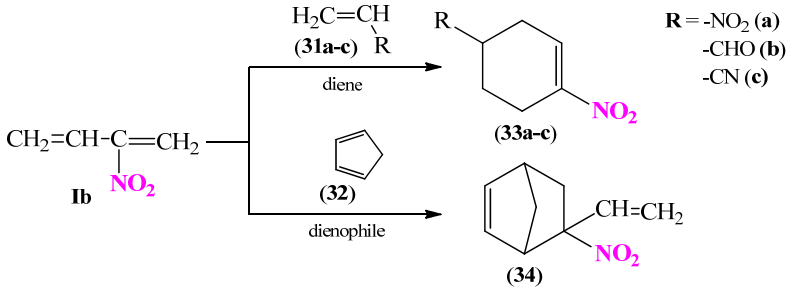
In 1955 *Kataev*[55] reported the application of 1-nitro-1,3-butadiene **Ia** in [4+2] cycloaddition (**Scheme 13**). In the article the geometric isomerism of compound **Ia** is not defined. In a role of dienophile the maleic anhydride (**29**) was applied. The yield reported by the author reached only 4.0 %.



Scheme 13. [4+2] cycloaddition between 1-nitro-1,3-butadiene **Ia** and maleic anhydride (**29**).

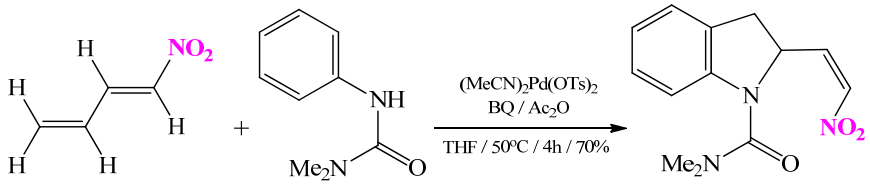
Kataev[55] reported also about, other [4+2] cycloaddition of 1-nitro-1,3-butadiene **Ia** with other dienes such as benzoquinone, α-naphothoquinone, and acrylonitrile, acrolein, and dimethyl acetylenedicarboxylate. The author described that these cycloaddition did not provide expected products.

In 1976 *Aleksiev et al.*[56] carried out a series of [4+2] cycloaddition reactions of 2-nitro-1,3-butadiene **Ib**. The authors indicated that nitrodiene **Ib** is a universal reagent to apply in Diels-Alder reactions. It is a very interesting fact due to the dual nature of compound **Ib**, because **Ib** can participate in [4+2] cycloaddition reactions both as the diene and the dienophile. This theory was tested in reactions of nitrodiene **Ib** with nitroethylene (**31a**), acrolein (**31b**), acrylonitrile (**31c**) as well as cyclopentadiene (**32**). The nitrodiene **Ib** in reaction with previous compounds forms corresponding cycloadducts **33a-c** and **34** (**Scheme 14**).



Scheme 14. [4+2] cycloaddition of 1-nitro-1,3-butadiene **Ia** with both dienophile **31a-c** and diene **32**.

The studies of mono-nitrodienes presented so far in this article come from the previous century. However, these compounds are still being researched by scientists. In 2008 *Houlden et al.*[61] and next, in 2017 *Chen et al.*[62] carried out a reaction of Pd(II)-catalyzed 1,2-carboamination of *1-trans*-1-nitro-1,3-butadiene **Ia-*1-trans*** with N,N-dimethyl-N′-phenylurea (**35**) (**Scheme 15**). In the role of precatalyst the authors used $(MeCN)_2Pd(OTs)_2$. The reaction is realised under mild conditions, in 50 °C, with tetrahydrofuran as a solvent and with addition of 4-benzoquinone and acetic anhydride. In these conditions the conversion of substrate takes 4 hours. As an effect the product (**36**) was obtained with 70.0 % yield.



Ia-*1-trans* (**36**) (**37**)

Scheme 15. [4+2] cycloaddition between 1-nitro-1,3-butadiene **Ia** and maleic anhydride (**29**).

