

ХИМИЯ

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*M. Mgkosza***SYNTHESIS OF INDOLES VIA REACTIONS OF NUCLEOPHILES WITH NITROARENES**

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It was shown that reactions between nitroarenes and carbon nucleophiles: Grignard reagents, enolate anions, α -halocarbanions etc. are valuable and versatile tools in synthesis of indoles. Reactions of vinylmagnesium halides with *o*-substituted nitroarenes that proceeds as multistep process initiated by single electron transfer, SET, the Bartoli indole synthesis leads to a variety 7-substituted indoles. A few variants of S_NArH reactions in nitroarenes with carbanions open an avenue to almost unlimited variety of substituted indoles and aza indoles. Refs 45.

Keywords: nitroarene, carbon nucleophiles, SET, indoles.

*M. Макоша***СИНТЕЗ ИНДОЛОВ ПРИ РЕАКЦИИ НУКЛЕОФИЛОВ С НИТРОАРЕНАМИ**

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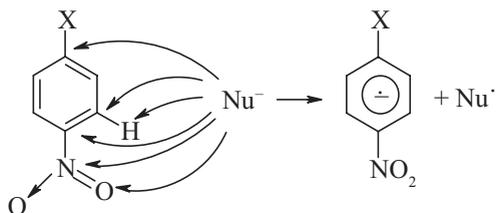
Показано, что реакция нитроаренов с углерод-нуклеофилами — реагенты Гриньяра, енолят-анионы, α -галогенкарбанионы — является удобным методом синтеза индолов. Реакции винилмагнийгалогенидов с *o*-замещёнными нитроаренами проходит как многостадийный процесс, инициируемый электронным переносом. Синтез индолов по Бартоли приводит к 7-замещённым индолам. Некоторые варианты S_NArH реакции нитроаренов с карбанионами открывают почти неограниченные возможности синтеза замещённых индолов и азаиндолов. Библиогр. 45 назв.

Ключевые слова: нитроарены, углеродные нуклеофилы, SET, индолы.

Indoles are very important heterocyclic systems because the indole rings form structural elements of many natural products, pharmaceuticals, agrochemicals, dyes etc. Construction of the indole ring systems is therefore of great importance and interest and is described in numerous original publications, reviews and monographs [1–4]. In recent years the major approaches to construction of the indole ring systems focus on the use of a variety of transition metal catalyzed reactions [2, 5–7], such as for instance Pd catalyzed intramolecular

cyclization of *ortho*-ethynyl anilines [8]. In spite of a wide scope and effectiveness of transition metals catalyzed reactions, they have substantial disadvantages — the products contain residual metals and cannot be directly applied hence they need laborious purification before use [9]. Additional disadvantage is use of costly transition metals and ligands as well as complicated starting materials [2, 5–7]. In this short review will be presented simple and efficient alternative approach to synthesis of indoles based on reactions between nucleophiles, mainly carbanions and nitroarenes. Nitroarenes are very interesting and versatile electrophilic compounds able to react with nucleophiles in a variety of ways presented in recent review [10]. The major ways are addition to the ring at positions occupied by hydrogen and halogens, addition to the oxygen and nitrogen atoms of the nitro group and single-electron transfer. These initial reactions between nucleophiles and nitroarenes are shown in scheme 1.

