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ortho-Functionalized nitroarenes in the synthesis of heterocycles

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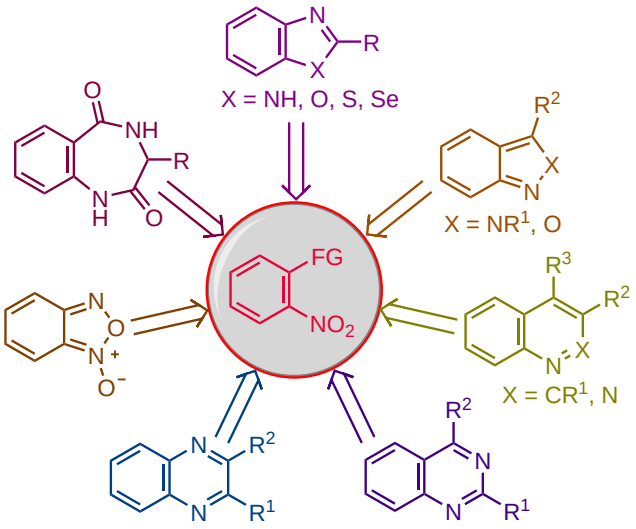
The development of convenient methods for the synthesis of heterocyclic compounds that are highly important for the search of pharmacological substances and in other spheres of human activity is among the most relevant fields of organic chemistry. Two functional groups in arenes located in adjacent positions of the benzene ring can form a fused ring. If at least one of the two *ortho*-functional groups contains a nitrogen atom, a nitrogen-containing heterocycle is formed upon the cyclization. The nitro group is often chosen as the nitrogen-containing group in *ortho*-substituted arenes to form heterocyclic systems, because of ready availability of *ortho*-functionalized nitroarenes, the ability of nitro group to undergo various reactions, and selectivity of the reactions. This review integrates and analyzes for the first time published data on the application of *ortho*-functionalized nitroarenes for the design of heterocyclic structures. Using numerous examples reported in the literature in the last decade, the mutually beneficial effect of two *ortho*-functional groups, one of which is the nitro group, for the formation of various heterocycles is demonstrated. Examples of both intramolecular cyclizations and reactions involving additional reagents are considered. The review gives a holistic view of the capabilities of functionalized *ortho*-nitroarenes in the design of various heterocyclic systems.



The bibliography includes 132 references.

Keywords: *ortho*-functionalized nitroarenes, intra- and intermolecular cyclizations, rearrangements, benzimidazoles, indazoles, indoles, quinoxalines, quinolines, benzodiazepines.

Contents

1. Introduction

Aromatic nitro compounds have attracted the attention of chemists since ancient times, especially after the discovery of nitrobenzene conversion to aniline under the action of ammonium sulfide made by Russian chemist N.N.Zinin in 1842. This reaction has opened up wide prospects for the production of dyes, synthetic rubbers, polyurethanes, explosives, pesticides, and pharmaceuticals. The choice of nitro group as one of the functional groups in *ortho*-substituted arenes implies, first of all, conversion of the nitro group to more reactive amino group, which reacts with a neighbouring substituent to form heterocycles. High reactivity of the amino group leads to restricted accessibility of functionalized anilines; therefore,

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functionalized nitroarenes are often used as precursors of anilines. In this connection, it is necessary to recall classical publications by Baeyer and Drewsen dealing with the synthesis of oxindoles and quinolines from *ortho*-nitrophenylacetic acids (Baeyer reaction)[a] and methyl *ortho*-nitrostyryl ketones (Baeyer–Drewsen reaction),[b] respectively, by reduction with tin in hydrochloric acid; the synthesis of indole by the reduction of *ortho*-nitrocinnamic acid with an iron powder in alkali (Baeyer reaction),[c] and the synthesis of indigo by treating the products of condensation of *ortho*-nitrobenzaldehydes with acetone with an aqueous solution of alkali (Baeyer–Drewsen reaction).[d] These studies initiated the synthesis of heterocyclic compounds from *ortho*-functionalized nitroarenes.

In 2001, Wiley–VCH published the monograph by N.Ono *The Nitro Group in Organic Synthesis*,[1] which considered in detail all sorts of transformations of the nitro group, paying little attention to reactions that involve other functional groups of nitroarenes, apart from the nitro group, to obtain heterocyclic compounds. All transformations of this type in this monograph included nitro group reduction to amino group and cyclization, leading to indole and quinoline derivatives. Since then, the interest in such reactions has markedly increased because of fast development of heterocyclic chemistry, which is important for the search for pharmacologically relevant substances and for other spheres of human activity, and in view of green chemistry principles, which imply decreasing number of steps in chemical synthesis. Therefore, numerous publications on the design of a variety of heterocyclic systems from *ortho*-functionalized nitroarenes appeared. Whereas the monograph by N.Ono[1] covers a small number of *ortho*-functional groups in nitroarenes (mainly, vinyl groups), the modern literature describes numerous *ortho*-functionalized nitroarenes that are converted to heterocycles *via* tandem and one-pot processes.[e] The diversity of heterocyclic compounds formed in these reactions is not limited to indoles and quinolines, but is quite extensive, as evidenced by the Contents to this review. In addition, the mentioned book[1] virtually neglects modifications of the *ortho*-substituent in nitroarenes (except for the methyl group in *ortho*-nitrotoluenes), while our review extensively addresses two- and three-component reactions in which substituents already present in the *ortho*-position of nitroarenes are modified. Finally, some recent publications describe the preparation of heterocycles from *ortho*-functionalized nitroarenes without the intermediate conversion of the nitro group to the amino group, and these reactions receive particular attention throughout the review.

Published data on the transformations of *ortho*-functionalized nitroarenes into heterocycles in tandem and one-pot processes make it possible to identify the main trends in the development of this field of chemical science and to formulate modern methodological approaches to the design of heterocyclic systems.

2. *ortho*-Nitroanilines in the synthesis of benzimidazoles and benzimidazolones

It is easy to predict that conversion of *ortho*-nitroaniline (**1a**) to benzimidazoles **2** requires building of the imidazole moiety using, apart from two nitrogen atoms of the substrate, a carbon atom from an external source.[f] Apparently, benzimidazoles are generated from *ortho*-nitroaniline **1a** through the intermediate formation of *ortho*-diaminobenzene **3a**; therefore, a reducing agent or transition metal-based catalyst ([M]) and a source of hydrogen atoms should be added to the reaction mixture. The conversion of *ortho*-nitroaniline **1a** to benzimidazoles **2** is depicted in Scheme 1. In this case, the use of *ortho*-diaminobenzenes is less expedient since they are produced in industry from nitro compounds.

In the synthesis of benzimidazoles **2** from *ortho*-nitroaniline **1a**, alcohols are used most often as sources of the carbon atom, as they are readily available and environmentally friendly. Transition metal-based catalysts initiate the generation of hydrogen from alcohols, which are thus converted to aldehydes. Hydrogen successively reduces the nitro group to nitroso, hydroxylamino, or amino group (intermediate compounds **A**, **B**, and **3a**, respectively), while the aldehyde condenses with the amino group to form an imine moiety in intermediate **C** (Scheme 2). The intramolecular nucleophilic addition of the

[a] See A.Baeyer. *Ber. Deutsch. Chem. Ges*., **11**, 582 (1878).
[b] See A.Baeyer, V.Drewsen. *Ber. Deutsch. Chem. Ges*., **15**, 2682 (1882).
[c] See A.Baeyer, A.Emmerling. *Ber. Deutsch. Chem. Ges*., **2**, 679 (1869).
[d] See A.Baeyer, V.Drewsen. *Ber. Deutsch. Chem. Ges*., **15**, 2856 (1882).
[e] The notions 'tandem' and 'one-pot' processes in this review differ by the fact that the former proceeds in one reactor without the addition of any other reagents, while the latter implies the addition of a reagent during the reaction.

[f] In the Schemes presented in this Section, the carbon atom involved in the formation of the imidazole moiety is marked in the reactant and in the product by a red circle (in the subsequent Sections, the red colour marks the carbon atoms that are involved in the construction of other heterocycles).

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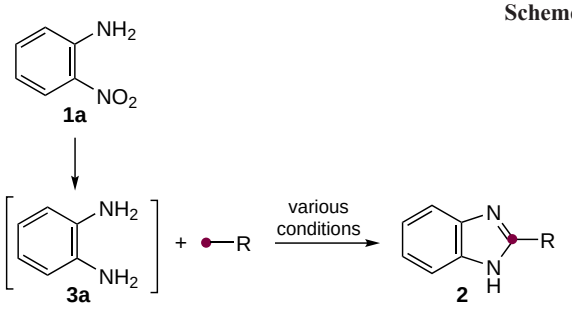
Translation: Z.P.Svitanko

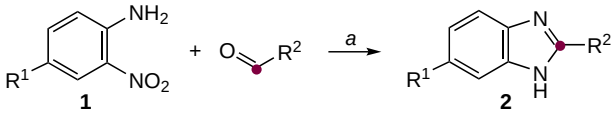
Scheme 1



amino group to the imine group of the Schiff base provides the formation of the dihydrobenzimidazole ring in intermediate **D**, which is reduced with hydrogen to give products **2**.[2,3] The possible catalysts [M] include iron,[3] iron salts,[4] Knölker complex (**I**);[5,6] palladium,[7] cobalt,[8–10] and copper[11] compounds; and Cu–Pd/γ-Al_2O_3 (Refs 12 and 13) and Ir/TiO_2 (Refs 14, 15) multifunctional systems.

The synthesis of benzimidazoles **2** from *ortho*-nitroanilines **1** and aldehydes may be performed using, for example, $Na_2S_2O_4$ in water, which selectively reduces the nitro group (Scheme 3),[16] or hydrogen activated by cobalt nanoparticles (Co-NPs) encapsulated into nitrogen-doped carbon nanotubes (68–99% yields).[17]

Scheme 3



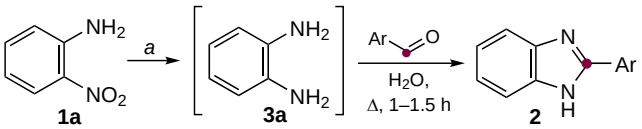
(>99%, 21 examples)

(a) $Na_2S_2O_4$ (3 equiv.), H_2O, EtOH, 50–60°C, 5 h;
R^1 = H, NH_2; R^2 = $(CHOH)_nCH_2OH$ (*n* = 3, 4), Ar

The Ghosh's research group[18] prepared 2-arylbenzimidazoles *via* a one-pot process in which *ortho*-nitroaniline was first treated with Zn and $NaHSO_3$ in an aqueous medium at room temperature, and then aldehyde was added to the reaction mixture (Scheme 4).