3.2. Analogues of 1,3-butadiene including two nitro groups in the structure

For analogues of 1,3-butadiene containing two nitro groups, due to their position in the structure, five isomers are possible. In the literature only one of them is described – 1,4-dinitro-1,3-butadiene **II** (**Fig. 7**). Early authors, such as *Novikov et al.*[64] and *Carroll et al.*[65,68] do not describe conformation of obtained dinitrodiene **II**, whereas *Durden et al.*[66] claim 1,4-dinitro-1,3-butadiene **II** to be stable in *1-trans-3-trans* form, which will be used to represent the compound.

II

CAS 26378-88-1

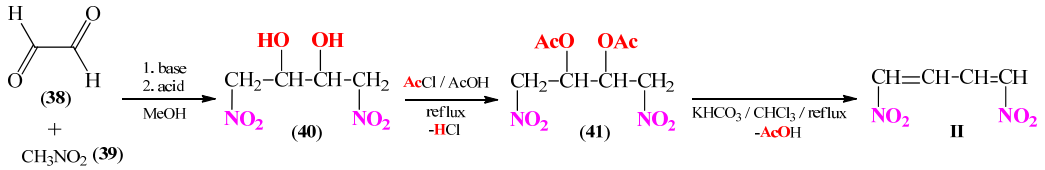
Fig. 7. 1,4-dinitrobuta-1,3-diene **II** as the only dinitro analogue of butadiene described in literature, according to *Reaxys* database[33].

According to *Reaxys* database[33], the only 13 publications contain information about 1,4-dinitro-1,3-butadiene **II** are available. The dinitrodiene **II** has been thoroughly researched and described in the literature. Basic physicochemical data for 1,4-dinitrobuta-1,3-diene **II** are included in **Table 2.**

Table 2. Basic physicochemical and spectroscopic data for 1,4-dinitrobuta-1,3-diene **II**.

	Physical form	Melting point [°C]	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]	IR υ [cm^{-1}]	UV-Vis λ [nm]
II		147.0-148.0 (from $CHCl_3$)[63]	7.52s, 7.55s ($CDCl_3$)[65]			
	Yellow needles (from $CHCl_3$)[63,64]	146.5-147.0 (from $CHCl_3$)[64]	7.43s, 7.49s ($CDCl_3$)[67]	130.7 147.3 ((CD_3)$_2$CO)[67]	1615 1525 1340 (2 % of $CDCl_3$)[64]	281 (MeOH)[65,66]
	Pale-brown needles (from EtOH)[63]	150.0-150.5 (from $CHCl_3$)[65]	7.90s ((CD_3)$_2$CO)[66]			
		146.0-148.0 (from $CHCl_3$)[66]	6.2m (C_6D_6)[66]			

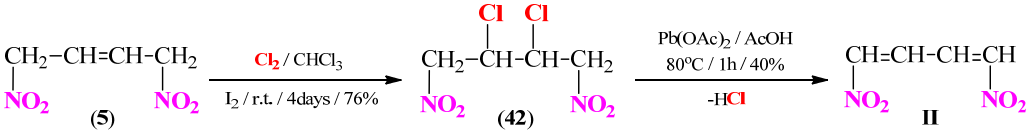
In 1960 *Novikov et al.*[64] proposed a three stepped method for obtaining 1,4-dinitro-1,3-butadiene **II** (**Scheme 16**). The method was later replicated by *Carroll et al.*[64,68] and *Durden et al.*[66] in 1966 and 1970, respectively.



Scheme 16. Synthesis of dinitrodiene **II** via three stepped process including a condensation (**38** + **39** → **40**), esterification (**40** → **41**) and AcOH thermal elimination (**41** → **II**) reactions.

