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N-ARYL-*C*-NITROAZOLES
1. *C*-NITRO-*N*-PHENYLAZOLES
(REVIEW)

Several synthetic approaches to differently substituted nitroazoles and their applications have been described in literature. Recently, some *N*-aryl-*C*-nitroazoles proved to be promising antibacterial, antiprotozoal agents, as well as explosives. However, their synthesis and applications are not well developed. Syntheses of *N*-aryl-*C*-nitroazoles are reviewed here for the first time. Part 1 is devoted to synthesis of *C*-nitro-*N*-phenylazoles treated in this review as parent compounds. Procedures of selected compounds have been given and their properties verified. Part 2 will contain related information on the derivatives containing additional substituents in one or both aromatic rings. In Part 3, *N*-aryl group in *C*-nitroazoles will be replaced by *N*-heteroaryl substituent. Non-aromatic compounds and nitroazoles containing ring heteroatom other than nitrogen will not be included in the review.

Keywords: nitroazole, nitration, phenylation.

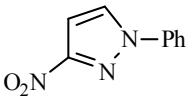
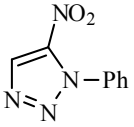
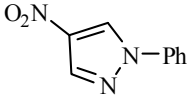
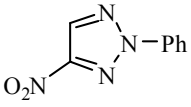
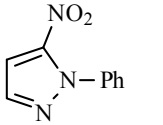
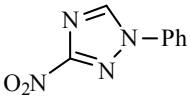
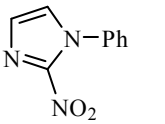
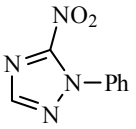
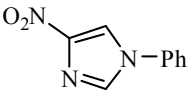
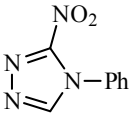
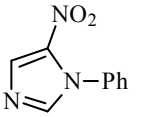
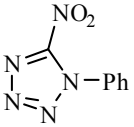
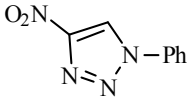
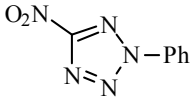
N-Aryl-*C*-nitroazoles described in this review include derivatives of five-membered heterocyclic rings containing two, three, or four nitrogen atoms with an aryl substituent at one of them. Names and structures of all possible fourteen *C*-nitro-*N*-phenylazoles **1**–**14** are collected in Table 1. The compounds belong to five groups of azoles: pyrazoles (1,2-diazoles **1**–**3**), imidazoles (1,3-diazoles **4**–**6**), 1,2,3-triazoles **7**–**9**, 1,2,4-triazoles **10**–**12** and 1,2,3,4-tetrazoles **13**, **14**. Compounds **13**, **14**, without additional substituents, have not been prepared yet. Compounds **1**–**14** will be treated here as the parent structures, and, as a consequence, other *N*-aryl-*C*-nitroazoles will be treated as their derivatives. Material in each sub-chapter on synthetic methods applied to preparation of the nitroazoles is presented depending on a type of azole in the same order as in Table 1.

Several synthetic approaches towards differently substituted nitroazoles have been described in literature. However, synthesis of *N*-aryl-*C*-nitroazoles and particularly parent *C*-nitro-*N*-phenyl compounds are not well developed. To our knowledge no review on this topic has been published yet. The very recent book by Larina and Lopyrev [1] on nitroazoles (their synthesis, structure and applications) and chapters on diazoles [2, 3] and triazoles [4, 5] in *Comprehensive Heterocyclic Chemistry III* have hardly mentioned *N*-aryl-*C*-nitroazoles. Even a specific review on synthetic nitroimidazoles published recently by Mital [6] has only shortly described antibacterial activity of some 1-aryl-4-nitroimidazoles not mentioning their synthesis. Synthesis and properties of nitro-1,2,3-triazoles were reviewed by Vereschagin, Pokatilov, and Kizhnyaev [7]. In contrast to other reviews this paper brought some substantial information on synthesis of *N*-aryl-1,2,3-triazoles. Older books and reviews written by Grimmett [8], Boyer [9], Kanishchev *et al.* [10], or

* Здесь и далее в номере фамилия автора, с которым следует вести переписку, отмечена звёздочкой.

Table 1

Names and structures of *C*-nitro-*N*-phenylazoles 1–14

Compound	Name	Structure	Compound	Name	Structure
1	3-Nitro-1-phenyl-1*H*-pyrazole		**8**	5-Nitro-1-phenyl-1*H*-1,2,3-triazole	
2	4-Nitro-1-phenyl-1*H*-pyrazole		**9**	4-Nitro-2-phenyl-2*H*-1,2,3-triazole	
3	5-Nitro-1-phenyl-1*H*-pyrazole		**10**	3-Nitro-1-phenyl-1*H*-1,2,4-triazole	
4	2-Nitro-1-phenyl-1*H*-imidazole		**11**	5-Nitro-1-phenyl-1*H*-1,2,4-triazole	
5	4-Nitro-1-phenyl-1*H*-imidazole		**12**	3-Nitro-4-phenyl-4*H*-1,2,4-triazole	
6	5-Nitro-1-phenyl-1*H*-imidazole		**13**	5-Nitro-1-phenyl-1*H*-tetrazole	
7	4-Nitro-1-phenyl-1*H*-1,2,3-triazole		**14**	5-Nitro-2-phenyl-2*H*-tetrazole	

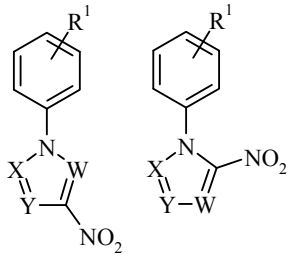
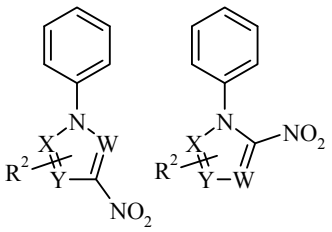
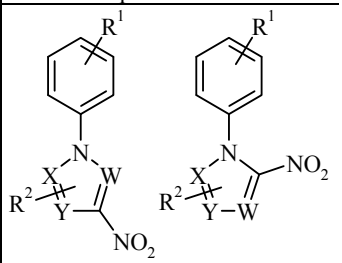
Adams and Box [11], brought either very little or no information on synthesis of *N*-aryl-*C*-nitroazoles. Several papers and patents concerned with syntheses and properties particularly of *C*-nitro-*N*-phenylazoles were published years ago, and the results reported there are uncertain. Very recently Chertkov, Shestakova and Davydow [12] have described regioselective *N*-arylation of a series of nitroazoles with diaryliodonium salts trying to correct some older reports.