Using a twofold or threefold excess of aromatic aldehyde in the reaction with compound **1a** in the presence of the $SnCl_2 \cdot 2H_2O$/ChCl system (Ch is choline), which acted as a catalyst and a deep eutectic solvent (DES),[g] Ochoa–Puentes and

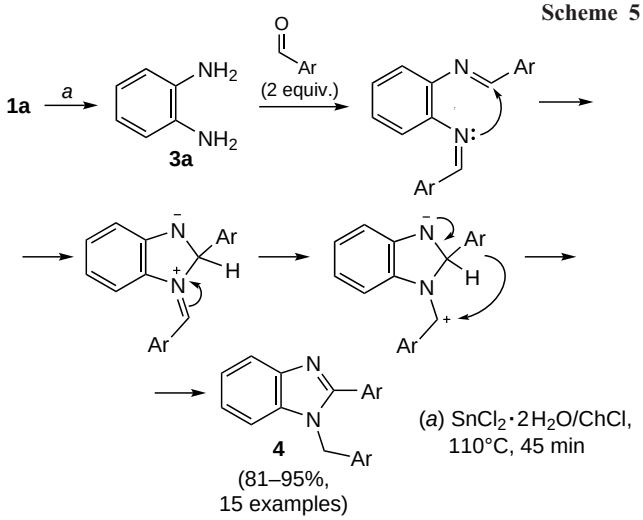
Scheme 4



(*a*) Zn (3 equiv.), $NaHSO_3$ (6 equiv.), H_2O, rt, 5–10 min

(83–93%, 12 examples)

Scheme 5



(81–95%, 15 examples)

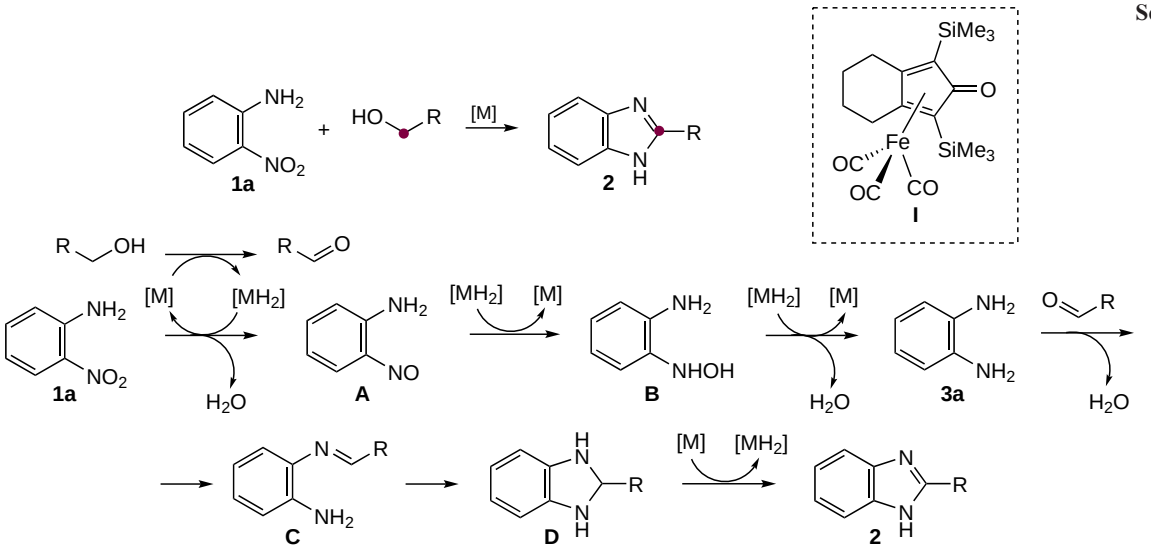
co-workers[19] prepared 2-aryl-1-benzylbenzimidazoles **4**, as shown in Scheme 5.

2-Unsubstituted benzimidazoles were synthesized by the microwave (MW)-assisted reaction of *ortho*-nitroanilines with an azeotropic mixture of formic acid and triethylamine in the presence of catalytic amounts of Pd/C.[20] When the authors used N-substituted anilines in these reactions, N-substituted benzimidazoles were obtained (Scheme 6).[h]

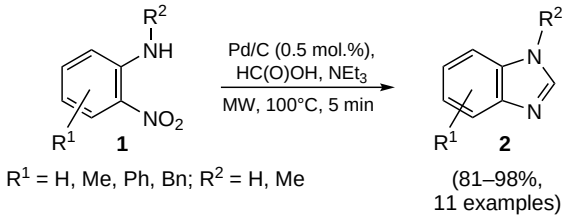
[g] Deep eutectic solvent (DES) is a solvent obtained by thermal mixing of two or more components, which has a melting point lower than the melting points of each component and low volatility, high stability, and the lack of toxicity.

[h] Here and below, substituents in the benzene ring indicated without locants means that the substituent can occupy any position.

Scheme 2



Scheme 6

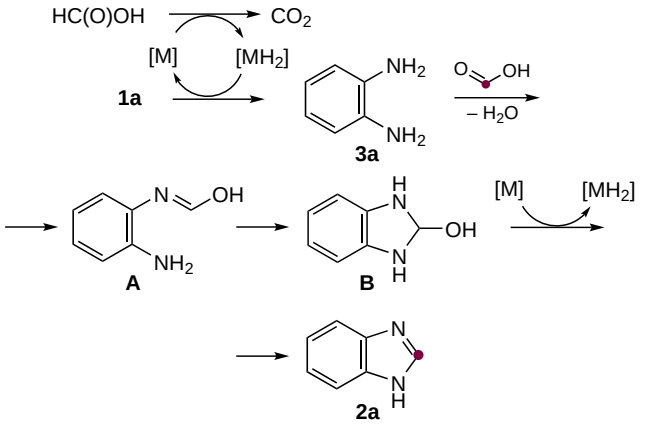


R^1 = H, Me, Ph, Bn; R^2 = H, Me

(81–98%, 11 examples)

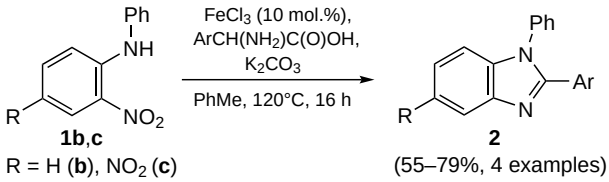
In these reactions, formic acid decomposes under the action of a catalyst to give carbon dioxide and hydrogen; the latter reduces the nitro group in nitroaniline **1a**, and after that, diaminobenzene **3a** reacts with formic acid to give intermediate imino compound **A** (Scheme 7). The intramolecular nucleophilic addition of the amino group to the imine bond in intermediate **A** forms a benzimidazole ring (compound **B**), while hydrogen released upon the decomposition of formic acid reduces **B** to benzimidazole **2** (see Scheme 7). Formic acid acts in these reactions as a reducing agent and provides a carbon atom for the formation of the imidazole moiety.

Scheme 7



Ferric chloride-initiated reactions of *N*-phenyl-2-*ortho*-nitroanilines with aryl-substituted glycine derivatives afforded benzimidazoles with a phenyl substituent at nitrogen in position 1 and aryl moiety in position 2 (Scheme 8).[21]

Scheme 8



R = H (**b**), NO_2 (**c**)

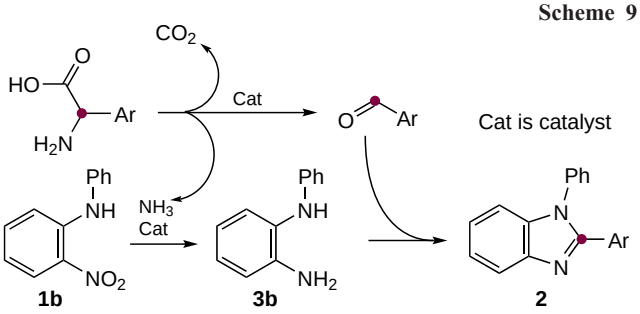
(55–79%, 4 examples)

In this reaction, in the presence of a catalyst, amino acid gives off ammonia and CO_2 being oxidized to the corresponding aldehyde. Under the action of a catalyst, ammonia promotes the conversion of nitroanilines **1b**,**c** to diaminobenzenes **3b**,**c**, which then react with aldehydes to give *N*-phenylbenzimidazoles **2** (Scheme 9).

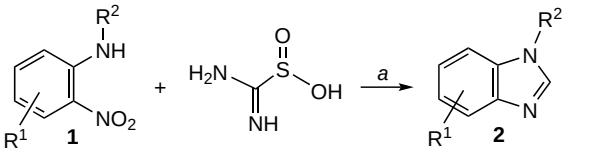
Porcheddy and co-workers[22] synthesized benzimidazoles from *ortho*-nitroanilines **1** and thiourea dioxide, which acted as a source of carbon and a reducing agent. The reaction was conducted without a solvent using mechanochemical activation[i] of reactants in a ball mill (Scheme 10).

[i] Mechanochemical activation is the acceleration or increase in the efficiency of chemical reactions by mechanical impact.

Scheme 9



Scheme 10

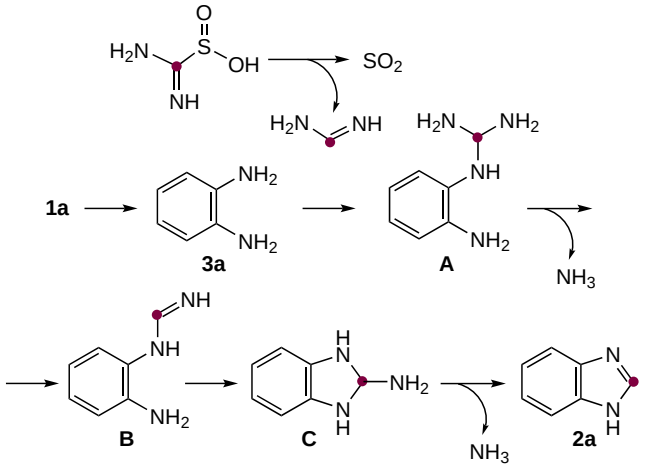


(45–94%, 9 examples)

(*a*) NaOH, H_2O, rt, 2–3 h, ball-milling, 30 Hz;
R^1 = H, Me, OMe, OCF_3, Br, Cl, NH_2; R^2 = H, Me

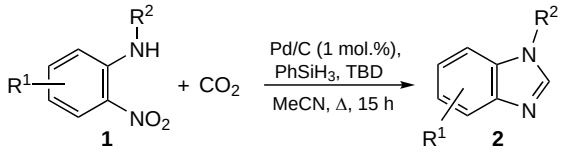
Scheme 11 shows a possible reaction pathway in which intermediate diaminobenzene **3** adds to the imine bond of formimidamide generated from thiourea dioxide to give compounds **A**. The elimination of ammonia leads to imine **B**, which undergoes intramolecular cyclization involving the amino group and the imine bond to give 2-amino-2,3-dihydrobenzimidazol **C**, while elimination of ammonia from compound **C** yields product **2**.

Scheme 11



2-Unsubstituted benzimidazoles are formed in the reactions of nitroanilines **1** with CO_2 catalyzed by Pd/C in which $PhSiH_3$ serves as a reducing agent and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) acts as a base (Scheme 12).[23]

Scheme 12

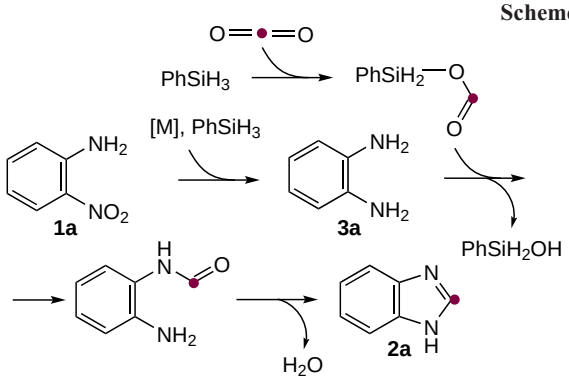


R^1 = H, Me, OMe, Br, F;
R^2 = H, Me, Et, Ph, C_6H_4Me-4

(70–95%, 12 examples)

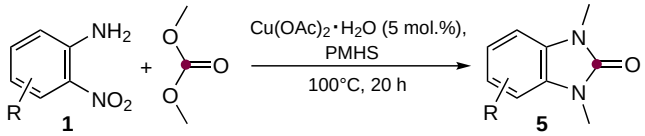
In this case, phenylsilane reacts with CO_2 to be converted to phenylsilyl formate, which reacts with diaminobenzene **3** to give *N*-(*ortho*-aminophenyl)formamide, which cyclizes to benzimidazole **2** (Scheme 13). Bhanage's reseach group[24] used ruthenium nanoparticles supported on polymer ionic liquids (IL) as catalysts and dimethylaminoborane as a reducing agent to perform reactions of nitroanilines **1** with CO_2 (the product yields were 75–90%).