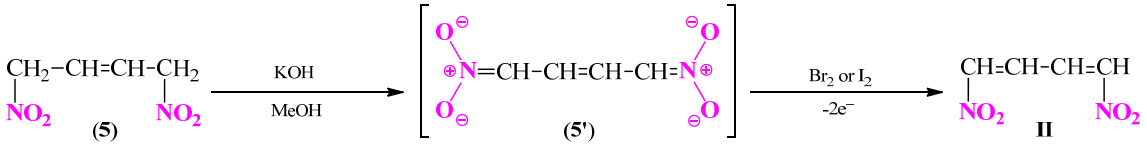
First stage (**Scheme 16**) is the condensation of glyoxal (**38**) and nitromethane (**39**), yielding 1,4-dinitrobutane-2,3-diol (**40**) with various yields *Novikov et al.*[64] claim yield of 80.5 %, whereas yield reported by *Carroll*[68] reaches only 36.4 %. Reaction occurs in an equal-volume mixture of nitromethane and methanol, in the presence of NaOH[64,66] or KOH[68] at temperature up to 10 °C. For acidification various acids can be used.[69] Second stage (**Scheme 16**) comprises acylation of previously obtained diol **40** with acetyl chloride. Reagents are refluxed in glacial acetic, producing 2,3-diacetoxy-1,4-dinitrobutane (**41**) with yields up to 87.0 %.[66] The last stage (**Scheme 16**) is the elimination of two acetic acid molecules from 2,3-diacetoxy-1,4-dinitrobutane (**41**). It should be underlined that the elimination process is released according to the E1cB mechanism. It occurs in the presence of $KHCO_3$, in refluxed $CHCl_3$.[64] *Novikov et al.*[64] claim quantitative yields of the reaction, while *Durden et al.*[66] report that yields circa 90.0 % are to be expected.

In 1959 *Perekalin et al.*[63] described a method for synthesis of 1,4-dinitrobuta-1,3-diene **II** starting from 1,4-dinitrobuta-2-ene (**5**). In the method (**Scheme 17**), compound **5** is chlorinated with gaseous chlorine, in the presence of iodine, reaction takes place in chloroform at room temperature, over 4 days, yielding 76.0 % of 2,3-dichloro-1,4-dinitrobutane (**42**). The resulting product **42** is dehydrochlorinated in glacial acetic acid at 80 °C in the presence of lead(II) acetate over a span of 1 hour, yielding 40.0 % of dinitrodiene **II**.



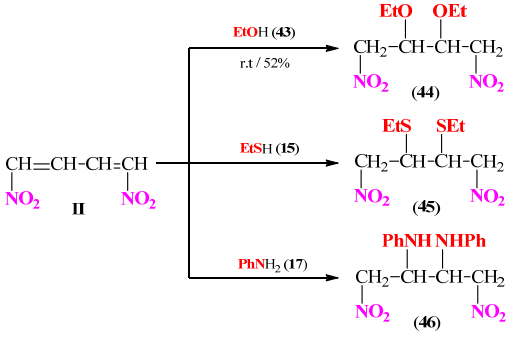
Scheme 17. Synthesis of dinitrodiene **II** via multistep process through the stadium of 2,3-dichloro-1,4-dinitrobutane (**42**).

One more method starting from 1,4-dinitrobut-2-ene (**5**) was described in 1968 by *Rowley et al.*[22] The authors described direct oxidation of nitroalkene **5** with bromine or iodine in the presence of KOH (**Scheme 18**). Reaction took place at temperature slightly below 0 °C in a methanolic KOH solution, over 1 hour span. Yield of raw product totalled 79.0 %.[22]



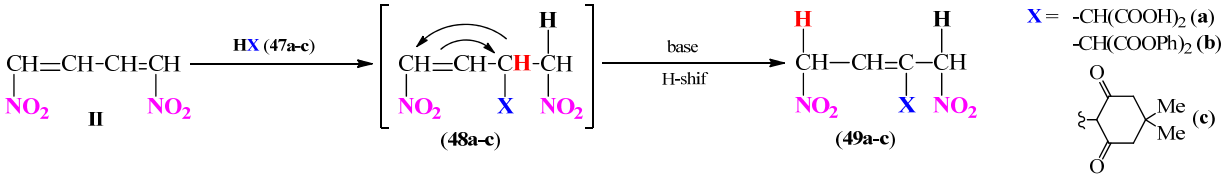
Scheme 18. Synthesis of dinitrodiene **II** via electrochemical processes.