In the framework of this review we decided to present in Part 1 information on *C*-nitro-*N*-phenylazoles **1**–**14** only and then in Part 2 on derivatives of these compounds bearing additional substituents on benzene **1**–**14 A**, azole **1**–**14 B** or on both rings **1**–**14 C** (Table 2). The information concerning synthesis of the derivatives presented in Part 2 will be classified according to the methods of their preparation being either modifications of an approach described for the parent compounds **1**–**10** or their transformations to the derivatives.

There exist several different synthetic routes to *N*-aryl-*C*-nitroazoles. These compounds can be obtained by nitration, ring closure, intramolecular rearrangements of cyclic molecules, transformation of functional groups, or by the introduction of an aryl substituent at the ring nitrogen atom in nitroazole. Depending on the starting materials, available reagents, and conditions one or another of the above methods can be applied for the required synthesis.

Table 2

Structures of six types of *N*-aryl-*C*-nitroazoles

Compounds **1**–**14 A**	Compounds **1**–**14 B**	Compounds **1**–**14 C**
		
W, X, Y = CH or N, but at least one is N	W, X, Y = CH or N, but at least one is N	W, X, Y = CH or N, but at least one is N

R^1, R^2 = one or more substituents of any kind

The simplest, but in general not selective approach is nitration. Conditions and the nature of the employed reagents significantly influence the structures of the final products. Though nitration enables syntheses of *C*-nitroderivatives of *N*-phenyl pyrazoles, imidazoles, 1,2,3-triazoles, and 1,2,4-triazoles, products usually contain two or more nitro groups. The nitro group is usually introduced into benzene ring first. Therefore, alternative approaches to some of compounds **1**–**14** have been developed, but the need for new methods still exists.

Research on functional group transformations revealed that these methods can be successfully applied for obtaining most of the nitroazoles. Examples include such processes as oxidation or Sandmeyer reaction of aminoazoles, as well as indirect nitration of the parent compounds through *C*-lithium or *C*-bromo derivatives. Investigations of other methodologies allowed a development of ring closure or transformation reactions as alternatives. The former approach besides the intramolecular cyclization spreads also over to two-step reactions leading to building of azole ring. For a long time direct *N*-arylation of nitroazole salts has been generally limited to compounds containing strong electron-withdrawing substituents on benzene ring. This situation has partly changed with publication by Chertkov, Shestakova and Davydow [12].

Nitroazoles are compounds of many applications. Some of them are used as antiprotozoal agents in human and veterinary medicine [13], as hypoxic cell sensitizers in radiation therapy of cancer (e. g. 2-nitroimidazoles) [14], as antiphlogistic medicines [15], they are applied in agrochemicals as plant growth regulators [16]. Their properties make them useful in preparation of many materials and therefore these compounds are versatile intermediates in organic synthesis (e. g. 4(5)-nitroimidazole) [17]. Some nitroazoles are used as propellants and explosive materials (tetrazoles, picrylamino- and nitro-substituted pyrazoles) [18–21]. What is more, they exhibit good heat resistance and, therefore, can be used in space programs and deep oil-well drilling [22].

Most of known nitroazoles of practical use contain *N*-alkyl substituent. *N*-Aryl-*C*-nitroazoles are much less common. Nevertheless, they increasingly generate interest, e. g., as candidates for new effective antimicrobial drugs [23]. The nitro group of these compounds undergoes reduction in several cases. The reduction plays particularly important role in pharmaceutical applications. Reduction potentials of parent *C*-nitro-*N*-phenylazoles **1**–**14** should depend on the type of the azole ring and the positions of the nitro as well as phenyl substituents. The

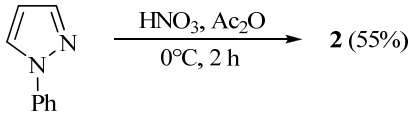
reduction potentials should be greatly affected by the presence of strong electron withdrawing or electron donating substituents in derivatives **1**–**14 A**–**C**. These effects of substituents in benzene ring of *N*-aryl-*C*-nitroazoles are expected to be much stronger in comparison with effects of substituents in *N*-alkyl chains of similar *C*-nitroazoles.

Syntheses of *C*-nitro-*N*-phenylazoles by nitration

Direct nitration of *N*-phenylazoles

Among nitrating agents, known in the literature, many have been investigated for the purpose of nitration of azoles. The list includes, e. g., mixed nitric and sulfuric acids, acetic anhydride and nitric acid, nitronium tetrafluoroborate. Because of differences in structures and consequently in the chemical properties of particular azoles, each group of the compounds exhibits a specific behavior during the nitration.

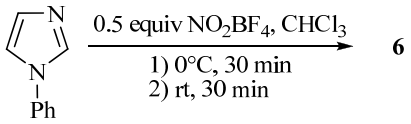
Nitration of the unsubstituted pyrazole ring takes place at C-4 position. However, introduction of *N*-phenyl substituent results in differentiation of products of nitration depending on the reaction conditions [22, 23]. The choice of conditions and consequently a form of starting compound, i. e., neutral or protonated one, seems to be the key for obtaining selectively substituted 4-nitro-1-phenylpyrazole derivative [24, 25]. The nature of the nitrating agent used and orientation of the substitution is related. When mixed acids are used the nitration takes place in the benzene ring to give 94% of 1-(4-nitrophenyl)pyrazole, while with nitric acid in acetic anhydride at low temperature the substitution occurs in the heterocyclic ring yielding 4-nitro-1-phenyl-1*H*-pyrazole (**2**) in 55% yield [26, 27]. Nitronium tetrafluoroborate in tetramethylene sulfone allows introducing nitro group into pyrazole ring too [25]. Kinetics of 1-phenylpyrazole nitration was studied in details [28].



Neither 3- nor 5-nitro derivatives **1** or **3** were obtained by direct nitration of 1-phenylpyrazole.