Scheme 13



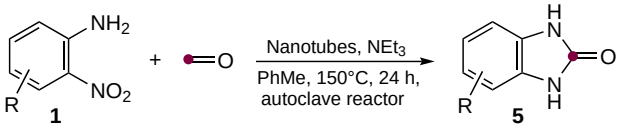
The reactions of nitroanilines **1** with dimethyl carbonate in the presence of $Cu(OAc)_2 \cdot H_2O$ as a catalyst and polymethylhydrosiloxane (PMHS) as a reducing agent resulted in the synthesis of benzimidazol-2-ones **5** (Scheme 14).[25]

Scheme 14



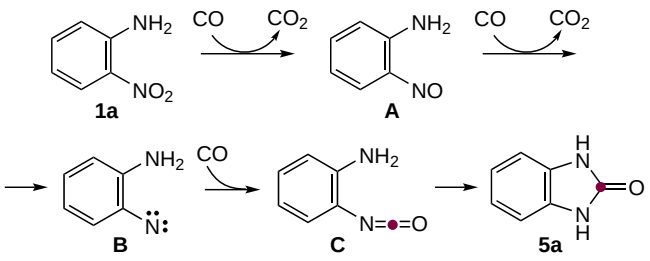
Benzimidazolones **5** were also synthesized by treatment of nitroanilines **1** adsorbed on nitrogen-doped carbon nanotubes with carbon monoxide (Scheme 15).[26]

Scheme 15



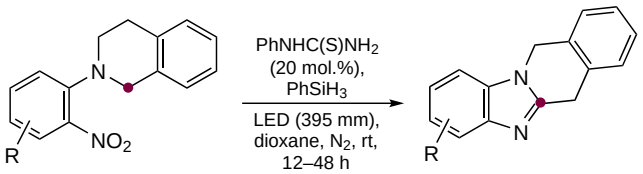
A putative pathway to benzimidazolones **5** in this reaction is depicted in Scheme 16. First, carbon monoxide reduces the nitro group, thus converting substrate **1** successively to nitroso compound **A** and nitrene **B**. Then CO adds to nitrene and serves as the source of a carbonyl group in the formation of the imidazolone moiety from isocyanoaniline **C** *via* intramolecular cyclization.

Scheme 16



When 2-(2-nitrophenyl)-1,2,3,4-tetrahydroisoquinolines were introduced in the reaction (Scheme 17), fused benzimidazoisoquinoline structures were formed.[27] This intramolecular reaction following a biradical mechanism is initiated by phenylthiourea and by irradiation with a light-emitting diode (LED); phenylsilane acts as a reducing agent, while the methylene group of the piperidine moiety adjacent to nitrogen is involved in the formation of the imidazole ring. In this case, there is no need in an external source of carbon for the generation of the imidazole system, as it is present in the molecule (marked with a red circle).

Scheme 17

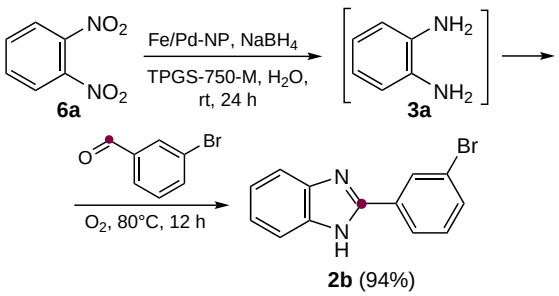


To summarize the above, it should be noted that in the design of the benzimidazole system from *ortho*-nitroanilines, alcohols are normally used as sources of the carbon atom, as they are readily available and environmentally friendly reagents. The conduction of these reactions requires transition metal-based catalysts, which trigger the reaction by oxidation alcohols to aldehydes; this is accompanied by the release of hydrogen needed to reduce the nitro group to amino group (see Scheme 2). When aldehydes are used as sources of the carbon atom, the catalyst is no longer needed; it is sufficient that the system contains a reducing agent for the nitro group (see Schemes 3–5). The methods for the synthesis of 2-unsubstituted benzimidazoles involving CO_2 (see Scheme 12) and the synthesis of benzimidazolones involving CO (see Scheme 15) comply with the green chemistry principles related to the prospects of recycling of industrial and domestic waste. The transformation depicted in Scheme 17 demonstrates the case in which the carbon atom needed for the formation of the imidazole moiety is already present in the starting molecule and, hence, the reaction is intramolecular.

3. *ortho*-Dinitrobenzenes in the synthesis of benzimidazoles

ortho-Dinitrobenzenes **6** are also used in the synthesis of benzimidazoles. For example, 2-(3-bromophenyl)benzimidazole (**2b**) was prepared in a one-pot process, which included the reduction of dinitrobenzene **6a** to diaminobenzene **3a** with sodium borohydride in water in the presence of DL-α-tocopherol methoxypolyethylene glycol succinate (TPGS-750-M) as a surfactant and the subsequent reaction of diaminobenzene with

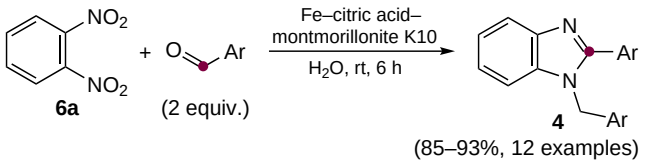
Scheme 18



3-bromobenzaldehyde (Scheme 18).[28] The reduction of dinitrobenzene is successfully performed with hydrogen in the presence of molybdenum sulfide catalyst (50–98% yield)[29] or activated cobalt nanoparticles (69–98% yields).[17]

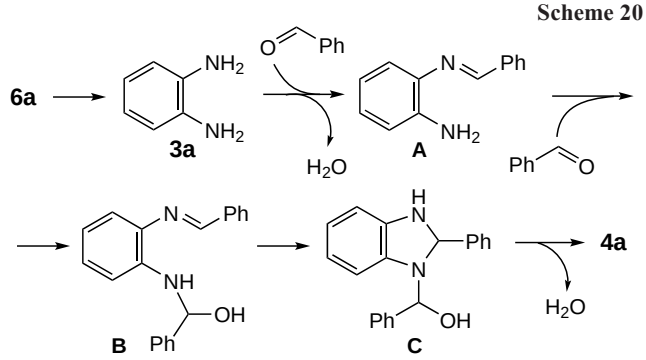
ortho-Dinitrobenzene (**6a**) was allowed to react with aromatic aldehydes in the presence of Fe–aqueous solution of citric acid–montmorillonite K10 catalytic system, which resulted in the formation of 2-aryl-1-benzylbenzimidazoles **4** (Scheme 19).[30]

Scheme 19



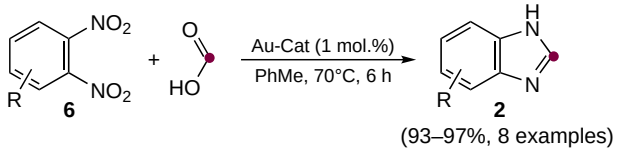
Scheme 20 shows the mechanism of this reaction, including the reduction of dinitrobenzene **6a** to diaminobenzene **3a**. One of the amino groups is involved in the condensation with benzaldehyde to give imino compound **A**, while the other amino group adds to the benzaldehyde carbonyl group, thus giving intermediate compound **B**. The intramolecular addition of the amino group in intermediate **B** to the imine bond leads to benzimidazole **C**, which eliminates water to give product **4**.

Scheme 20



In the catalytic reaction involving EtOH, *ortho*-dinitrobenzene is converted to 2-methylbenzimidazole;[31] in the reaction with formic acid, 2-unsubstituted benzimidazole is formed.[32,33] A number of 2-unsubstituted benzimidazoles have been prepared by the reactions of dinitrobenzenes **6** with formic acid in the presence of a gold-based catalyst (Scheme 21).[33]

Scheme 21



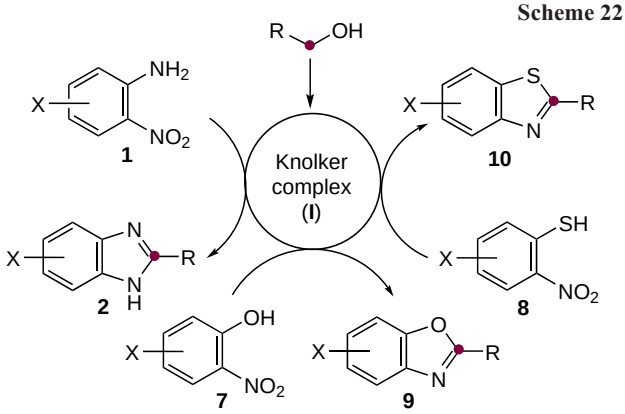
The photocatalytic reduction of dinitrobenzene in the presence of potassium polyheptazinimide in a mixture of ammonium formate and glycolic acid as a reagent and DES gave benzimidazole in 85% yields.[34] In essence, this reaction is reduced to the interaction of diaminobenzene **3a** with formic acid, which results from the reaction of ammonium formate with glycolic acid.

Thus, *ortho*-dinitrobenzenes can be used in the synthesis of benzimidazoles under approximately the same conditions as *ortho*-nitroanilines.

4. *ortho*-Nitrophenols and *ortho*-nitrothiophenols in the synthesis of benzoxazoles and benzothiazoles

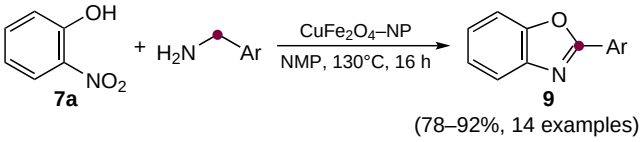
In the same way as *ortho*-nitroanilines **1** are converted to benzimidazoles, *ortho*-nitrophenols **7** and *ortho*-nitrothiophenols **8** are converted to benzoxazoles **9** and benzothiazoles **10**, respectively. This may be done *via* reactions with alcohols,[6,12,35,36] aldehydes,[37–39] CO_2,[24] benzylamines,[40] and aryl isothiocyanates.[41] The reactions of compounds **1**, **7**, and **8** with alcohols in the presence of the Knölker complex are shown in Scheme 22.[6]

Scheme 22



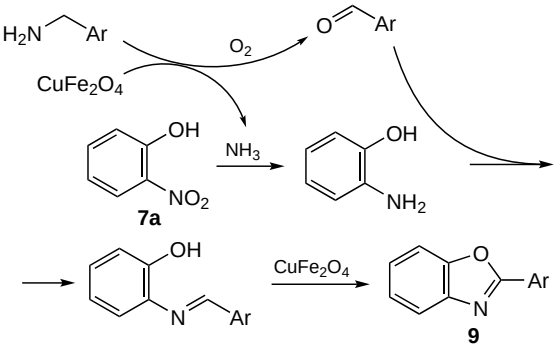
ortho-Nitrophenol (**7a**) reacts with benzylamines in *N*-methylpyrrolidin-2-one (NMP) with copper ferrite as a catalyst at 130°C (Scheme 23).[40] 2-Arylbenzoxazoles **9** are formed in high yields.

Scheme 23



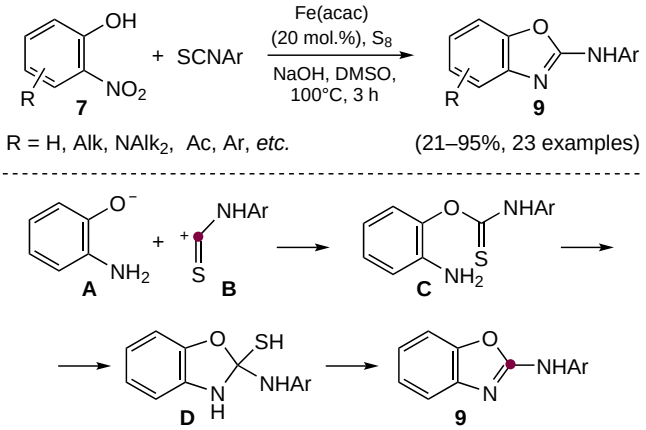
The following processes occur in the system: oxidation of benzylamine to benzaldehyde accompanied by the evolution of ammonia, the reduction of the nitro group in nitrophenol to amino group, the condensation of intermediate benzaldehyde with *ortho*-hydroxyaniline, and cyclization of the condensation product to give 2-arylbenzoxazoles **9** (Scheme 24).