Scheme 1



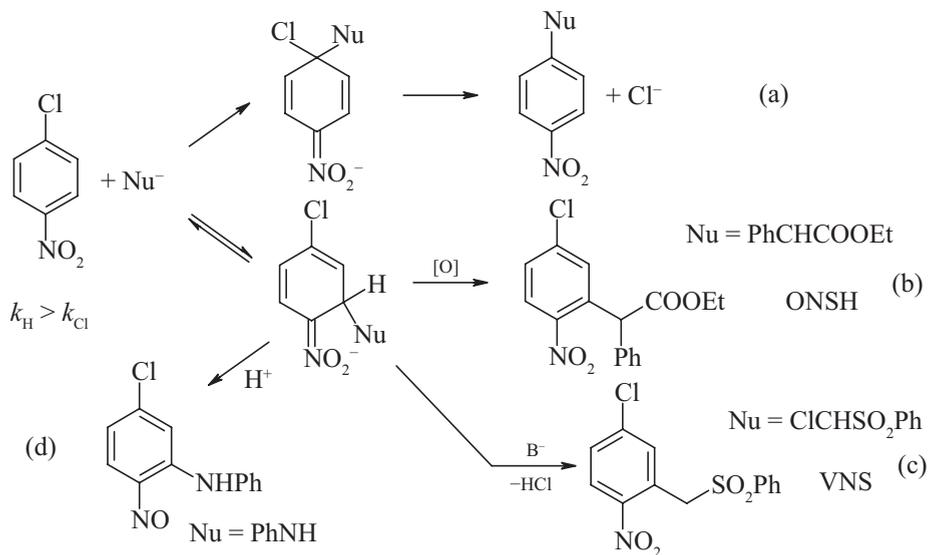
These initial reactions between nucleophiles and nitroarenes are followed by a variety of transformations therefore reactions of nucleophiles with nitroarenes create rich field of organic synthesis. Undisputable the most important reactions between nucleophiles and nitroarenes are initiated by the addition of nucleophiles to the electron deficient rings in positions occupied by halogens X and hydrogen to form intermediate σ^X and σ^H adducts respectively. The former process followed by fast departure of X^- from the σ^X adducts is a well-known reaction of nucleophilic aromatic substitution, S_NAr . However addition of nucleophiles to nitroarenes proceeds much faster at positions occupied by hydrogen. Since spontaneous departure of hydride anions from the initially formed σ^H adducts does not proceed, usually they dissociate hence slower formation of σ^X adducts and subsequently S_NAr can occur. Nevertheless σ^H adducts can undergo fast conversion into products of nucleophilic substitution of hydrogen, S_NArH reaction. Three major ways of conversion of these σ^H adducts are: oxidation with external oxidants — ONSH, elimination of HL when nucleophiles have nucleofugal groups L at the nucleophilic centers — vicarious nucleophilic substitution, VNS and conversion of the σ^H adducts into substituted nitrosoarenes.

In scheme 2 a general picture of reactions between nucleophiles and nitroarenes exemplified by *p*-chloronitrobenzene, initiated by the addition to the ring is presented. Fast addition at position *ortho* to form σ^H adducts is a reversible process. Dissociation of the σ^H adducts followed by slow addition at position *para* and subsequent departure of Cl^- results in S_NAr reaction (2a). On the other hand fast oxidation of the σ^H adducts with an external oxidants gives products of ONSH (2b). Further conversion of the σ^H adducts of α -chlorocarbanions e.g. chloromethyl phenyl sulfone proceeds as base induced β -elimination to give products of VNS (2c). The reaction of *p*-chloronitrobenzene with aniline carried out at $-40^\circ C$ in the presence of strong base results in the formation of σ^H adducts that upon protonation give *o*-nitroso diarylamines (2d).

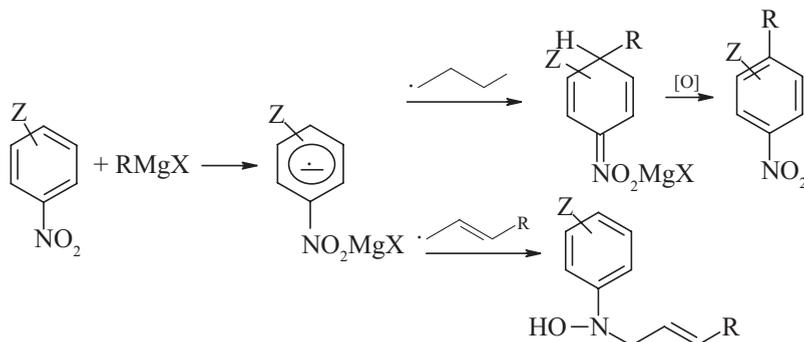
Detailed discussion of many variants of S_NArH reactions is presented in monograph [11] and reviews [12–14]. Contrary to anionic nucleophiles — the Grignard reagents react with nitroarenes not via direct addition but via initial single electron transfer — SET to form nitroaromatic anion-radicals and radicals. Further fate of these paramagnetic species

depends on the structure of the generated radicals. Primary alkyl radicals add to the ring of the nitroaromatic anion radicals in positions *ortho*- and *para*- to form anionic σ^H adducts that can be further oxidized to form products of ONSH-alkylated nitroarenes [15, 16]. On the other hand allyl and aryl radicals add to the nitrogen atom of the nitro group giving substituted hydroxylamines and diaryl amines (scheme 3) [15, 16].