Khan, Lynch and Hung [24] gave a possible explanation of the differences in the substitution pattern based on the fact that bromination of 1-phenylpyrazole in inert solvent leads to substitution at C-4 position in heterocyclic ring while nitration of the compound with mixed acids resulted in substitution in benzene ring. The conjugate acid of 1-phenylpyrazole formed in this way contains deactivated pyrazole ring, which does not undergo electrophilic substitution. Therefore, the substitution takes place at *para*-position of phenyl ring. However, in acetyl nitrate, pyrazole is involved in nitration as the free base and the substitution in this ring occurs [24, 26]. The described mechanism of nitration with acetyl nitrate, which can be obtained from nitric acid (70%) and an excess of acetic anhydride [29], according to a proposal from 1964 year involves two major steps. The nucleophilic nitrogen atom N-2 of pyrazole ring attacks electron-deficient carbon atom of protonated acetyl nitrate, and subsequent electron shifts in the intermediate lead to 4-nitropyrazole formation [25]. Such mechanism should be treated as uncertain, but newer proposals have not been published yet.

Nitration of imidazole itself proceeds with introduction of nitro group in the C-4 or C-5 positions [30]. However, when phenyl substituent is present on the azole ring, the reaction with standard acidic nitrating agents occurs on phenyl substituent at first and then, if forcing conditions are applied, on imidazole ring too [31]. The only described example of direct nitro group introduction exclusively on imidazole ring in 1-phenylimidazole, without preceding or simultaneous nitration of phenyl substituent, was nitration of 1-phenylimidazole with insufficiency of nitronium tetrafluoroborate in chloroform at room temperature, patented forty years ago [32]. According to the authors of this patent nitro group enters the position 5 of imidazole ring, affording nitroimidazole **6**. Yield of the product is not given. Other papers or patents have not confirmed that result. Thus, the position of nitro group and, therefore, the structure of product seem doubtful.

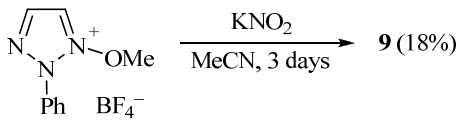


The presence of three nitrogen atoms in five-membered azole ring strongly reduces its susceptibility to electrophilic substitution, and, therefore, triazole rings cannot be nitrated if no activating substituent is present in the starting material.

All attempts of selective nitration of the azole ring in *N*-aryl-1,2,3-triazoles failed. 1-Phenyl-1,2,3-triazole is nitrated in the position 4 of benzene ring. The same concerns 2-phenyl-1,2,3-triazole, even when the reaction is carried out at temperatures below 20°C [33]. Remaining *C*-nitro-*N*-phenyltriazoles **7**, **8** and **10**–**12** as well as *C*-nitro-*N*-phenyltetrazoles **13**, **14** have not been prepared by nitration of *N*-phenyltriazoles.

Indirect nitration of *N*-phenylazoles

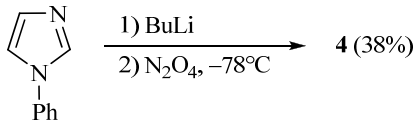
Since nitration of 2-phenyl-1,2,3-triazole exclusively leads to products substituted at benzene ring, Begtrup and Holm [34] described an alternative way of introduction of nitro group to 1,2,3-triazole ring. The method is based on activation of the azole ring by *N*-oxide or *N*-methoxy grouping. Because all attempts of oxidations of 2-phenyl-1,2,3-triazole with a series of different oxidizing agents (peracetic acid, *meta*-chloroperbenzoic acid, dichloropermaleic acid, trifluoroperacetic acid, peroxydisulfuric acid, *t*-pentyl hydrogen peroxide) failed, 2-aryl-1,2,3-triazole-1-oxides were prepared through oxidative cyclization of *vic*-arylhydrazone oximes. *N*-Oxides subjected to alkylation with trimethyloxonium tetrafluoroborate resulted in *N*-methoxytriazolium salts, which have a strongly electrophilic carbon atom at the position 5 of the ring. Then the introduction of nitro group into the activated position is possible by the nucleophilic addition of nitrite ion and subsequent elimination of methanol to afford 4-nitro-2-phenyl-2*H*-1,2,3-triazole (**9**) [34, 35]. Besides compound **9** (18%) also 4-hydroxy-2-phenyltriazole (1%), 4-hydroxy-5-nitro-2-phenyltriazole (32%) and 2-phenyltriazole-1-oxide (11%) were obtained as side-products from the reaction.



Introduction of nitro group through lithium derivatives of *N*-phenylazoles

The lithiation can be a convenient way of introduction of several substituents into heterocyclic rings. The first step of indirect nitration includes introduction of lithium atom into a molecule of azole and then subsequent substitution of lithium with nitro group. The literature describes a series of lithiating agents used: lower alkyllithium (e. g. methyllithium, ethyllithium) or aryllithium (e. g. phenyllithium); the choice of the lithiating reagent seems not to influence the reaction [36]. A list of nitrating agents used in the second step of the process includes nitrogen tetraoxide, nitronium tetrafluoroborate, *n*-propyl nitrate and tetranitromethane [14]. From among *C*-nitro-*N*-phenylazoles **1**–**14** only 2-nitro-1-phenyl-1*H*-imidazole (**4**) was obtained *via* this method until now.

The reaction of 1-phenylimidazole with butyllithium followed by treatment of the obtained lithiated derivative with N_2O_4 gave 2-nitro-1-phenyl-1*H*-imidazole (**4**) in 38% yield [37].



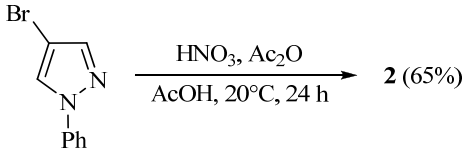
The reactions of 2-lithium derivatives of 1-triphenylmethylimidazole or 4-methyl-1-triphenylmethylimidazole with *n*-propyl nitrate as a source of nitro group have also been reported to afford moderate yields of the expected products [14].

Lithiation of 1-phenyl-1,2,3-triazole with *n*-butyllithium preferentially occurs at the C-5 position [38]. Therefore, this method would be suitable for synthesis of 5--nitroderivative **7**. Unfortunately, nitrotriazole **7** has not been prepared according to this approach yet.

ipso-Nitration of *C*-bromo-*N*-phenylazoles

ipso-Nitration is a substitutive nitration, where the displacement of an atom or a functional group other than hydrogen or metal atom by nitro group takes place. Among *C*-nitro-*N*-phenylazoles only 4-nitro-1-phenyl-1*H*-pyrazole (**2**) was obtained by this method.