Scheme 24



The reactions of *ortho*-nitrophenols **7** with aryl isothiocyanates were carried out in the presence of iron acetylacetonate (acac) and sulfur in a solution of NaOH in DMSO (Scheme 25).[41] In this process, intermediates **A** and **B** formed under the action of the base and the catalyst are combined with each other to form compound **C**, which contains all groups needed for cyclization

Scheme 25



to dihydrobenzoxazole **D**, which is subsequently converted to benzoxazole with the arylamine moiety in position 2 (see Scheme 25).

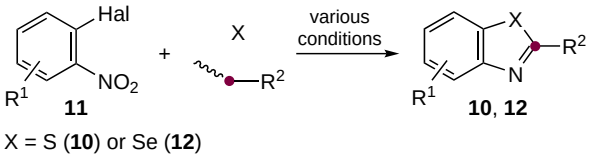
Hence, the formation of benzoxazoles and benzothiazoles from *ortho*-nitrophenols and *ortho*-nitrothiophenols requires the presence of a carbon atom source and conditions ensuring the reduction of the nitro group, similarly to the formation of benzimidazoles from *ortho*-nitroanilines and *ortho*-dinitrobenzenes.

5. *ortho*-Halonitroarenes in the synthesis of benzothiazoles and benzoselenazoles

Several research groups studied three-component reactions involving *ortho*-halonitrobenzenes **11**, sulfur (or selenium), and sources of carbon atoms such as benzaldehydes,[42] benzyl alcohols,[42] acetophenones,[43] arylacetic acids,[44,45] and benzyl chlorides.[46,47] These reactions performed in the presence of *N*-methylmorpholine (NMM) resulted in benzothiazoles or benzoselenazoles. According to the authors,[42,43] the role of NMM was to initially react with sulfur to give zwitter-ion **A**, which then reacts with, for example, *ortho*-chloronitrobenzene (**11a**), yielding intermediate **B**. The subsequent course of the process is shown in Scheme 26 in relation to the reaction with acetophenone as a source of carbon atom.[43] The reduction of nitrone **C** to 2-benzoylbenzothiazole occurs with participation of zwitter-ion **A**. The mechanism has not been finally clarified, but it can be seen in the Scheme that no conversion of the nitro group to the amino group takes place in these processes.

Table 1 summarizes data on the synthesis of benzothiazoles **10** and benzoselenazoles **12** from halonitroarenes, a chalcogen (S or Se), and carbon atom sources (Scheme 27). The data of the Table indicate that highly diverse substituents can be introduced into position 2 of benzothiazoles and benzoselenazoles. If the carbon atom source has two functions that can provide a carbon atom to the thiazole moiety, *e.g.*, isophthalaldehyde (see line 2) or pyridine-2,6-diyldimethanol (see line 4), bis-products with two benzothiazole moieties are obtained.

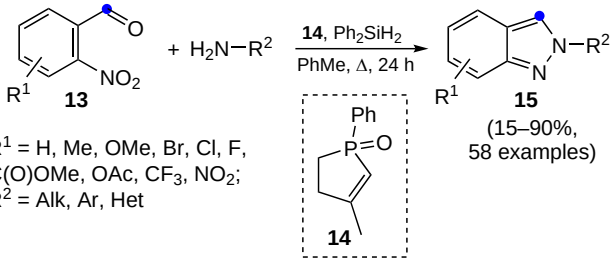
Scheme 27



6. *ortho*-Nitrobenzaldehydes and various *ortho*-nitrobenzyl derivatives in the synthesis of indazoles and indazolones

Nazare and co-workers[48] performed reactions of *ortho*-nitrobenzaldehydes **13** with primary amines in the presence of a reducing system composed of commercially available 3-methyl-1-phenyl-2-phospholene 1-oxide (**14**) and diphenylsilane and thus synthesized indazoles **15** (Scheme 28).[j]

Scheme 28



In this system, the reaction of *ortho*-nitrobenzaldehyde **13** with amine affords *N*-(*ortho*-nitrobenzylidene)aniline **16** (Scheme 29). Phosphine **17** generated from phospholene oxide **14** under the action of diphenylsilane adds to the nitro group of **16** to give intermediate compound **A**, which is stabilized *via* elimination of phospholene oxide **14**, being converted to nitroso derivative **B**. Phosphine **17** adds again to the nitroso group of intermediate **B**, which gives zwitter-ion **C**. This product undergoes intramolecular nucleophilic addition and elimination of phospholene oxide **14** to afford indazole **15**.

[j] Here and in the subsequent schemes, the carbon atom in nitroarene involved in the formation of the C–N bond is marked by a blue circle.

Scheme 26

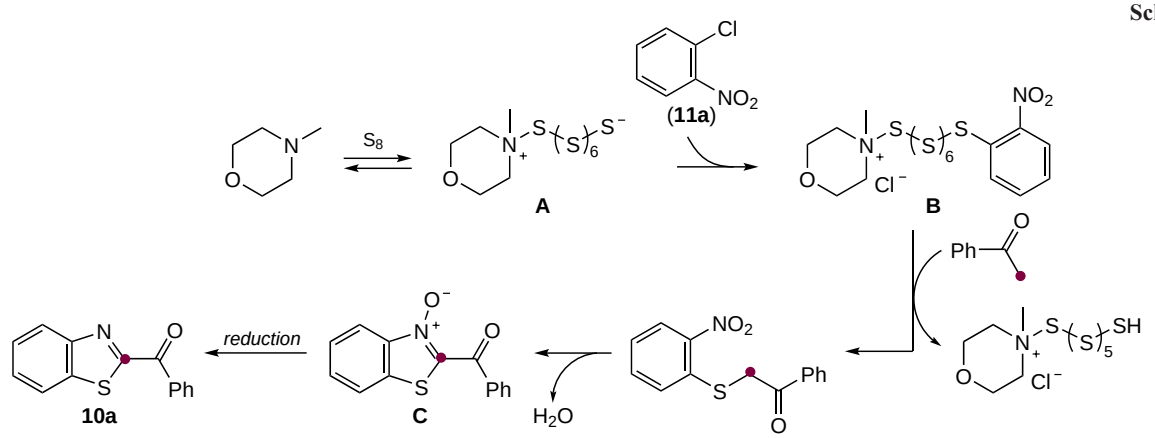
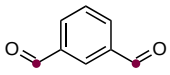
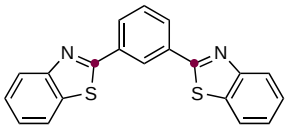
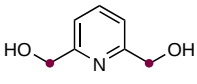
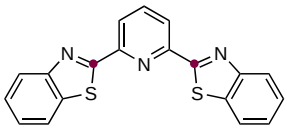
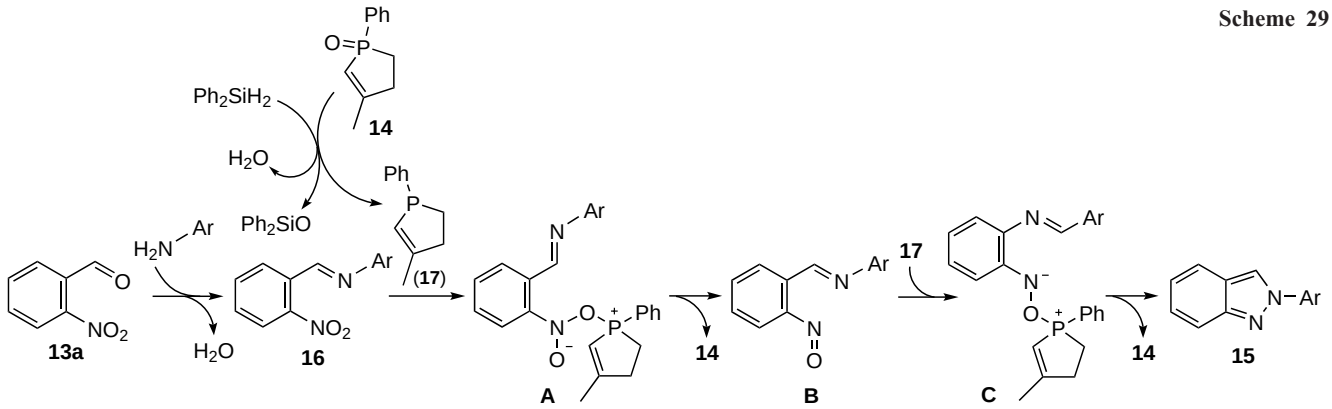


Table 1. Synthesis of benzothiazoles и benzoselenazoles from halonitroarenes, chalcogen (S or Se), and carbon atom sources (see Scheme 27).

Line	R^1	Hal	Carbon source	X	Conditions	Number of examples	Yields (%)	Product	Refs
1	H, Me, OMe, OH, Cl, F, CF_3, CN, NO_2	Cl	ArC(O)H HetC(O)H	S	NMM, 130°C, 16 h	26	61–80	**10**: R^2 = Ar, Het	42
2	H	Cl		S	NMM, 130°C, 16 h	1	67		42
3	OMe, Br, F, CF_3	Cl	$ArCH_2OH$	S	NMM, 130°C, 16 h	4	31–85	**10**: R^2 = Ar	42
4	H	Cl		S	NMM, 130°C, 16 h	1	68		42
5	H, Me, OMe, Br, Cl, F, CF_3	I, Br, Cl, F,	ArC(O)Me HetC(O)Me	S	NMM, 120°C, 16 h	25	41–92	**10**: R^2 = C(O)Ar, C(O)Het	43
6	H, Me, Cl, C(O)OH, NHC(S)Ph	Cl	$ArCH_2C(O)OH$	S	NMM, 110°C, 15 h	23	50–75	**10**: R^2 = Ar, Het	44
7	H, Me, OMe, Br, Cl, F, CF_3	Cl, Br	$ArCH_2C(O)OH$	Se	NMM, 130°C, 24 h	30	41–82	**12**: R^2 = Ar	45
8	H, Me, OMe, Br, Cl, F	Cl	$ArCH_2Cl$	S	NMM, 110°C, 24 h	30	47–95	**10**: R^2 = Ar	46
9	H, Me, OMe, Br, Cl, F, CF_3	Cl	$ArCH_2Cl$	Se	NMM, 160°C, 18 h	28	39–89	**12**: R^2 = Ar, Het	47

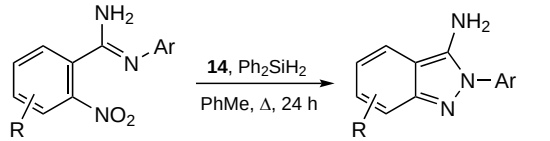
Scheme 29



When *N*-(*ortho*-nitrobenzylidene)anilines were directly used under the same reaction conditions, the reaction was intramolecular. A series of 3-amino-2-arylindazoles were prepared in this way from substrates with amino group at the imine carbon atom (Scheme 30).[48]

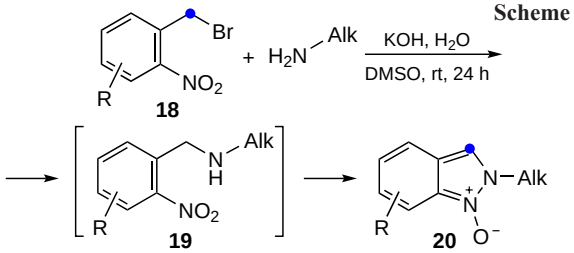
The reaction of *ortho*-nitrobenzyl bromides **18** with primary amines in the presence of KOH in DMSO involves the formation of intermediate *ortho*-nitrobenzylamines **19** and ends in the formation of indazole *N*-oxides **20** (Scheme 31).[49] Indazole *N*-oxides **20** were also obtained under the same conditions by the intramolecular cyclization of compounds **19** (33–72% yields).[49]

Scheme 30



R = 4-Me, 4-OMe, 4-Cl, 6-Cl, 5-F, 4,5-$(OMe)_2$ (34–85%, 6 examples)

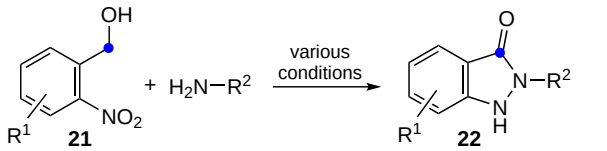
Scheme 31



R = H, OMe, CF_3; rt is room temperature (29–95%, 13 examples)

ortho-Nitrobenzyl alcohols **21** react with primary amines under the action of UV radiation[50–52] or on heating with KOH in aqueous Pr^{i}OH[53] and are thus converted to indazol-3-ones **22** (Scheme 32).