In the literature several examples of the dinitrodiene **II** application as a substrate in chemical reactions are available. All of them include a nucleophilic reaction. According to *Pavlova et al.*,[67] *Mostyaeva*,[70] and *Lipina et al.*[70] 1,4-dinitrobuta-1,3-diene **II** can undergo nucleophilic addition of many compounds such as of ethanol (**43**), ethanethiol (**15**) as well as aniline (**17**). In effect the appropriate 2,3-adducts are obtained (**Scheme 19**).



Scheme 19. Nucleophilic addition of ethanol (**43**), ethanethiol (**15**) and aniline (**17**) to 1,4-dinitro-1,3-butadiene **II**.

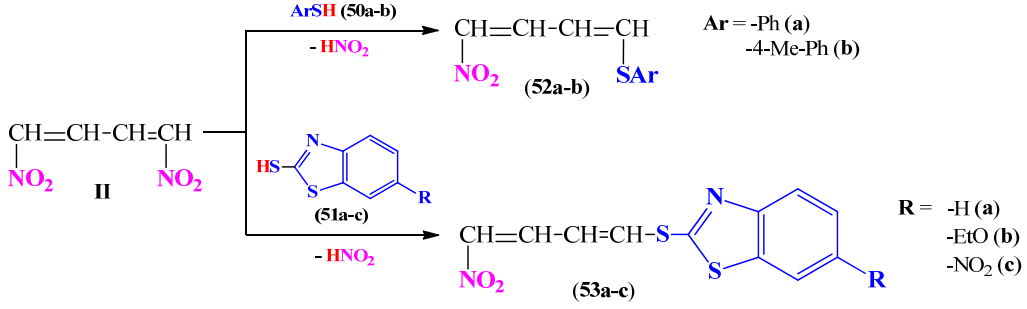
In 1964, *Lipina and Perekalin*[48] and next, in 1984, *Nekrasova et al.*[72] reported about another example of nucleophilic addition of dicarbonyl compound type CH-acids, namely malonic acid (**47a**), its diphenyl ester **47b** as well as 3,3-dimethylcyclohexane-1,3-dione (**47c**) to 1,4-dinitrobuta-1,3-diene **II**. The dinitrodiene **II** reacts with CH-acids to give the addition product at one of the nitrovinyl fragments. In turn, the other nitrovinyl fragment isomerises in the presence of a base. In effect the appropriate 1,2-adducts with changed position of the double bond are obtained (**Scheme 20**).



Scheme 20. Nucleophilic addition of CH-acids type **47a-c** to 1,4-dinitro-1,3-butadiene **II**.

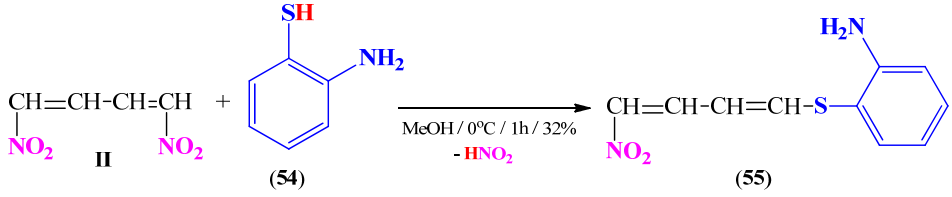
Nitro group of 1,4-dinitrobuta-1,3-diene **II** can also undergo substitution, in the presence of thiols, forming thioethers of vinyl type.[67,73-75] Three such reactions were found presenting reactions both with aliphatic and aromatic thiols.