Scheme 2

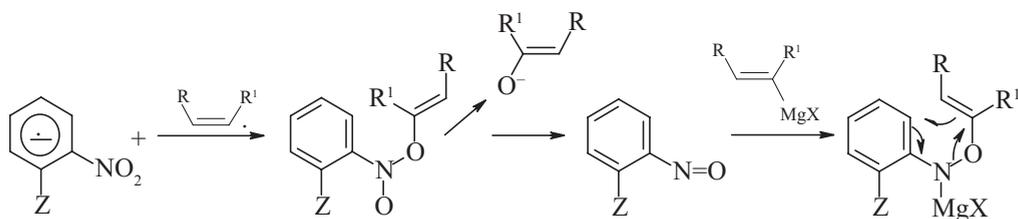


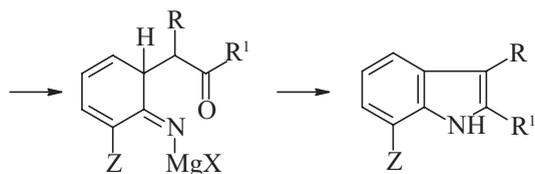
Scheme 3



The most interesting are reactions of vinyl radicals generated via SET between nitroarenes and vinylmagnesium halides. They add to the oxygen atom of the nitroaromatic anion radicals, subsequent elimination of enolate anion initiate multistep transformation giving, as ultimate products, substituted indoles (scheme 4) [17].

Scheme 4





This reaction, the Bartoli indole synthesis proceeds efficiently provided that nitroarene contains a substituent *ortho* to the nitro group. Due to its steric effect the desired process shown in scheme 4 proceeds selectively. The Bartoli indole synthesis has found wide application in organic synthesis [16].

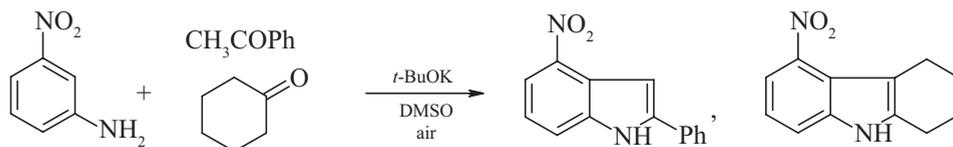
Much more general and versatile are pathways of syntheses of indoles that consist in introduction of functionalized carbon substituents into nitroaromatic rings followed by further transformations. The most efficient ways of introduction of such substituents into nitroarenes is nucleophilic aromatic substitution of hydrogen S_NArH with carbanions via ONSH and VNS reactions. Synthesis of indoles via S_NArH reactions in nitroarenes can be achieved on two ways:

- Substitution of hydrogen with carbanions in *m*-nitroaniline and related nitroarenes — the amine group nitrogen atom is in the heterocyclic ring.
- Introduction of functionalized carbon substituents *ortho* to the nitro group — the nitrogen atom of the nitro group is in the heterocyclic ring.

Perhaps the simplest synthesis of substituted indoles is reaction of enolate anions of ketones with *m*-nitroanilines that proceeds via addition of the enolates in vicinity of the amino group. The intermediate σ^H adducts are oxidized with the atmospheric oxygen whereas the produced *o*-aminobenzyl ketones undergo intramolecular Baeyer condensation to produce indoles [18].

Although the amino groups deactivate nitroaromatic ring toward nucleophilic addition, formation of the intermediate σ^H adducts of enolates to *m*-nitroanilines is promoted by the interaction of the ketone carbonyl and amino groups. Because of this additional interaction the enolate anions add in vicinity (*ortho*) to the amino group. The reaction is of general character, some examples are given in scheme 5. It is also feasible for practical synthesis [19]. Under similar conditions proceed reactions of carbanions of acetonitrile or phenylacetonitrile with *m*-nitroaniline giving 2-amino-4- or -6-nitroindoles (scheme 6) [20].