Scheme 32



R^1 = H, Me, OMe, Hal, C(O)NHAlk, CF_3, Ar, 3-furyl, 3-thienyl;
R^2 = Alk, Cy, Ar, Bn; Cy is cyclohexyl

Zhu *et al*.[50] assumed that this process follows the pathway shown in Scheme 33. In the first step, electron density redistribution takes place in substrate **21** under the action of radiation, giving rise to intermediate **A**, which cyclizes to dihydroxydihydrobenzisoxazole **B**. This is followed by oxazole ring opening to give nitroso-containing *gem*-diol **C**, dehydration to *ortho*-nitrosobenzaldehyde **D**, and the addition of amine to either the carbonyl group or the nitroso group to give intermediates **E** or **F**, respectively. The dehydration of these intermediates leads to the formation of indazolones **22**. In these processes, amines act as sources of the nitrogen atom, contributing to the formation of the indazolone system.

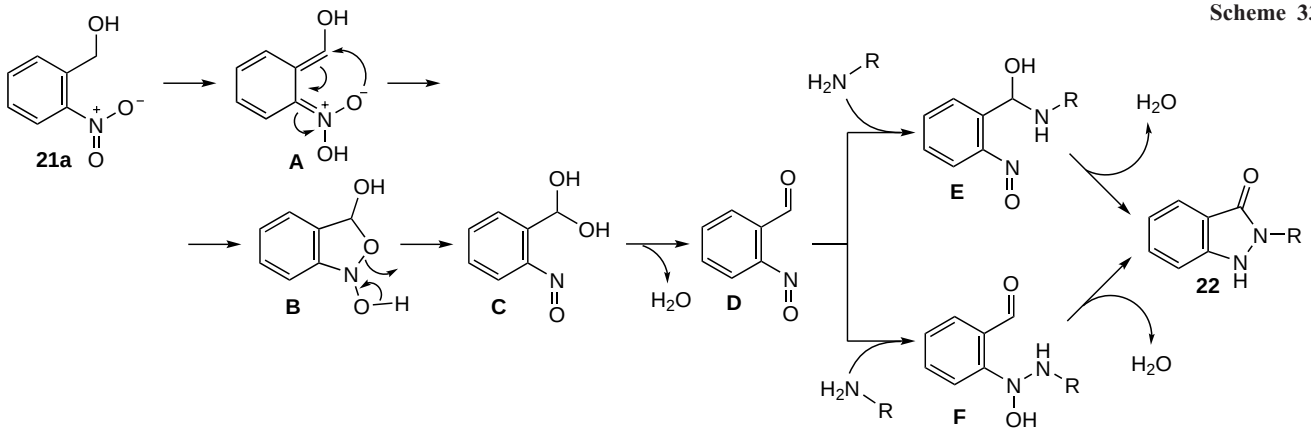
When benzyl-, allyl-, and propargylamines were used to convert *ortho*-nitrobenzyl alcohol **21a** (see Scheme 34) in the KOH–H_2O–Pr^{i}OH system at 100°C, it was impossible to isolate indazolones **22** from the reaction mixtures, unlike examples with alkylamines and anilines. In the case of benzylamine, 2-phenylquinazoline (**23a**), and 3-phenylcinnoline (**24a**) were obtained in relatively low yields; the pathways to these compounds from intermediates **D** and **E** (designations from Scheme 33) are shown in the left- and right-hand parts of Scheme 34.[53] In this transformation, benzylamine acts as a source of not only the nitrogen atom, but also the carbon atom for building the pyrimidine and pyridazine rings.

The reaction of *ortho*-nitrobenzyl alcohols **21** with anilines under conditions indicated in Scheme 35 resulted in the formation of the Davis–Beirut reaction products,[k] 3-alkoxyindazoles **25**.[54]

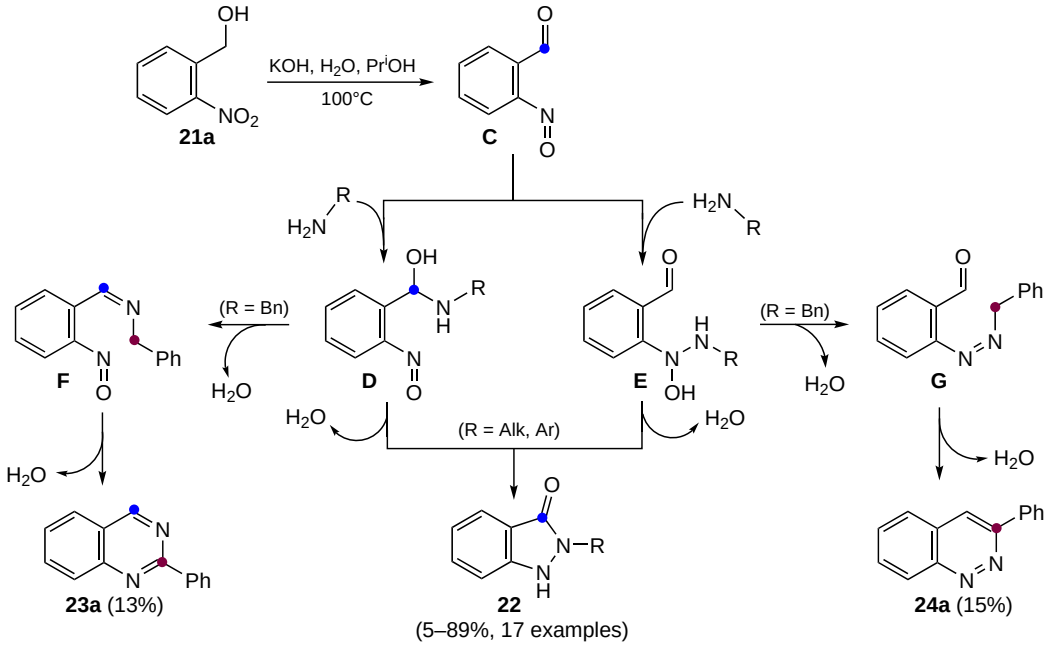
The reactions involving alcohols, which also serve as solvents, follow the mechanism depicted in Scheme 36. However, testing of various alcohols demonstrated that not any alcohol participates in the product formation: in the case of, for

[k] See J.S.Zhu, M.J.Haddadin, M.J.Kurth. *Acc. Chem. Res*., **52**, 2256 (2019); https://doi.org/10.1021/acs.accounts9b00220.

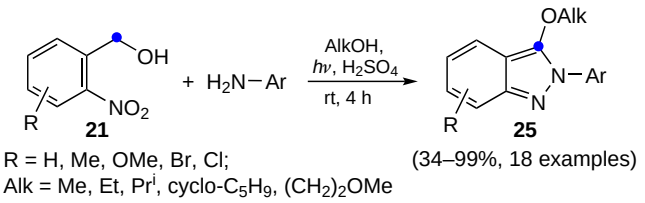
Scheme 33



Scheme 34



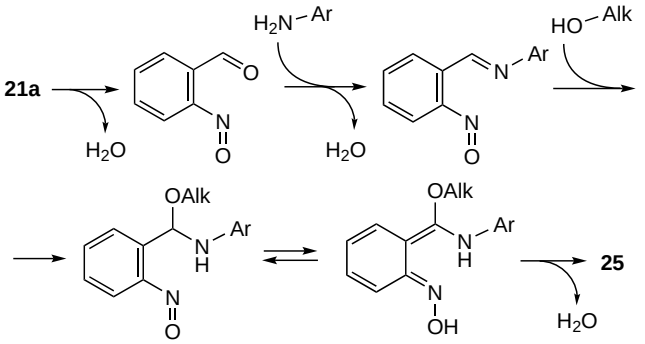
Scheme 35



R = H, Me, OMe, Br, Cl;
Alk = Me, Et, Pr^i, cyclo-C_5H_9, $(CH_2)_2OMe$

(34–99%, 18 examples)

Scheme 36



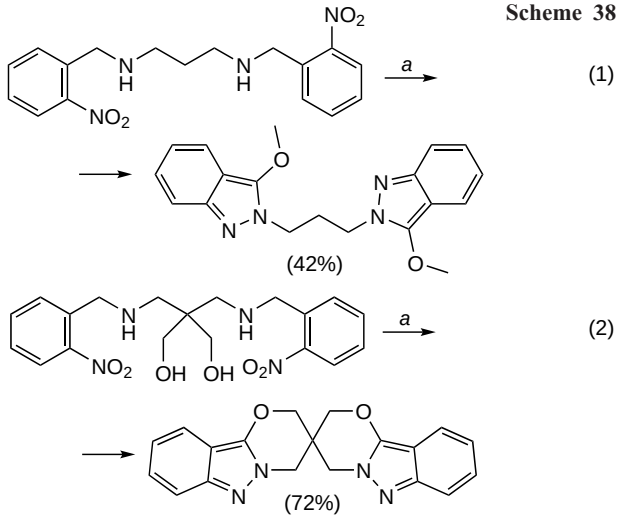
example, Bu^{t}OH, indazolones **22** [R^1 = H: R^2 = Ph (**a**, 64%), C_6H_4OMe-4 (**b**, 71%)] were obtained (see Scheme 32). The reaction of *ortho*-nitrobenzyl alcohol with butylamine in Pr^{i}OH proceeded by the same pathway: 2-butylindazol-3-one **22c** (R^1 = H, R^2 = Bu^n) was isolated in 63% yield.

The reactions of *ortho*-nitrobenzyl alcohol **21a** under conditions indicated in Scheme 35 were also carried out for *ortho*-substituted anilines containing a hydroxyl group in the benzene ring or in a side chain (Scheme 37). These reactions gave annulated indazoles **26a–e**, the yields of which depended on the solvent (Pr^{i}OH or DMSO). In the reactions carried out in Pr^{i}OH, in addition to tetracycles **26a** and **26b**, 3-isopropoxyindazole (**25a**) and indazolo[2,1-*a*]indazol-6-one (**27**) were isolated when 2-aminophenol and 2-aminobenzyl alcohol were used.[54]

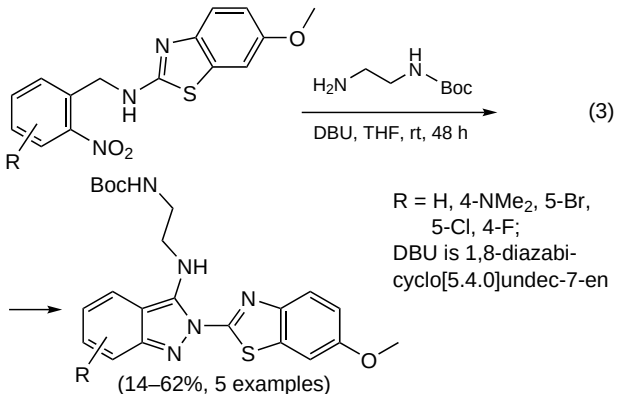
Kurth and co-workers[55] performed the double Davis–Beirut reactions, which gave bis(3-alkoxyindazoles) when compounds with two terminal *ortho*-nitrobenzylamino groups were taken as substrates [reactions (1) and (2) in Scheme 38].