The first reports on the use of dinitrodiene **II** in nucleophilic substitution reactions come from 1985. *Pavlova et al.*[67] described a reaction 1,4-dinitrobuta-1,3-diene **II** with thiophenol (**50a**). In a result the 4-nitro-1-phenylthio-1,3-butadiene (**52a**) was obtained in 42% yield (**Scheme 21**). In turn, in 1990 *Mukhina et al.*[73] carried out a similar reaction with 4-toluenethiol (**50b**). The reaction proceeds analogously and gives 4-nitro-1-(4-tolylthio)-1,3-butadiene (**52b**) with 28.0 % yield (**Scheme 21**).



Scheme 21. Nucleophilic substitution of thiols **50a-b** and **51a-c** to 1,4-dinitro-1,3-butadiene **II**.

In 2005 *Kretser et al.*[73] reported a nucleophilic substitution of 1,4-dinitrobuta-1,3-diene **II** with benzothiazolyl-2-thiol (**51a**) and its analogues **51b-c** (**Scheme 21**). Reactions of dinitrodiene **II** with thiols **51a-c** took place in methanolic suspension of appropriate thiol at room temperature, for thiols **51a-b**, or in a boiling methanol, for thiol **51c**. In these conditions the reaction times were reported on 2 hours for thiols **51a-b** as well as 48 hours for thiol **51c**. The products **53a-c** were obtained in 32.0 % (**53a**), 5.0 % (**53b**) and 33.0 % (**53c**) yield respectively. A very interesting example of nucleophilic substitution is presented by a reaction of 1,4-dinitrobuta-1,3-diene **II** with 2-amino-benzenethiol (**54**) (**Scheme 22**). The reaction was presented in 2010 by *Kretser and Lipina.*[75] The Authors reported that the reaction is realised only on thiolic fragments of molecule **54**. The reaction took place in a methanolic solution at 0 °C. In this condition the reaction time was 1 hour. The product **55** was obtained with 32.0 % yield.



Scheme 22. Nucleophilic substitution of 2-amino-benzenethiol (**54**) to 1,4-dinitro-1,3-butadiene **II**.

1,4-dinitrobuta-1,3-diene **II** was found to be active against *Staphylococcus aureus* and *Aspergillus niger* at 100 p.p.m. concetration in growing media. What is more the compound prevented bean rust (*Uromyces phaseoli*) infection in *in vivo* tests. In the same research some other nitrodienes were tested, showing promising results.[66] In the literature none tests of toxicity of discussed compounds were identified, so drawing any conclusions of possible application in agriculture is impossible, more research is still required.

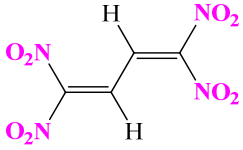
3.3. Analogues of 1,3-butadiene including three nitro groups in the structure

None representants of this group have been found in the literature. Hereby a gap in the research is identified. More research is required on the topic of stability and synthesis of the trinitro analogues of 1,3-butadiene.

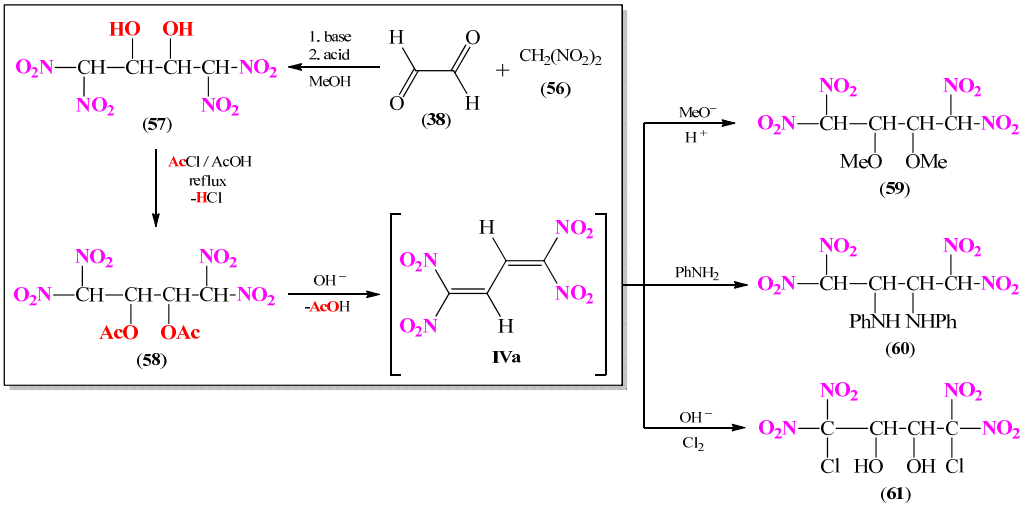
3.4. Analogues of 1,3-butadiene including four nitro groups in the structure