Results of 4-bromo-1-phenylpyrazole nitration depend on the nitrating agents used. When the reaction was carried out with mixed acids 4-bromo-1-(4-nitrophenyl)derivative was obtained. On the other hand, in acetic anhydride and nitric acid the *ipso*-nitration has occurred giving 4-nitro-1-phenyl-1*H*-pyrazole (**2**) in 65% yield [39].

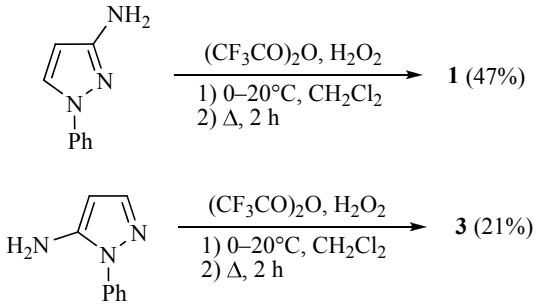


Besides compound **2** the reaction produced also a mixture of bromo, dibromo and dinitro products [39].

Syntheses by oxidation of aminoazoles

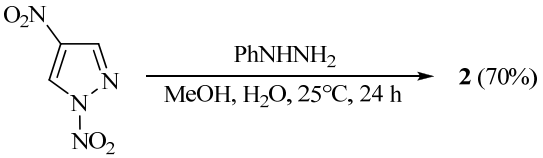
Some reports describe oxidation of aminoazoles leading to nitroazoles. The suitable oxidizing agent used for this purpose is anhydrous peroxytrifluoroacetic acid. Stabilization of the molecule by the presence of *N*-phenyl substituent allows oxidation of the amino group without cleavage of the azole ring. Lancini *et al.* investigated microbial oxidation of aminoimidazoles to nitro derivatives. The *Streptomyces* strain can oxidize series of 2-aminoimidazoles substituted with lower alkyl at 4 and 5 positions. However, when methyl or phenyl group was present on the ring no transformation occurred [40].

3-Amino-1-phenylpyrazole and 5-amino-1-phenylpyrazole treated with peroxytrifluoroacetic acid, generated *in situ* from trifluoroacetic anhydride and hydrogen peroxide, gave the corresponding 3-nitropyrazole **1** and 5-nitropyrazole **3** derivatives, while 3-aminopyrazole underwent degradation when subjected to the reaction conditions [41].

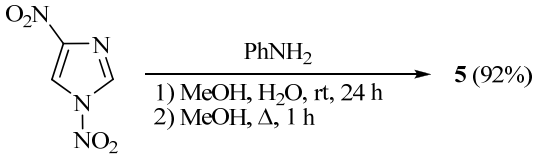


Syntheses from other *C*-nitro-*N*-substituted azoles by the degenerated ring transformation reactions

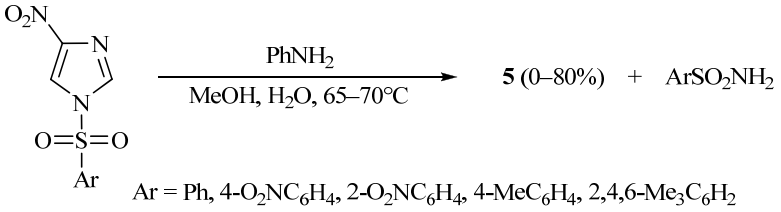
Because of some limitations of the previously described methods of synthesis of *N*-aryl-*C*-nitroazoles, e. g., nitration of 1-arylazoles usually led to substitution at benzene ring as carbon atoms in azole rings are less susceptible to electrophiles, alternative ways have been searched. Attention of the chemists, focused so far on the introduction of nitro group into arylazoles, was later attracted by the methods of introduction of aryl ring onto already nitrated azole molecule. Successful methods of *C*-nitro-*N*-phenylazole synthesis were reactions involving degenerated ring transformations. Syntheses described below in this sub-chapter occur according to so called ANRORC (Addition of the Nucleophile, Ring Opening, and Ring Closure) mechanism. Mechanisms of the described here ANRORC reactions have been published elsewhere in details [42]. Until now, from among *C*-nitro-*N*-phenylazoles only compounds **2** and **5** have been obtained according to this approach. 1,4-Dinitropyrazole (prepared by nitration of pyrazole with an excess of trifluoroacetyl nitrate in trifluoroacetic acid) reacts with phenylhydrazine under mild conditions to afford 4-nitro-1-phenyl-1*H*-pyrazole (**2**) in 70% yield [43].



1,4-Dinitroimidazole (prepared by nitration of 4(5)-nitroimidazole with acetyl nitrate in acetic acid) treated with aniline in aqueous methanol at room temperature afforded 4-nitro-1-phenyl-1*H*-imidazole (**5**) in high yield [44–47]. Nitrogen monooxide and water are formed as side products. The so called "atom economy" of this reaction, describing the conversion efficiency of a chemical process in terms of all atoms involved, exceeds 80% [44].



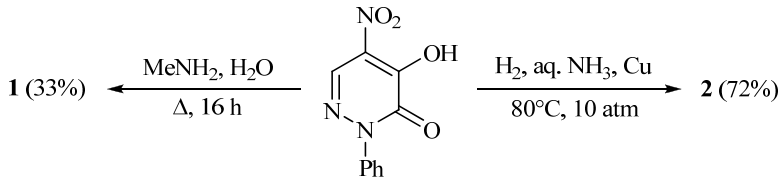
Also 1-arenesulphonyl-4-nitroimidazoles (obtained from 4(5)-nitroimidazole in reaction with arenesulfonyl chloride and triethylamine) can be used as starting materials in similar syntheses of 4-nitro-1-phenyl-1*H*-imidazole (**5**) [46, 47].