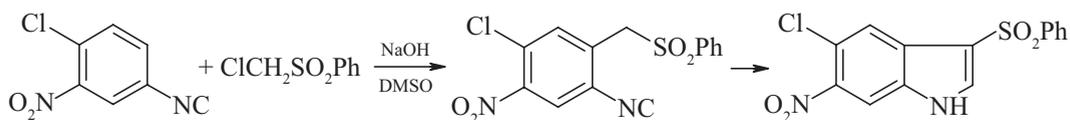
Scheme 5



Scheme 6



Alternatively *m*-nitroanilines can be converted into *m*-nitrobenzoizocyanides that can enter VNS with a variety of carbanions. The produced nitrobenzyl carbanions undergo intramolecular addition to the isocyanide group to form indoles (scheme 7) [21].



Particularly valuable and general approach to synthesis of indoles from nitroarenes consists in introduction of functionalized carbon substituents in positions *ortho* to the nitro group via VNS or ONSH reactions followed by a variety of further transformations.

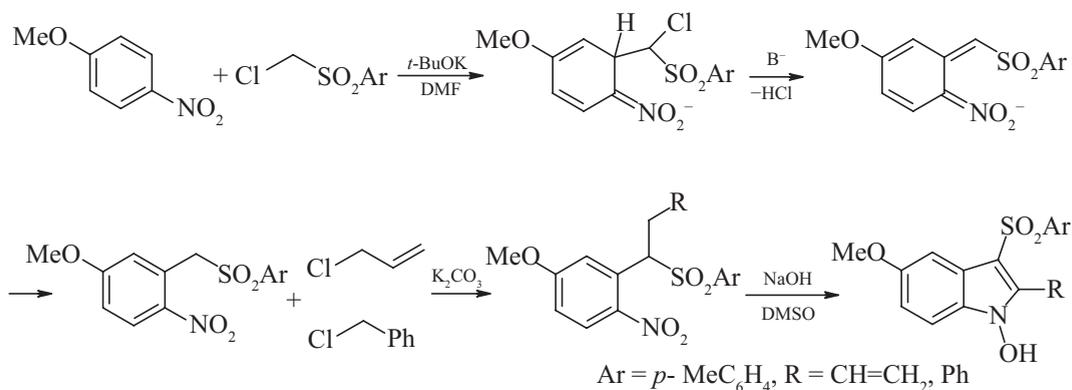
The VNS reaction of carbanions of chloroacetonitrile, or more convenient, aryloxyacetonitriles and chloromethyl phenyl sulfone with a variety of nitroarenes — carbo and heterocyclic, proceeds preferentially in positions *ortho* to the nitro group to provide *o*-nitroaryl acetonitriles [22] and *o*-nitroarylmethyl phenyl sulfones [23, 24] — versatile starting materials for synthesis of substituted indoles. It should be mentioned that the reaction can be directed in the *ortho* position by the proper conditions [24]. These nitriles and sulfones can be converted into indoles on two major ways:

a) Alkylation of the methylenic groups with allyl or benzyl halides or the Knoevenagel reaction with aldehydes followed by base induced intramolecular condensations. These reactions do not require reduction of the nitro group.

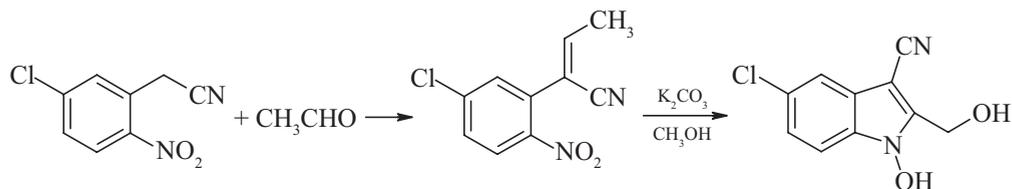
b) Reduction of the nitro group and subsequent reactions.