Substituted *N*-(*ortho*-nitrobenzyl)benzothiazole-2-amines react with *tert*-butyl 4-aminobutanoate ($NH_2CH_2CH_2NHBoc$, Boc is *tert*-butoxycarbonyl) to give indazole in which the primary amino group of the reagent replaces the hydrogen atom at position 3 [see reaction (3) in Scheme 38; the positions of substituents in the substrate are indicated].[56]

Scheme 38



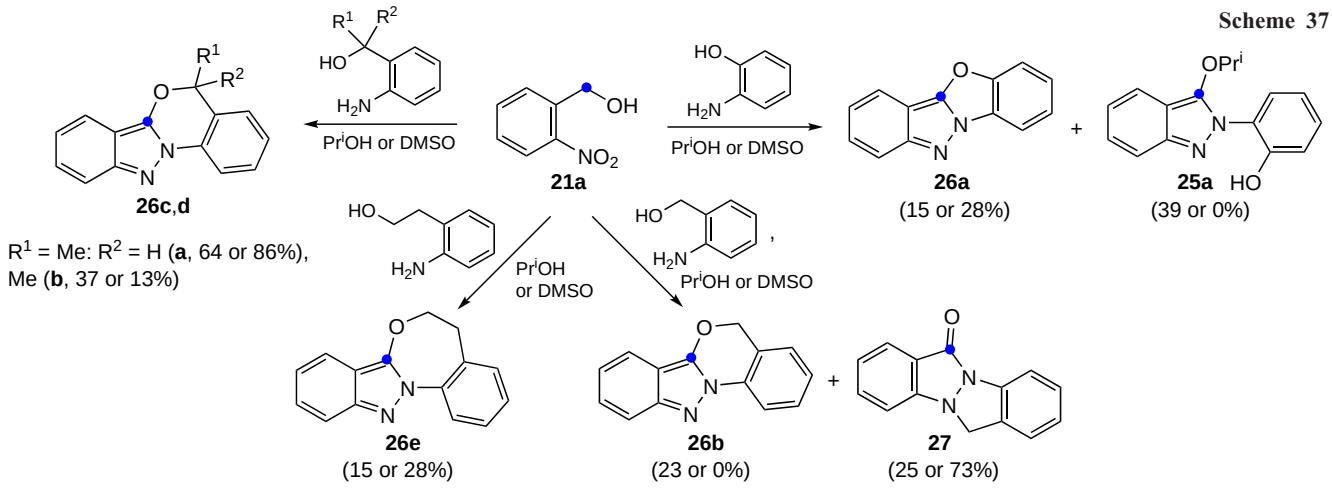
(*a*) KOH, MeOH, H_2O, MW, 100°C, 1 h, sealed tube



R = H, 4-NMe_2, 5-Br, 5-Cl, 4-F;
DBU is 1,8-diazabicyclo[5.4.0]undec-7-en

Thus, under certain conditions, reactions of *ortho*-nitro-substituted benzaldehydes, benzyl bromides, and benzyl alcohols with primary amines result in the synthesis of indazoles (see Scheme 28), indazole oxides (see Scheme 31), and indazolones (see Scheme 32). The reactions of *ortho*-nitrobenzyl alcohols with primary amines in alcohol solutions lead to 3-alkoxyindazoles (Davis–Beirut reactions; see Scheme 35). *ortho*-Nitrobenzylamines in alcohols can provide an

Scheme 37



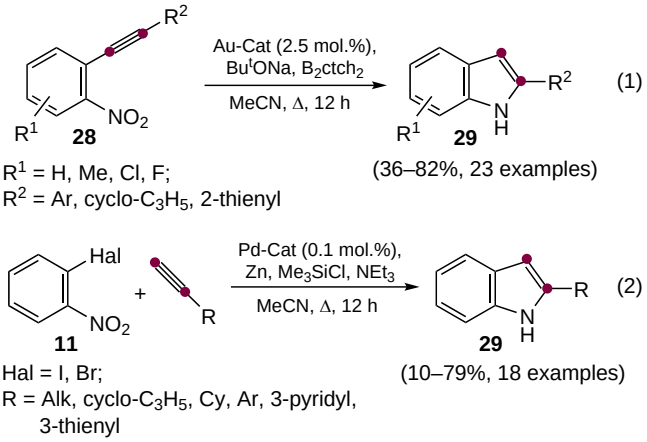
intramolecular course of the Davis–Beirut reaction. In this case, compounds with two terminal *ortho*-nitrobenzylamine groups were converted to bis(3-alkoxyindazoles) [see reactions (1) and (2) in Scheme 38]. Most often, the reactions discussed in this Section do not require the presence of a reducing agent in the system (except for the reaction shown in Scheme 28) and involve the intermediate formation of nitroso compounds.

7. Various *ortho*-functionalized nitroarenes in the synthesis of indoles and carbazoles

Below we consider numerous methods for the design of indole and carbazole systems from nitroarenes *ortho*-functionalized in different ways, either with or without participation of a second reactant.

Indoles are prepared, for example, from *ortho*-alkynylnitroarenes **28** by a catalyzed reduction of the nitro group with bis(catecholato)diboron (B_2ctch_2) and intramolecular closure of the heterocyclic ring involving the triple bond and the amino group [Scheme 39, reaction (1)].[57] The intermolecular reaction of acetylene derivatives with *ortho*-halonitroarenes **11** under the action of zinc, which reduces the nitro group, also gives indoles **29** [see reaction (2) in Scheme 39].[58]

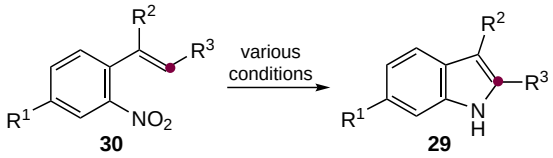
Scheme 39



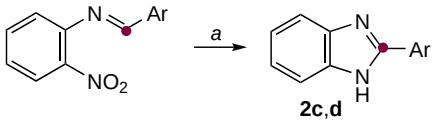
The conversion of *ortho*-nitrostyrene derivatives **30** to indoles (Scheme 40) was called the Cadogan–Sundberg indole synthesis.[59–61] The data on these reactions are summarized in Table 2.

Driver's research group[59] carried out the transformation of *N*-benzylidene-*ortho*-nitroanilines, besides *ortho*-nitrostyrene derivatives **30**, under conditions described in line 1 of Table 2, and thus obtained benzimidazoles **2c**,**d** (Scheme 41).

Scheme 40



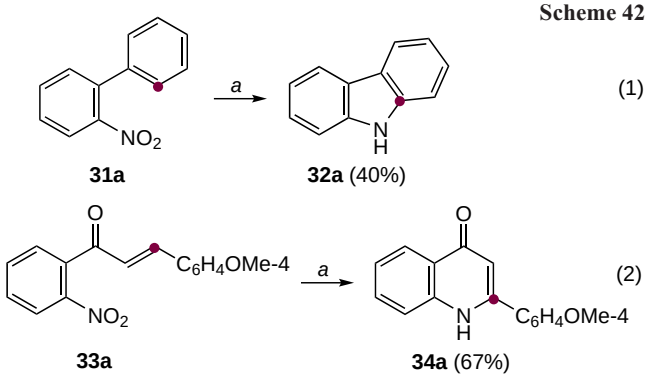
Scheme 41



(*a*) $Pd(OAc)_2$ (5 mol.%), tmphen (10 mol.%), DMF, 100°C, 10 h; Ar = Ph (**c**, 62%), C_6H_4Me-4 (**d**, 52%)

Under conditions presented in line 3 (see Table 2), Ragaini and co-workers[61] converted 2-nitro-1,1′-biphenyl (**31a**) to carbazole **32a** [Scheme 42, reaction (1)], while chalcone derivative **33a** was converted to quinolin-4-one **34a** [see Scheme 42, reaction (2)].

Scheme 42



(*a*) $Pd(MeCN)_2Cl_2$ (1 mol.%), phen (2.5 mol.%), HC(O)OPh, NEt_3, MeCN, 140°C

The research group headed by Professor V.A.Mamedov[62–64] reported the reactions of (*ortho*-nitrophenyl)pyruvic acid (**35a**) and esters **35b–d** and amide **35e** of this acid [Scheme 43, reaction (1)] and methyl 3-(*ortho*-nitrophenyl)glycidate (**36**) [see Scheme 43, reaction (2)] induced by sodium dithionite in aqueous dioxane, which gave indole-2-carboxylic acid (**37a**) and esters **37b–d** and amide **37e** of this acid.

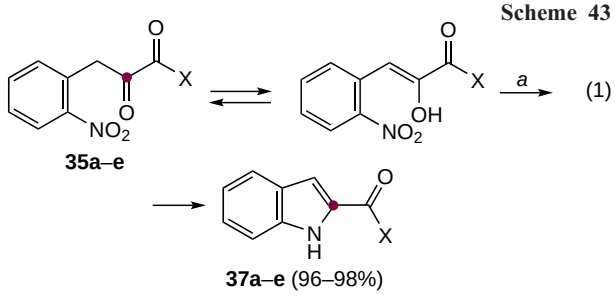
The conversion of glycidate **36** to indolecarboxylic acid **37b** is accompanied by the reduction of the nitro groups, the Meinwald rearrangement with hydrogen migration from the first

Table 2. Synthesis of indoles from *ortho*-nitrostyrene derivatives (see Scheme 40).

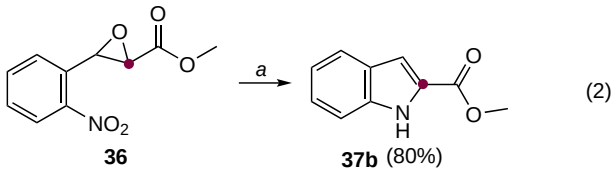
Line	Substrate			Catalyst (amount)	Reducing agent	Base	Solvent	Temperature, °C	Time, h	Number of examples	Yields (%)	Refs
	R^1	R^2	R^3									
1	H	H, Me, Et, Ph	H, Pr, Ar	$Pd(OAc)_2$ (5 mol.%), tmphen (10 mol.%)	$Mo(CO)_6$	–	DMF	100	10	10	40–95	59
2	H	H, Me, C(O)OEt, CN, Ph, Bn	H, Ar, Bz, 2-thienyl	–	B_2pin_2	KF	EtOH	Δ	12	25	25–95	60
3	H, Me, Br, Cl, CF_3	H, Cl, CO_2Me, CN	H, C(O)H, CO_2Me, Ar, Bz	$Pd(MeCN)_2Cl_2$ (1 mol.%), phen (2.5 mol.%)	HC(O)OPh	NEt_3	MeCN	140	3–12	21	45–98	61

Note. The following abbreviations are used: tmphen is 3,4,7,8-tetramethyl-1,10-phenanthroline, pin is pinacolate, phen is phenanthroline.

Scheme 43

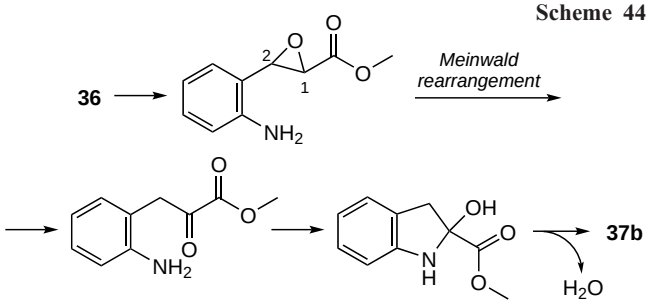


X = OH (**a**), OMe (**b**), OEt (**c**), OPr^i (**d**), NH_2 (**e**)



(*a*) $Na_2S_2O_4$, H_2O, dioxane, Δ, 3 h for (1) and 12 h for (2)

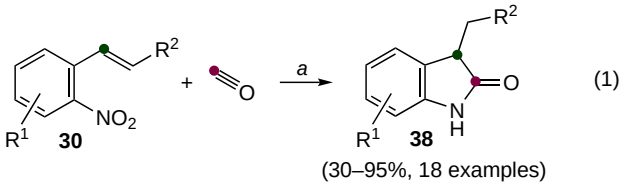
Scheme 44



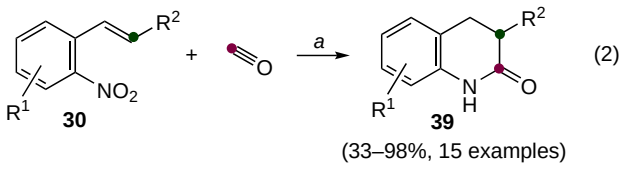
atom of the epoxide ring to the second atom and C(2)–O bond cleavage, intramolecular cyclization involving amino and carbonyl groups, and aromatization of the system accompanied by release of water (Scheme 44).