1-Arenesulphonyl-4-nitroimidazoles when treated with aniline at 25°C give colored azolide–aniline adducts (1:1), which heated to 65–70°C in aqueous methanol (1:1), undergo transformation leading to mixtures of products, where besides of product **5** (80% yield from 4-nitro-1-(2-nitrobenzenesulfonyl)imidazole) and 4(5)-nitroimidazole respective arenesulfonanilides, arenesulfonamides were present [46, 47]. Results of the reaction with aniline depend on a kind of arene-sulfonyl substituent and a solvent, e. g. 4-nitro-1-(2-nitrobenzenesulfonyl)imidazole afforded product **5** in 80% yield, 4-nitro-1-(*p*-toluenesulfonyl)imidazole in aqueous methanol gave imidazole **5** in 45% yield while a similar reaction carried out in pyridine led to 4(5)-nitroimidazole as a main product [47].

Syntheses by ring transformation reactions

Contractions of the pyridazine ring can be brought about by the action of mineral acids and alkalis [48]. The formation of 3-nitro-1-phenylpyrazole (**1**) in 33% yield (together with similar amounts of 5-methylamino-4-nitro-1-phenyl-pyridazin-6-one) by heating 5-hydroxy-4-nitro-1-phenylpyridazin-6-one with aqueous solution of methylamine is an example of such ring contraction [49].



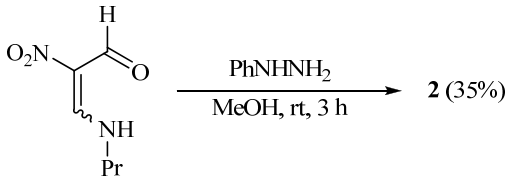
5-Hydroxy-4-nitro-1-phenylpyridazin-6-one also reacts with hydrogen and concentrated aqueous ammonia at 80°C under pressure of 10 atm in the presence of copper powder to afford 4-nitro-1-phenyl-1*H*-pyrazole (**2**) in 72% yield [50].

Syntheses by azole ring closure

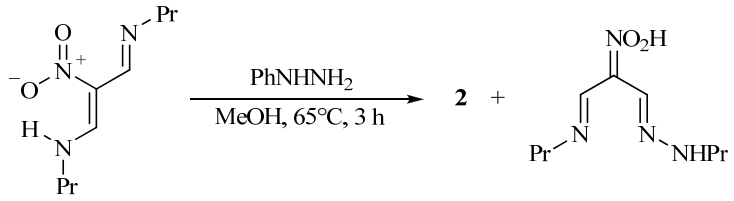
Reactions involving azole ring closure are of wide potential possibilities in *N*-aryl-*C*-nitroazoles synthesis. Such reactions include building azole rings from different starting reagents.

Nitromalonaldehyde found applications in the synthesis of nitroheterocyclic compounds already several years ago [51]. However, its use is limited due to instability, and, therefore, synthetic equivalents have been sought. One of them, currently used, is sodium salt of nitromalonaldehyde [31]. But the limitations still exist. Reactions carried out with salt require aqueous media or highly polar solvents, which often causes difficulties. Since, in addition, sodium salt of nitromalonaldehyde is explosive and difficult to handle other equivalents have been found to replace it [52, 53].

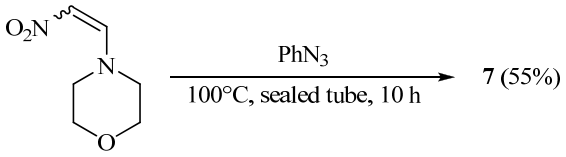
Nitroformylenamine (3-propylamino-2-nitropropenal) in methanol stirred with phenylhydrazine at room temperature for 3 h gave 4-nitro-1-phenyl-1*H*-pyrazole (**2**) in 35% yield. The starting β-nitroenamine can be regarded as an equivalent of nitromalonaldehyde being soluble in organic media and more safe [52, 53].



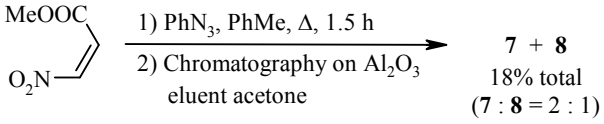
Also 4,8-diaza-6-*aci*-nitroundeca-4,7-diene can be used directly for synthesis of 4-nitro-1-phenyl-1*H*-pyrazole (**2**) without its conversion through the hydrolysis of an imino group into formylated nitroenamine. The reaction with hydrazines, carried out in organic media, gives the desired heterocycle [52].



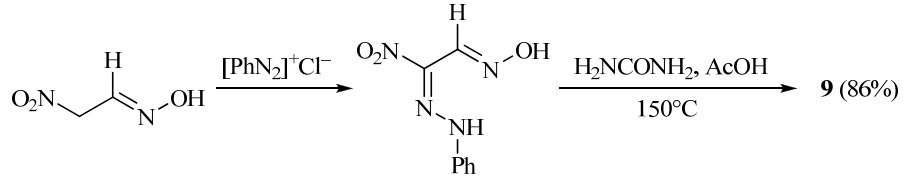
Another convenient ring closure method for azole synthesis involves 1,3-dipolar cycloaddition of 2-morpholino-1-nitroethene with aryl azides. The process, when carried out with phenyl azide, gives 4-nitro-1-phenyl-1*H*-1,2,3-triazole (**7**) [54–56].



Other unsaturated compounds, like alkyl 3-nitroacrylates, can be applied for a similar synthesis of nitrotriazoles. 3-Nitroacrylates treated with phenyl azide give 1,2,3-triazole carboxylic acid esters, which subsequently hydrolyzed afford 4-nitro-1-phenyl-1*H*-1,2,3-triazole (**7**) and 5-nitro-1-phenyl-1*H*-1,2,3-triazole (**8**) [57, 15].



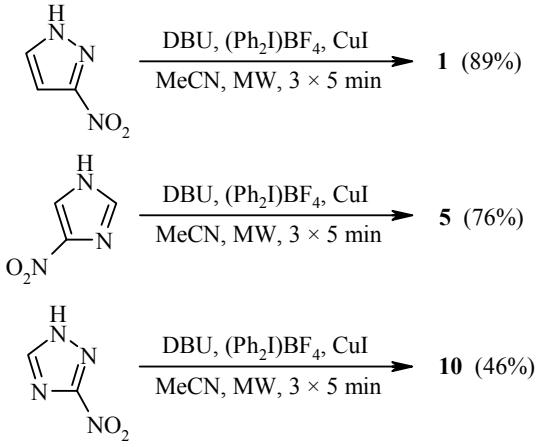
A preparation of 2-aryl-4-nitro-1,2,3-triazoles using nitroglyoxal oxime arylhydrazones as starting materials has been described. The latter compounds were obtained as a result of condensation of aryl hydrazones with α-oximinoketones, followed by acylation. The azole ring closure occurred in urea melt environment (100–210°C) leading to formation of the desired products. 4-Nitro-2-phenyl-2*H*-1,2,3-triazole (**9**) was prepared in 86% yield [58].