Only one analogue of 1,3-butadiene that includes four nitro group is described in literature (**Table 3**).

Table 3. Basic physicochemical and spectroscopic data for 1,1,4,4-tetranitro-1,3-butadiene **IVa**.

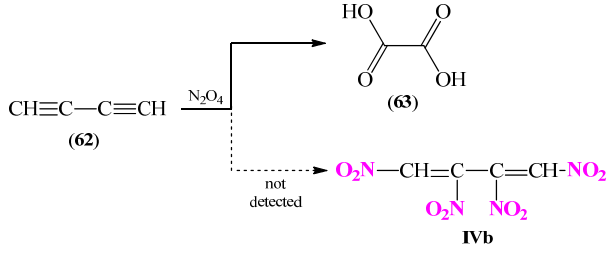
		Decomposition temperature [°C]	IR υ [cm^{-1}]	UV-Vis λ [nm]
 **IVa**		87	1585-1330	307 (CH_3OH)
CAS: 84717-06-6	**Ref.**	72	72	72

In 1984 *Nekrasova et al.*[72] reported possibilities of synthesis of symmetric 1,1,4,4-tetranitro-1,3-butadiene **IVa**. The Authors carried out a synthesis of nitrodiene **IVa** in three stepped process (**Scheme 23**) including condensation reaction between glyoxal (**38**) and dinitromethane (**56**), esterification of obtained alcohol **57** and thermal decomposition of 1,1,4,4-tetranitrobutane-2,3-diol diacetate (**58**), in an analogous way to synthesis of 1,4-dinitro-1,3-butadiene **II** (**Scheme 16**). The deacetylation product **IVa** is generated *in situ* using an alkaline environment (**Scheme 23**). The same Authors[72] described that non-stabilised nitrodiene **IVa** can be used to obtain bis-adducts **59-61** in a nucleophilic addition (**Scheme 23**). The reaction took place in the presence of a bases such as OH^-, MeO^- or aniline.



Scheme 23. Synthesis of 1,1,4,4-tetranitro-1,3-butadiene **IVa** and its application in nucleophilic additions.

In 1955 *Schlubach and Rott*[76] explored the possibility of obtaining another symmetric tetranitrodiene analogue, namely 1,2,3,4-tetranitro-1,3-butadiene **IVb**. The authors reported a reaction of butadiyne (**62**) with dinitrogen tetroxide. Unfortunately, the synthesis was unsuccessful. The reaction was accompanied by explosions. The only product which could then be isolated was oxalic acid (**63**) (**Scheme 24**).



Scheme 24. Nitration of butadiyne (**62**) using dinitrogen tetroxide.

4. Working with a nitro compound - hazards and safety principle

Undoubtedly, nitrodienes as well as other nitro compounds are a valuable and useful component commonly used in modern organic chemistry. It should be underlined that most extensively applied explosives are nitro compounds exactly due to the presence of $-NO_2$ fragment.[77] Pure organic nitro compounds such as aromatic or aliphatic nitro compounds pose a real threat to health and safety. It is related with the possibility of these compounds to decompose at high temperatures and their decomposition's large exothermic effect. In most cases, the decomposition is violent or explosive.[78]

It is well known that organic nitrogen-containing compounds are explosive.[79] Particular attention should be paid to the fact that organic compounds containing additional oxygen atoms present a unique hazard.[80] **Table 4** includes a percentage content of nitrogen in nitrobutadiene depending on number of nitro groups contained in the molecule.