For instance 2-nitro-5-methoxybenzyl tolyl sulfone, readily available via VNS in *p*-nitroanisole, is rapidly alkylated with allyl chloride or benzyl chloride under liquid-solid PTC conditions (K_2CO_3 anh., $Bu_4N^+Br^-$) to give expected alkylation products. These products treated with powdered NaOH in DMSO undergo a series of reactions giving as ultimate products *N*-hydroxy-2-vinyl (or 2-phenyl)-3-tosyl-5-methoxyindoles in excellent yields (scheme 8) [25].

Scheme 8



Similar transformations proceed with *o*-nitroarylacetonitriles. Thus alkylation of 2-nitro-5-halophenyl acetonitriles with allyl chloride followed by treatment of the product with sodium hydroxide in methanol provides *N*-hydroxy-2-vinyl-3-cyano-5-haloindoles [25]. On the other hand Knoevenagel condensation of these nitriles with acetaldehyde followed by treatment of the produced unsaturated nitriles with K_2CO_3 in methanol gave *N*-hydroxy-2-hydroxymethyl-3-cyano-5-haloindoles (scheme 9) [26].

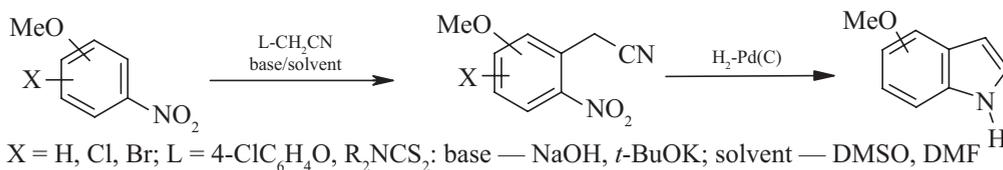


The *N*-hydroxy functionality can be easily removed by a variety of reagents, thus these reactions provide a general way of synthesis of substituted indoles. Surprisingly, in spite of simplicity and great potential value of these reactions, they have attracted only small interest in chemical community.

Even more attractive and general way of construction of substituted indoles consists in reduction of the nitro group in *ortho* nitroaryl acetonitriles and *ortho* nitrobenzyl sulfones.

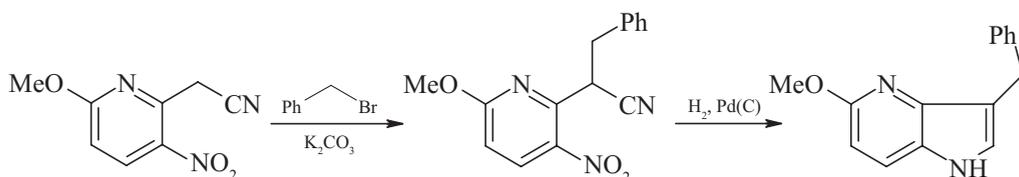
Hydrogenation of *o*-nitroarylacetonitriles was recognized as a way of synthesis of indoles as early as 1955 [27]. However the nitriles were not readily accessible thus this synthesis of indoles was without practical value. For instance, *o*-nitroarylacetonitriles were prepared via S_NAr of fluorine in *o*-fluoronitrobenzenes with carbanion of methyl cyanoacetate followed by partial hydrolysis and decarboxylation [28]. Introduction of VNS reaction into practice of organic synthesis opened possibility of direct cyanomethylation of nitroarenes [22]. Since VNS of hydrogen in halonitroarenes with carbanions proceeds much faster than S_NAr of halogens, whereas halogen substituents activates nitroaromatic rings towards nucleophilic addition [29] halogens in halonitroarenes can play double role: protect position they occupied against the reaction and facilitate synthesis of the desired isomers. Further hydrogenation results in formation of indoles and, if desired removal of protecting and activating halogens. Thus VNS cyanomethylation of isomeric chloronitroanisoles gave access to all isomeric 4-, 5-, 6- and 7-methoxyindoles (scheme 10) [30, 31].