An alternative way of carrying out the process has also been reported. The starting α-oximinoarylhydrazones were reacted with isocyanate or carbamic acid halide, or with pyrocarbonic acid ester, preferentially in the presence of a solvent. Sometimes addition of a base catalyst (e. g. alkali metal halides, carbonates, pyridine, quinoline, dimethylaniline, 0.05–0.10% by weight) was suggested. The modifications provide the advantage of no urea waste produced. In addition, lower temperatures are used: 60–80°C for the reaction with isocyanate and 30–40°C for pyrocarbonic acid esters [58].

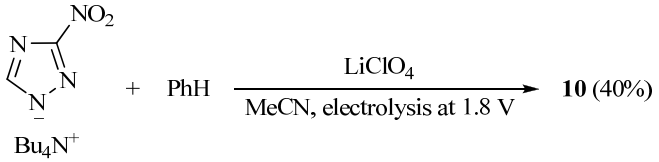
Syntheses by direct *N*-phenylation of nitroazole salts

N-arylation of a series of nitroazoles has been studied with the aid of diaryliodonium salts in the presence of CuI under the action of microwave radiation. It was found that alkylation proceeds regioselectively with the formation of one of two possible isomers. Among others, three *C*-nitro-*N*-phenylazoles, namely compounds **1**, **5** and **10**, have been prepared by this method [12].



Another synthetic route to *N*-aryl-*C*-nitroazoles involves electrochemical processes. Such method was applied to direct *N*-phenylation of a series of nitroazoles and led to formation of respective *C*-nitro-*N*-phenylazoles. It has been described that

3-nitro-1,2,4-triazole tetrabutylammonium salt and benzene in acetonitrile containing $LiClO_4$ during electrolysis at 1.8 V in an undivided cell equipped with platinum electrodes yielded mixture of 3-nitro-1-phenyl-1*H*-1,2,4-triazole (**10**) (18%) together with small amounts of 5-nitro-1-phenyl-1*H*-1,2,4-triazole (**11**) and 3-nitro-4-phenyl-4*H*-1,2,4-triazole (**12**). A higher yield of compound **10** (up to 40%) was obtained when the nitrotriazole itself was added to the reaction mixture [59, 60].



A similar process of *N*-phenylation of 3-nitro-1,2,4-triazole was observed when, instead of carrying the reaction electrolytically, difluoroxenon was used to oxidize 3-nitro-1,2,4-triazole anion to the respective radical [61]. Yield of 3(5)-nitrotriazole and 3-nitro-1-phenyl-1*H*-1,2,4-triazole (**10**) together was ca. 70%; while the ratio of the compounds was 3:2 as measured by integration of H-5 proton signals (9.35 and 8.85 ppm, respectively) in ^{1}H NMR spectrum of the reaction mixture.

Syntheses by other methods

4-Nitro-1-phenyl-1*H*-pyrazole (**2**) was obtained from 4-nitro-1-(4-nitrophenyl)-pyrazole by a selective reduction with ammonium hydrogen sulfide of the nitro group at phenyl. In this way 1-(4-aminophenyl)-4-nitropyrazole was obtained. Its subsequent deamination afforded the desired nitropyrazole **2** [62].

Probably a similar approach could be used for other *C*-nitro-*N*-phenylazoles preparation, but it has not been reported yet.

Selected synthetic procedures for the preparation of *C*-nitro-*N*-phenylazoles

3-Nitro-1-phenyl-1*H*-pyrazole (1).

Warning! Two different melting points are reported; in our experiment, *N*-phenylation of 3(5)-nitropyrazole leads to a product with mp 98–99°C like in [39], and it is characterized by NMR spectra very similar to those shown in [12].

A. Trifluoroacetic anhydride (34 ml, 0.24 mol) is added dropwise with stirring to slurry of 90% H_2O_2 (5.4 ml, 0.20 mol) in CH_2Cl_2 (100 ml) at 0–10°C. After the addition is completed, the solution is allowed to warm to 20°C and a solution of 3-amino-1-phenylpyrazole (4.77 g, 0.03 mol) in CH_2Cl_2 (25 ml) is added dropwise. During the addition the exothermic reaction causes the solution to reflux. The solution is refluxed 2 h after the addition, cooled, and extracted first with water (2 × 100 ml), then with aqueous sodium bicarbonate (100 ml). The solution is dried over $MgSO_4$ and evaporated to dryness under reduced pressure. The residue is crystallized from EtOH–H_2O. Yield 2.68 g (47%). Mp 98–99°C. No other details given [41].

B. Into the vessel containing absolute MeCN (10 ml), 3-nitropyrazole (0.11 g, 1 mmol), DBU (0.15 g, 1 mmol), and diaryl iodonium salt (1 mmol) are added with stirring. After solution of the components of the mixture, CuI is added (0.04 g, 20 mol %). The vessel is sealed and left in the microwave oven, the reaction mixture is irradiated 3–4 times for 5 min each time with intermediate cooling of the reactor to room temperature with stirring. The end of the reaction is checked by TLC and visually (the color of the reaction mixture stopped changing). After this the solvent is distilled in vacuum, the residue treated with hot CCl_4, and passed through a layer of alkaline Al_2O_3 to remove residues of ArI and MeCN. Product is isolated by flash chromatography, using EtOAc as eluent. The eluate is evaporated and the residue recrystallized from aq. MeOH. Yield 0.17 g (89%). Mp 127°C.