Table 4. Contents of nitrogen in nitrobutadiene depending on number of nitro groups present in the molecule.

$C_4H_5NO_2$	$C_4H_4(NO_2)_2$	$C_4H_3(NO_2)_3$	$C_4H_2(NO_2)_4$	$C_4H(NO_2)_5$	$C_4(NO_2)_6$
$\%_N$ = 14.1 %	$\%_N$ = 19.4 %	$\%_N$ = 22.2%	$\%_N$ = 23.9 %	**$\%_N$ = 25.1 %**	**$\%_N$ = 25.9 %**
three compounds avaliable	one compound avaliable	**absence**	one compound avaliable	**absence**	**absence**

It can be assumed that in nitro compounds used in the laboratory, the nitrogen content should not exceed 25.0 %.[78] Therefore, based on the information in **Table 4** it can be concluded that penta and hexa substituted analogues of 1,3-butadiene are extremely hard and hazardous to obtain from both synthetic and storage point of view. This may explain why there is no mention of these compounds in the literature. In turn, as shown in **Table 4**, working with 1,1,4,4-tetranitro-1,3-butadiene **IVa** is extremely dangerous,[72] while attempts to obtain 1,2,3,4-tetranitro-1,3-butadiene **IVb** failed, due to an explosion of reaction mixture.[76]

5. Conclusions and future perspective

The present review comprehensively summarizes information about physicochemical properties, synthesis methods, chemical transformations and biological activity of nitro-functionalised analogues of 1,3-butadiene. These compounds have attracted a growing interest in recent years because some of them are promising candidates regarding biological activity, as well as because of their recognized importance as reaction intermediates in the preparation of polyfunctionalized products. Thanks to presented review, it is possible to identify scientific gaps that create potential research topics in future.

In general, for all 35 possible combinations of nitro-functionalised analogues of 1,3-butadiene only 5 are described in literature. This provides an opportunity to further explore this class of organic compounds. What is interesting, for nitro-functionalised 1,3-butadiene analogues including two and four nitro groups are represented only by symmetrical molecules. In turn 1,3-butadiene analogues that include three nitro groups are not known at all. The phenomenon can be due to the lack of possibility of such a connection in the form of asymmetrical relationship. Due to the explosive properties, the increasing content of nitrogen in the molecule and, additionally, the presence of oxygen, 1,3-butadiene analogues with five and six nitro groups are practically impossible to achieve.

1,4-dinitrobuta-1,3-diene was found to be active against *Staphylococcus aureus* and *Aspergillus niger*. What is more, the compound prevented bean rust infection in plants. Unfortunately in the literature none tests of toxicity of nitrodienes were identified, so possibility of application in agriculture uncertain.

In order to obtain nitro-functionalised analogues of 1,3-butadiene two main methods are used. The first synthesis method includes the direct nitration of butadiene derivatives by different nitrating agents such as nitrogen oxides, also in combination with halogens. The second synthesis method is the multistep process containing the synthesis of nitro derivatives of esters, and then, the elimination of small molecules such as hydrogen halides, acetic acid and others via thermal decomposition process.

Reactions undergone by nitro-functionalised analogues of 1,3-butadiene are mainly limited to nucleophilic additions and substitutions with thiols and amines as well as, less numerous examples of electrophilic additions of halogens, especially bromine. The synthesis of heterocyclic organic compounds using this class of organic compounds is still not strongly developed. In the literature only several examples of application nitro-functionalised analogues of 1,3-butadiene in a cycloaddition reaction are described. The main limitations of employment of these compounds include small yields for processes as well as problems with polymerization of titled compounds. In the future the application of nitro-functionalised analogues of 1,3-butadiene as building blocks for heterocyclic chemistry can be a promising direction of development.

This work confirms that heterocycle chemistry is one of the most developing branches of science due to its various applications as reported before.

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