Scheme 10

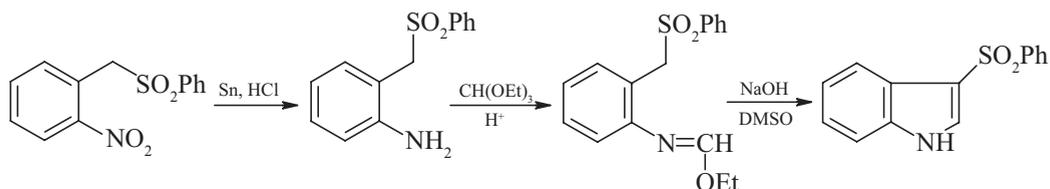


Since carbanions of these nitroaryl acetonitriles can be easily alkylated combination of VNS, alkylation and hydrogenation is a simple way to prepare indoles having a variety of substituents in position 3 (scheme 11) [30, 31].

Scheme 11

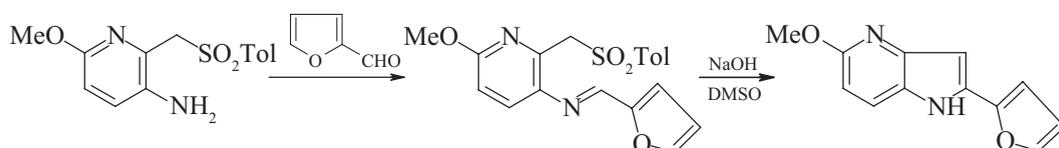


Equally productive is synthesis of indoles via reduction of the nitro group in *ortho*-nitroarylmethyl aryl sulfones. Contrary to the nitriles, the sulfones can be reduced to *ortho*-amionarylmethyl sulfones without cyclization (scheme 12) [32, 33].



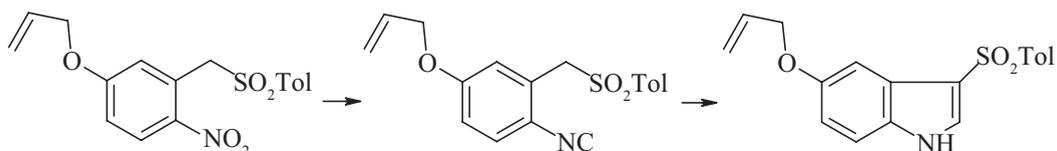
A few ways of conversion of these sulfones into indoles were developed. The base catalyzed condensation of such aminosulfones with aromatic aldehydes provides 2-aryl indoles, probably via formation of imines followed by intramolecular addition of the sulfone carbanion and subsequent sulfinate elimination (scheme 13) [33]. On the other hand acid catalyzed condensation of the amines with *ortho* esters produces imidates that enter intramolecular addition of the carbanion followed by elimination of the alcohol to form 3-arylsulfonyl indoles (scheme 12) [32].

Scheme 13



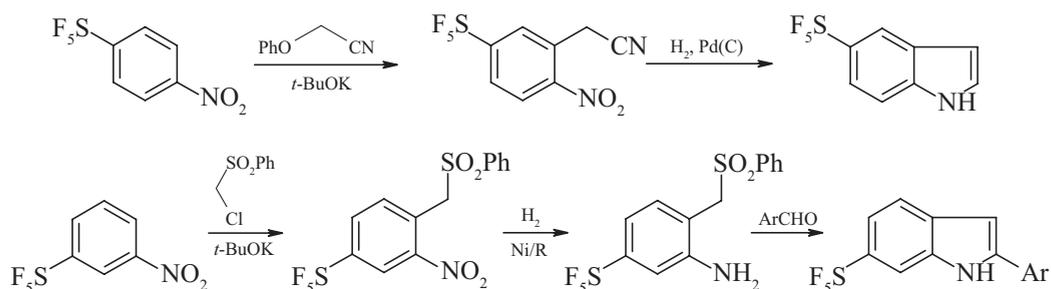
Yet another way consists in conversion of the amino group into isocyanato functionality and further intramolecular addition of the sulfone carbanion (scheme 14) [34].