^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.10 (1H, d, ^3J = 2.6, H-4); 7.43 (1H, m, H-4 Ph); 7.52 (2H, m, H-3,5 Ph); 7.75 (2H, m, H-2,6 Ph); 7.98 (1H, d, ^3J = 2.6, H-5). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 104.3 (C-4, $^1J_{C\text{-}4,H\text{-}4}$ = 188.0, $^2J_{C\text{-}4,H\text{-}5}$ = 8.4); 120.1 (C-2,6 Ph); 128.7 (C-4 Ph); 129.5 (C-5, $^1J_{C\text{-}5,H\text{-}5}$ = 192.0, $^2J_{C\text{-}5,H\text{-}4}$ = 8.2); 129.8 (C-3,5 Ph); 138.9 (C-*ipso*, $^4J_{C\text{-}ipso,H\text{-}4}$ ~1.0, $^3J_{C\text{-}ipso,H\text{-}5}$ ~1.0); 157.1 (C-3, $^2J_{C\text{-}3,H\text{-}4}$ = 2.0, $^3J_{C\text{-}3,H\text{-}5}$ = 10.2). Mass spectrum, *m/z* (I_{rel}, %): 189 $[M]^+$ (100), 142 $[M–HNO_2]^+$ (21), 77 [Ph] (60). [12]. Mp 126–128 °C for compound **1** is also reported in [49] where it is obtained as a by-product.

4-Nitro-1-phenyl-1*H*-pyrazole (2).

A. 4-Bromo-1-phenylpyrazole (1.00 g, 0.004 mol) dissolved in glacial AcOH (72.8 ml) and cooled to 0°C, is treated with a chilled mixture of fuming HNO_3 (17.0 ml) and Ac_2O (72.8 ml). After standing overnight at 20°C, the mixture is poured onto ice, neutralized with Na_2CO_3 and extracted with Et_2O. The obtained oil contains a number of products. A column chromatography on alumina with benzene gives desired 4-nitro-1-phenylpyrazole. Yield 0.49 g (65%). Mp 126–128°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.65 (1H, s); 8.26 (1H, s); 7.62 (5H, m). Mass spectrum, *m/z*: 189 $[M]^+$ [39].

B. A solution of fuming HNO_3 (1.5 ml) in Ac_2O (4.0 ml), prepared at 15–20°C, is cooled to –5°C and added to solution of 1-phenylpyrazole (3.0 g) in Ac_2O (6 ml) at –5°C in a period of 30 min. The reaction mixture is allowed to reach room temperature, and then poured onto ice. The precipitate is collected and recrystallized from EtOH, yielding 4-nitro-1-phenyl-1*H*-pyrazole (**2**). Yield 2.1 g (53%). Mp 125–127 °C. The reactions on a larger scale generally gives lower yields, although unchanged 1-phenylpyrazole is recovered. IR spectrum (KCl), ν, cm^{-1}, 690, 751, 770, 820, 950, 1325, 1545; UV-VIS spectrum ($CHCl_3$), λ_{max}, nm (log ε_{max}): 228 (4.11), 295 (4.07) [24].

C. A solution of phenylhydrazine (0.22 g, 2 mmol) in aq. MeOH (1.0 : 2.5 ml) is added with stirring to 1,4-dinitropyrazole (0.32 g, 2 mmol) in MeOH (10 ml) at 25°C. The forming precipitate of crude product is collected after 24 h by filtration; the filtrate is evaporated to dryness to give an additional amount of crude product. Both portions of the product are combined; flash chromatographed on silica gel with MeOH–$CHCl_3$ (1:9) as eluent, followed by crystallization from MeOH. Yield 0.26 g (70%). Mp 126–128°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.42–7.52 (1H, m, H Ar); 7.54–7.64 (2H, m, H Ar); 7.92–8.00 (2H, m, H Ar); 8.36 (1H, s, H-3); 9.26 (1H, s, H-5) [43].

5-Nitro-1-phenyl-1*H*-pyrazole (3).

5-Amino-1-phenylpyrazole (4.77 g, 0.03 mol) is oxidized with peroxytrifluoroacetic acid according to the foregoing procedure (synthesis of 3-nitro-1-phenyl-1*H*-pyrazole (**1**)). The product is recrystallized from EtOH–H_2O followed by C_6H_6–hexane. Yield 1.20 g (21%). Mp 99–100°C. No other details given [41].

2-Nitro-1-phenyl-1*H*-imidazole (4).

Solution of butyl bromide (4.50 g, 0.033 mol) in Et_2O (10 ml) is added within 45 min under nitrogen atmosphere with stirring to ground lithium (0.45 g, 0.065 mol) in Et_2O (15 ml). The stirring is continued for the next 15 min and the mixture is cooled to –15°C. 1-Phenylimidazole (1.95 g, 0.018 mol) dissolved in Et_2O (10 ml) is dropped into the mixture within 40 min. One hour later a solution of forming 2-lithium-1-phenylimidazole is cooled to –78°C. Solution of N_2O_4 (5.00 g, 0.054 mol) in Et_2O (50 ml) is then introduced to vigorously stirred solution and the mixture is left without cooling. When temperature of the mixture reaches 0°C it is alkalized with aq. NH_3 (10%). The phases are separated, and aqueous layer is a few times extracted with $CHCl_3$. Both organic layers are combined, dried over Na_2SO_4 and evaporated to dryness. The residue is crystallized from petroleum ether. Yield 1.35 g (38%). Mp 141–142°C (MeOH). No other details given [37].

4-Nitro-1-phenyl-1*H*-imidazole (5).

A. Aniline (0.93 g, 0.01 mol) is added to a stirred suspension of 1,4-dinitroimidazole (1.58 g, 0.01 mol) in aq. MeOH (1:1, 40 ml) at the temperature of ~20°C. The stirring is continued for 2 h, and the resulting mixture is left overnight in the darkness. The colored deposit is collected and heated for 1 h in boiling MeOH (10 ml). Colorless crystals, which have precipitated on cooling, are recrystallized from acetone, MeOH or aq. MeOH. Yield 1.74 g (92%). Mp 186–187°C (acetone). UV-VIS spectrum (MeOH), λ_{max}, nm (ε_{max}): 292 (11600). ^{1}H NMR spectrum (acetone-d_6), δ, ppm (*J*, Hz): 8.14 (1H, d, *J* = 1.6); 8.53 (1H, d, *J* = 1.6); 7.46–7.83 (5H, m) [44].

B. Aniline (0.93 g, 10.0 mol) is added to a stirred solution of 1-(4-chlorobenzenesulfonyl)-4-nitroimidazole (0.72 g, 2.5 mmol) in MeOH–H_2O solution (1:1, 20 ml). The whole mixture is agitated for 2 h at 65–70°C and then left at 25°C until next day. The mixture is subjected to steam distillation. Around 250 cm^3 of the distillate is collected and rejected. Hot aqueous solution from the distillation flask is evaporated under reduced pressure at a temperature below 80°C to dryness yielding the residue. The residue is crystallized from aq. MeOH using activated carbon. Yield 0.27 g (57%). Mp 183–185°C [46].

5-Nitro-1-phenyl-1*H*-imidazole (6).

Warning! Our attempts to obtain compound **6** following the procedure given below have failed.

1-Phenylimidazole (10 g, 0.069 mol) is dissolved in $CHCl_3$ (30 ml), and the solution is stirred in an ice bath while nitronium fluorborate (5 g, 0.037 mol) is added in small portions over 0.5 h. After stirring for additional 0.5 h at room temperature, the two dark phases are diluted with $CHCl_3$ (200 ml) and the mixture extracted with an excess of 1N HCl. The chloroform extract is evaporated, and the residue dissolved in acetone–Et_2O (1:1) and chromatographed on 12 g of a charcoal–Supercel mixture to yield 5-nitro-1-phenyl-imidazole. No yield was given. Mp 150–165°C, sublimation at less than 1 Hg mm pressure at 120°C raises the melting point to 160–170°C. UV-VIS spectrum, λ_{max}, nm (ε_{max}): 292 (5000) [32].

4-Nitro-1-phenyl-1*H*-1,2,3-triazole (7).

4-(2-Nitrovinyl)morpholine (4.76 g, 30 mmol) and phenyl azide (7.17 g, 60 mmol) are mixed, and the mixture is divided among five Carius tubes. The tubes are sealed and heated at 100°C for 10 h, then tubes cooled and carefully opened (with release of a considerable volume of gas). The black residue is dissolved in $CHCl_3$, and the solution is filtered through alumina. The solvent is distilled off, and the residue is triturated with light petroleum (bp 60–80°C). Yield 3.17 g (55%). Mp 132–133°C. No other details given [56].

4-Nitro-1-phenyl-1*H*-1,2,3-triazole (**7**). Yield 60%. Mp 134°C (EtOH). IR spectrum, ν, cm^{-1}: 3100, 1515, 1330. No other details given [55].

5-Nitro-1-phenyl-1*H*-1,2,3-triazole (8).

Phenyl azide (0.63 g, 5.3 mmol) is added to a solution of methyl 3-nitroacrylate (0.70 g, 5.3 mmol) in abs. toluene (20 ml). The resulting mixture is heated under reflux for 1.5 h. The solvent is removed under reduced pressure, and the oily residue is subjected to chromatography on aluminum oxide. Elution with Et_2O gives 5-nitro-1-phenyl-1*H*-1,2,3-triazole (**8**) (0.05 g, 5%). Elution with acetone affords 0.18 g (18%) of 5-nitro-1-phenyl-1*H*-1,2,3-triazole (**8**) and 4-nitro-1-phenyl-1*H*-1,2,3-triazole (**7**) mixture (1:2, R_f 0.86 and 0.80, respectively). Mp 120–122°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1540. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.70 (1H, s); 7.60–7.80 (5H, m) [57].

4-Nitro-2-phenyl-2*H*-1,2,3-triazole (9).

Nitroglyoxaloxime phenylhydrazone (104 g, 0.5 mol) (prepared by coupling benzene diazonium chloride with nitroacetaldoxime) is introduced, while stirring, into a mixture of urea (800 g) and glacial acetic acid (120 g) heated to 140°C and stirred at 140–150°C for 15 min. Water (600 ml) is subsequently slowly added, and, after cooling the mixture, the precipitated yellow triazole is filtered off with suction, washed with water and dried. Yield 81 g (86%). Mp 123–125°C. No other details given [58].

4-Nitro-2-phenyl-2*H*-1,2,3-triazole (**9**). Yield 18%. Mp 124–126°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.34 (1H, s); 8.20–8.00 (2H, m); 7.65–7.45 (3H, m). Mass spectrum, *m*/*z* (I_{rel}, %): 190 $[M]^+$ (100) [34].

3-Nitro-1-phenyl-1,2,4-triazole (10).

3-Nitro-1,2,4-triazole (0.11 g, 1 mmol), DBU (0.15 g, 1 mmol), and diphenyl iodonium tetrafluoroborate (0.37 g, 1 mmol) were introduced with stirring into the vessel containing absolute MeCN (10 ml). After dissolution of the components of the mixture, CuI (0.04 g, 20 mol %) is added. The vessel is sealed and left in a microwave oven, and the reaction mixture is irradiated 3–4 times for 5 min each time with intermediate cooling of the reactor to room temperature with stirring. The progress of the reaction is observed by TLC. Then the solvent is distilled off in vacuum, the residue treated with hot CCl_4 and passed through a layer of alkaline Al_2O_3 to remove residues of ArI and MeCN. The product is isolated by

flash chromatography, eluent EtOAc. The eluate is evaporated and the residue recrystallized from aq. MeOH. Yield 0.09 g (46%). Mp 133°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.51 (1H, m, H-4 Ph); 7.57 (2H, m, H-3,5 Ph); 7.74 (2H, m, H-2,6 Ph); 8.65 (1H, s, H-5). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 120.5 (C-2,6 Ph); 130.0 (C-4 Ph); 130.1 (C-3,5 Ph); 135.7 (C-*ipso* Ph); 142.3 (C-5); 163.3 (C-3). Mass spectrum, *m/z* (I_{rel}, %): 190 $[M]^+$ (100), 117 $[M–HCN–NO_2]^+$ (16), 77 [Ph] (42) [12].

***C*-Nitro-*N*-phenylazoles 11–14**.

Until now compounds **11** and **12** have been obtained as by-products in very low yields only together with their isomer **10**. No physicochemical properties are given [60]. Compounds **12**–**14** without additional substituents remain unknown.

Several N-aryl-C-nitroazoles, among them some of the compounds reported here, have been prepared by us via N-arylation of C-nitro-NH-azoles with arylboronic acids. Preliminary results were reported on a conference (Annual Polish Chem. Soc. meeting Gliwice, Poland, IX. 2011) and will be sent for publication soon.

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