Scheme 14



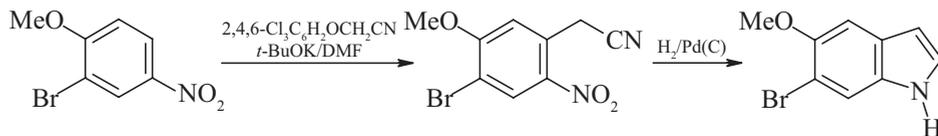
The reductive ways of synthesis of indoles have found wide application in practical synthesis of a variety of indoles [35–40] some examples are given in schemes 15–17.

Scheme 15 [39]

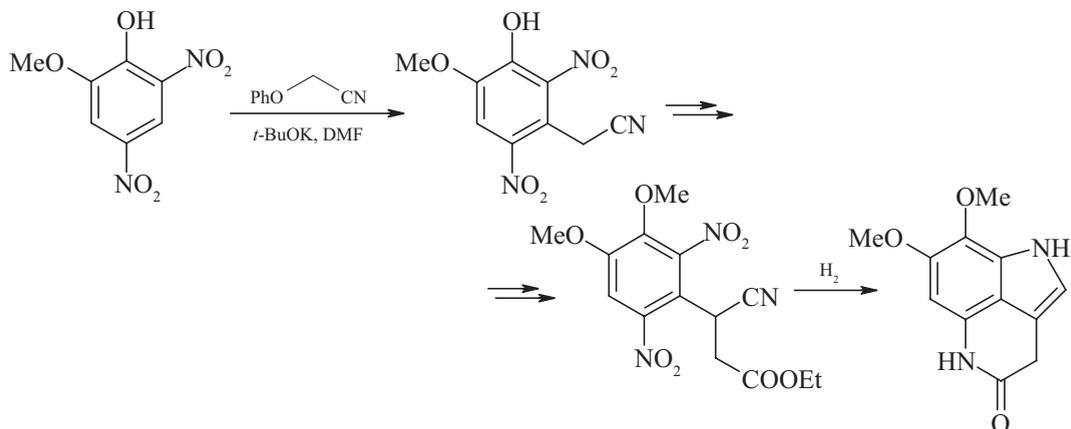


Indoles can be also synthesized via reduction of *o*-nitroarylmethyl ketones, followed by instantaneous Baeyer type condensation [41, 42]. However introduction of acylmethyl substituents into nitroarenes via S_NAr reaction (VNS or ONSH) is less general, because of moderate nucleophilicity of enolate anions. It is therefore limited to highly active nitroarenes such as dinitrobenzene or nitronaphthalene.

Scheme 16 [38]

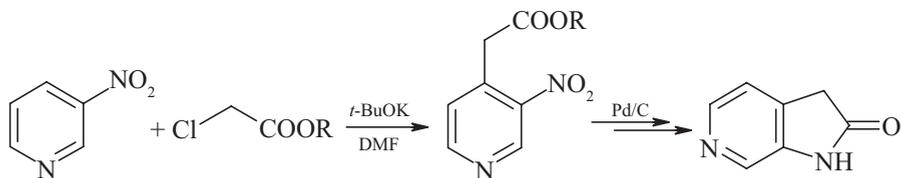


Scheme 17 [40]



S_NArH reactions are also efficient tool in synthesis of oxindoles. Thus intramolecular VNS and ONSH reactions of *m*-nitroanilides of chloroacetic or alkanic acids give directly 5-nitrooxindoles [43, 44]. Even more efficient and versatile way to oxindoles is synthesis of alkyl *o*-nitroarylacetaes via VNS in nitroarenes with alkyl chloroacetates followed by reduction of the nitro group and nitromolecular acylation (scheme 18) [45].

Scheme 18



In this short paper it was shown that reactions between nitroarenes and carbon nucleophiles: Grignard reagents, enolate anions, α -halocarbanions etc. are valuable and versatile tools in synthesis of indoles. Reactions of vinylmagnesium halides with *o*-substituted nitroarenes that proceeds as multistep process initiated by single electron transfer, SET, the Bartoli indole synthesis leads to a variety 7-substituted indoles [17]. A few variants of S_NAr reactions in nitroarenes with carbanions open an avenue to almost unlimited variety of substituted indoles and aza indoles.

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