Li and co-workers[65] selected conditions for the formation of pyrrolidine and piperidine rings in the reactions of *ortho*-nitrostyrenes **30** with CO as a carbon atom source in Pd-catalyzed reactions in the presence of $B(OH)_3$ and $TsOH \cdot H_2O$ [Ts is *para*-toluenesulfonyl (tosyl)] as acidic agents [reactions (1) and (2) in Scheme 45, respectively]. Depending on which

Scheme 45



(*a*) $PdCl_2/PPh_3$ (5 mol.%), $B(OH)_3$, THF, 80°C, 2 h;
R^1 = H, Me, OMe, Cl, C(O)OMe, OAc, Ac, CF_3;
R^2 = H, Me, C(O)OMe, $C(O)NEt_2$

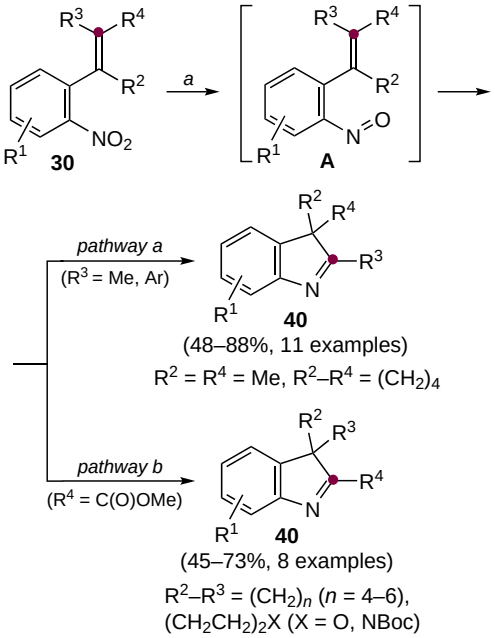


(*a*) $Pd(tfa)_2$/BINAP (5 mol.%), $TsOH \cdot H_2O$, THF, 80°C, 2 h;
R^1 = H, Me, OMe, Cl, C(O)OMe, OAc, Ac; R^2 = H, Me;
tfa is trifluoroacetate, BINAP is 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl

carbon atom of the double bond in styrene **30** the CO carbon atom binds to, the reaction gives indolin-2-ones **38** or 3.4-dihydroquinolin-2-ones **39** (the carbon atom in styrenes involved in the C–C bond formation is coloured green).

Driver and co-workers[66] demonstrated that in the presence of a palladium catalyst and $Mo(CO)_6$ as a reducing agent, *ortho*-nitrostyrenes **30** with the fully substituted double bond undergo cyclization to 3*H*-indoles **40** accompanied by migration of one terminal substituent. The reaction involves the intermediate formarion of *ortho*-nitrososstyrene derivative **A** (Scheme 46).

Scheme 46



(*a*) Pd(OAc) (10 mol.%), phen (20 mol.%), $Mo(CO)_6$ (1 equiv.), $(CH_2Cl)_2$, 120°C, 16 h; R^1 = H, Me, OMe, F, C(O)OMe, CF_3

Scheme 47 demonstrates two special cases of implementation of pathways *a* and *b* giving 3*H*-indoles **40a**,**b** and presents a possible mechanism of conversion of compound **30a** to product **40a**. In these reactions, complete reduction of the nitro group to the amino group does not take place; the nitro group is reduced to a nitroso group, and this is followed by cyclization and migration of substituents.

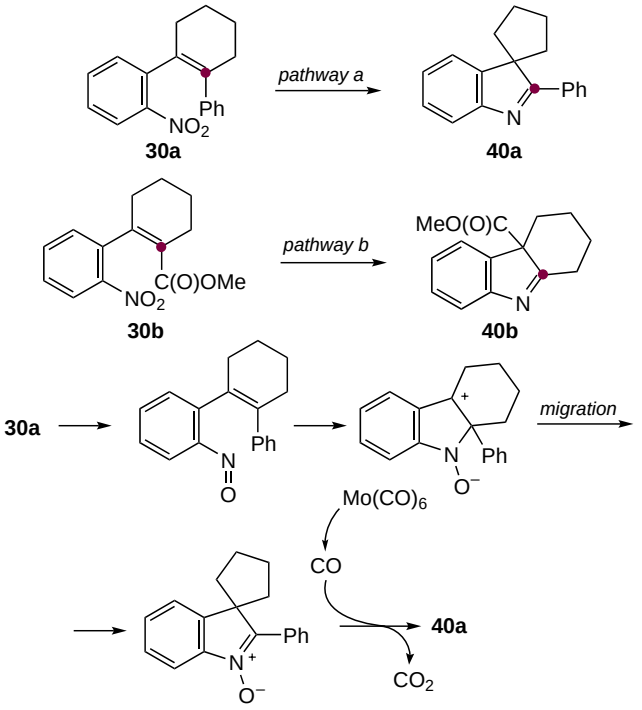
2-Arylindoles **29** were prepared by a catalyzed one-pot process involving *ortho*-nitrobenzyl bromides and *N*-tosylarylhydrazones. Triphenylphosphine added in the first step reduces the nitro group in the intermediate *ortho*-nitrostyrenes **30** (Scheme 48).[67]

The use of *N*-tosyldiarylhydrazones under the same reaction conditions results in the formation of 2.3-diarylindoles **29′** [Scheme 49, reaction (1), conditions *a* and *b* correspond to those shown in Scheme 48],[1] the formation of which from the intermediate styrene derivatives is accompanied by migration of the aryl group [reaction (2)].[67]

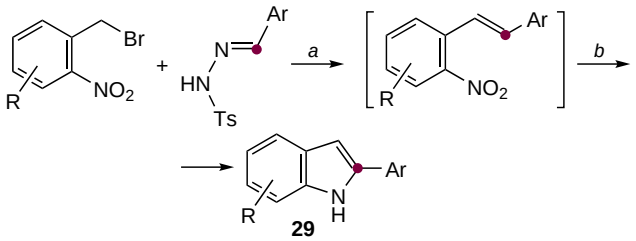
3-Arylindoles **29′** were prepared from *ortho*-nitrobromobenzenes **11** and *N*-tosylhydrazones **41** under similar reaction conditions [Scheme 50, reaction (1)].[68] If the hydrazone contains ethyl or benzyl group instead of methyl, this group forms the substituent in position 2 of indoles **29″** [see Scheme 50,

[1] The primed number of a compound designates the same heterocyclic skeleton, but different substituents.

Scheme 47



Scheme 48



29

(35–72%, 21 examples)

(*a*) $Pd_2dba_3 \cdot CHCl_3$ (2.5 mol.%), $P(2\text{-furyl})_3$ (10 mol.%), $LiOBu^t$, dioxane, 110°C, 3 h, sealed tube;
(*b*) PPh_3, 160°C, 24 h; R = H, OMe, F, CN;
dba is dibenzylideneacetone

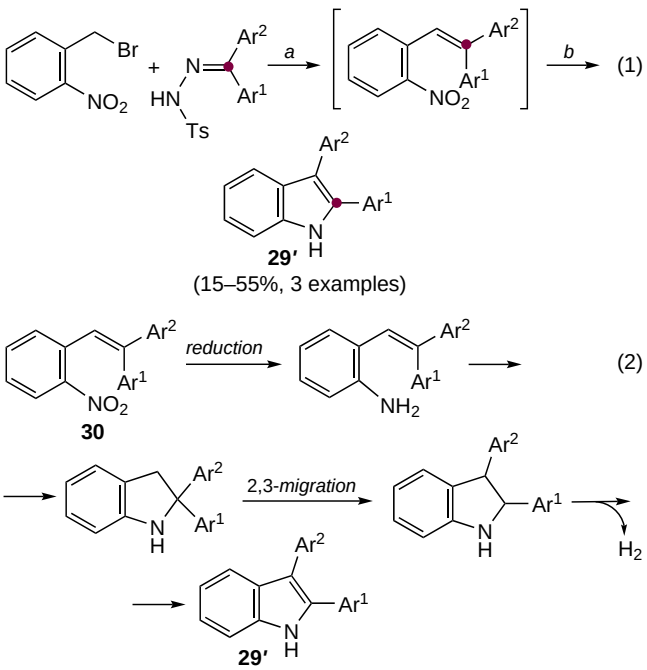
reaction (2)]. In this case, *N*-tosylarylhydrazone **41** supplies two carbon atoms to the indole system.

4(or 5)-Bromo-*ortho*-nitro-substituted biphenyls **31** react with *N*-tosylaryl(methyl)hydrazones **41** under the same conditions to give 4(or 5)-(1-arylvinyl)carbazoles **42** (Scheme 51).[68]

Similarly to the reactions of *ortho*-nitrobromobenzenes **11** with *N*-tosylaryl(methyl)hydrazones **41**, resulting in the synthesis of 3-arylindoles (see Scheme 50), 2-chloro-3-nitroimidazo[1.2-*a*]pyridine (**43**) were first converted to intermediate 3-nitro-2-(1-arylvinyl)imidazo[1.2-*a*]pyridines **44** and then to 3-arylpyrroloimidazo[1.2-*a*]pyridines **45** [Scheme 52, reaction (1)].[69] Compounds **45** were also directly obtained from substrates **44** [see Scheme 52, reaction (2)].[69]

Carbazoles **32** are formed in reactions of *ortho*-nitrobromobenzenes **11** with arylboronic acids catalyzed by palladium acetate. This reaction takes place in the presence of the triphenylphosphine ligand and a base, apparently, through the intermediate formation of *ortho*-aminobiphenyls **46** (Scheme 53).[70]

Scheme 49



29′

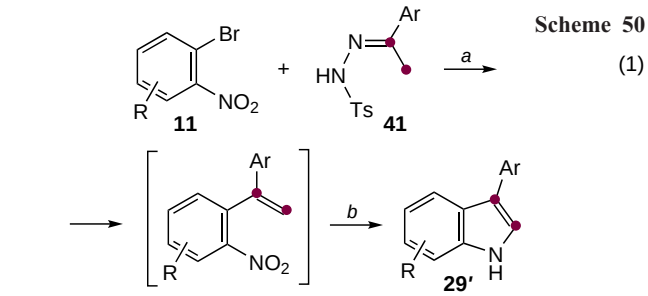
(15–55%, 3 examples)

(2)

30

(*a*) $Pd_2dba_3 \cdot CHCl_3$ (2.5 mol.%), $P(2\text{-furyl})_3$ (10 mol.%), $LiOBu^t$, dioxane, 110°C, 3 h, sealed tube;
(*b*) PPh_3, 160°C, 24 h; R = H, OMe, F, CN;
dba is dibenzylideneacetone

Scheme 50



11 **41** **29′**

R = H, OMe, F, CF_3, CN (54–92%, 19 examples)

(1)

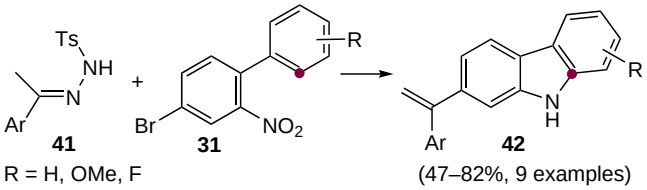
(2)

29″

(66–82%, 4 examples)

(*a*) $Pd_2dba_3 \cdot CHCl_3$ (2.5 mol.%), XPhos (10 mol.%), $LiOBu^t$, dioxane, 110°C, 5 h; (*b*) PPh_3, 160°C, 24 h;
R^1 = H, 4-OMe, 2,4-$(OMe)_2$; R^2 = Me, Ph, C_6H_4OMe-4;
XPhos is 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl

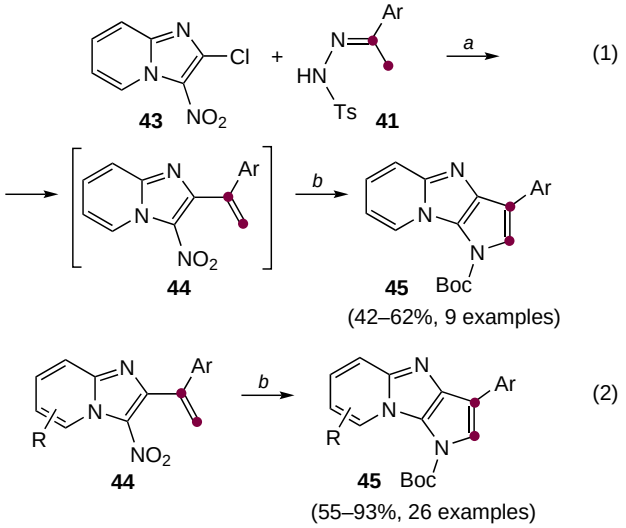
Scheme 51



41 **31** **42**

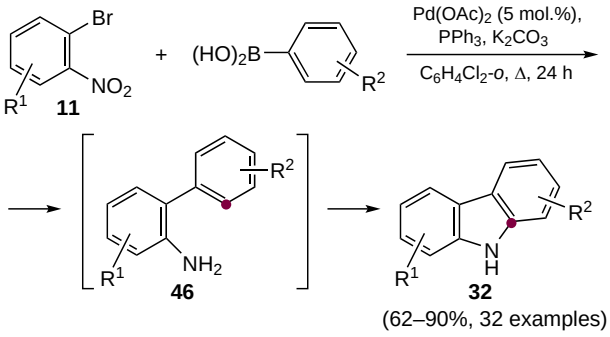
R = H, OMe, F (47–82%, 9 examples)

Scheme 52



(*a*) $Pd_2dba_3 \cdot CHCl_3$ (2.5 mol.%), XPhos (5 mol.%), $LiOBu^t$, dioxane, Δ, MW, 30 min;
(*b*) 1) $MeO_2Cl(DMF)_2$ (10 mol.%), PPh_3, dioxane, Δ, MW, 4 h; 2) Boc_2O, NEt_3, DMAP; DMAP is 4-dimethylaminopyridine;
R = H, Ar

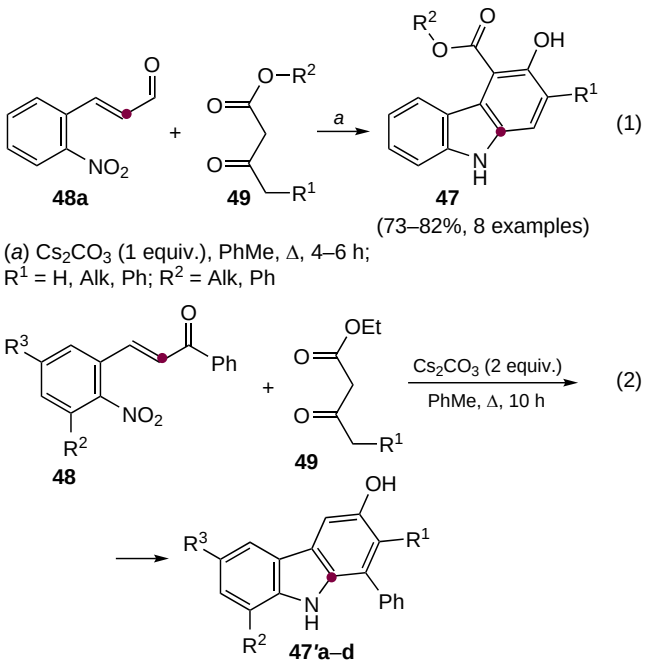
Scheme 53



R^1 = H, Me, OMe, Cl, F; R^2 = H, Alk, OMe, Cl, F, C(O)OMe

Poudel and Lee[71] reported the carbazole synthesis in which they used, on the one hand, *ortho*-nitroaryl-containing α,β-unsaturated aldehydes and ketones and, on the other hand, β-oxocarboxylic acid esters or dibenzyl ketones as reactants (68–88% yields). Scheme 54 shows two synthetic routes to

Scheme 54



(*a*) Cs_2CO_3 (1 equiv.), PhMe, Δ, 4–6 h;
R^1 = H, Alk, Ph; R^2 = Alk, Ph

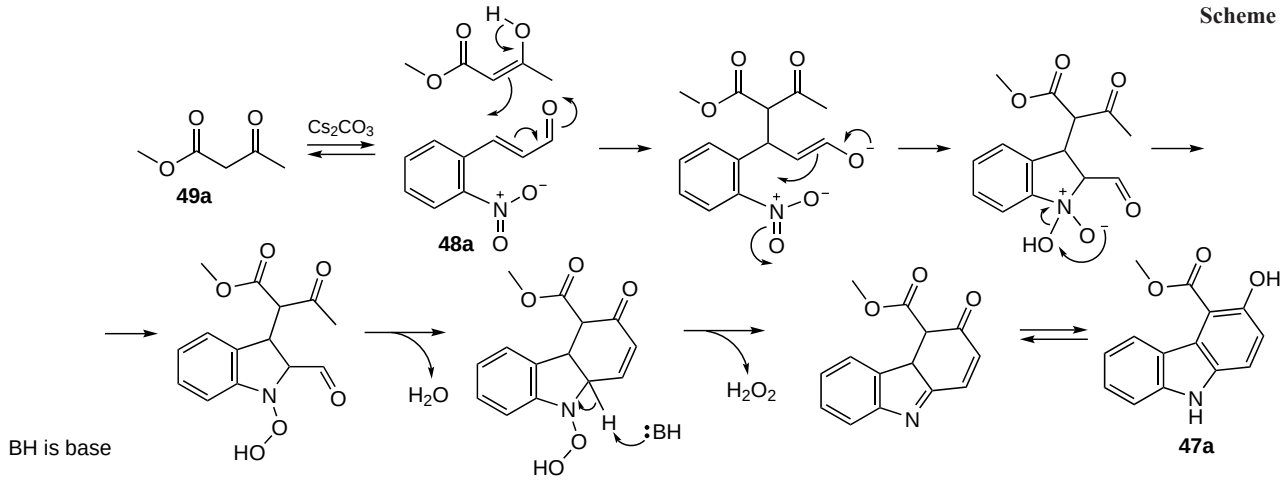
$R^1 = R^2 = R^3$ = H (**a**, 74%); R^1 = Me, $R^2 = R^3$ = H (**b**, 71%);
$R^1 = R^3$ = H, R^2 = OMe (**c**, 75%); R^1 = Me, R^2 = H, R^3 = Cl (**d**, 68%)

carbazoles **47**: the reaction of *ortho*-nitrocinnamaldehyde (**48a**) with ethyl β-oxocarboxylates **49** in the presence of an equimolar amount of Cs_2CO_3 in toluene [reaction (1)] and the reaction of *ortho*-nitrochalcones **48** and ethyl β-oxocarboxylates with a double amount of the base, which afforded deethoxycarbonylated products **47′a–d**.

The mechanism of reaction (1) between *ortho*-nitrocinnamaldehyde (**48a**) and methyl acetoacetate (**49a**) is depicted in Scheme 55. It can be seen that the formation of the indole moiety involves atoms of only the first reactant [compound **48a** or *ortho*-nitrochalcone in reaction (2)], while the second component, β-dicarbonyl compound, takes part in completing the indole ring to carbazole.

The material of this Section demonstrates that the indole system is mainly formed *via* reductive cyclization of *ortho*-nitrostyrene derivatives [see Schemes 40, 45, reaction (1), and Scheme 47]. Even when differently functionalized *ortho*-nitroarenes in combination with other reagents are used to build the indole system, the reactions involve the intermediate

Scheme 55

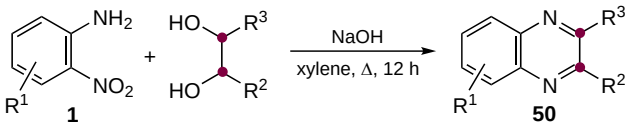


formation of *ortho*-nitrostyrene derivatives (see Schemes 48–50). Carbazoles are formed *via* the reductive cyclization of *ortho*-aryl-substituted nitroarenes (see Schemes 42, 51, and 53) or *via* building-on to the indole system by means of an additional group present in the molecule, as shown in Scheme 55. If CO is introduced as a reactant in the reaction with *ortho*-nitrostyrenes, then indolin-2-ones are formed [see reaction (1) in Scheme 45]. Acetylene derivatives of *ortho*-nitroarenes are also used to build the indole system [see reaction (1) in Scheme 39]. Mention should be made of the reactions that proceed without complete reduction of the nitro group through the formation of intermediate nitroso compounds, in particular, the formation of indoles polysubstituted in the heterocyclic moiety from *ortho*-nitrostyrenes containing the fully substituted double bond (see Scheme 47) and the synthesis of carbazoles by reactions of *ortho*-nitrocinnamaldehyde or *ortho*-nitrohalcones with alkyl β-oxocarboxylates or dibenzyl ketones (see Schemes 54, 55).

8. *ortho*-Nitroanilines and *ortho*-dinitrobenzenes in quinoxaline synthesis

The reactions of *ortho*-nitroanilines **1** or *ortho*-dinitrobenzenes **6** with vicinal diols catalyzed by transition metal compounds in the presence or in the absence of reducing agents give quinoxalines **50**. The catalysts used in these reactions include the Knölker complex[5,72] and other iron complexes,[4] and also cobalt,[73–75] copper,[76] iridium,[77] ruthenium,[78] and nickel[79] compounds. There are examples of transformation of nitroanilines **1** to quinoxalines **50** in reactions with vicinal diols without metal catalysts under the action of NaOH in refluxing xylene (Scheme 56)[80] or in toluene (4–98% yields).[81] Under these conditions, quinoxalines **50** are also formed from *ortho*-dinitrobenzenes **6** (33–54% yields). α-Keto alcohols can serve as carbon sources in reactions with nitroanilines **1** (46–98%).[81]

Scheme 56



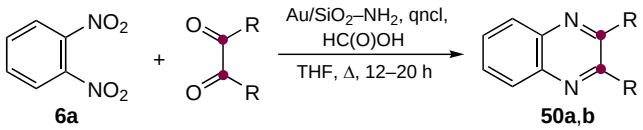
1 **50** (38–94%, 42 examples)

R^1 = H, Me, OH, OMe, NH_2, NMe_2, Br, Cl, C(O)OH, Bz, CF_3, CN;
R^2 = R^3 = Me, Ar, 2-thienyl; R^2 = H, R^3 = Alk;
R^2 = H, R^3 = Ar; R^2–R^3 = $(CH_2)_4$

When α-diketones that bring two carbon atoms to the newly formed quinoxaline system are used in the reactions with nitroanilines **1** or dinitrobenzenes **6**, a reducing agent is required. The nitro group is reduced by formic acid (Scheme 57),[82] hydrazine hydrate,[83] or H_2.[84,85]

The reactions of nitroanilines **1** or dinitrobenzenes **6** with α-diketones carried out in water in the presence of diboronic acid (Scheme 58)[86] or B_2ctch_2 (Ref. 87) give 1,2,3,4-tetrahydroquinoxalines **51**. In these reactions, boron-containing compounds

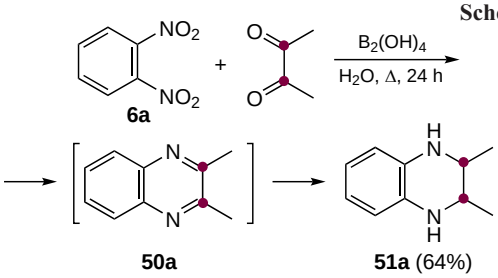
Scheme 57



6a **50a**,**b**

R = H (**50a**, 70%), Ph (**50b**, 50%); qncl is quinuclidine

Scheme 58

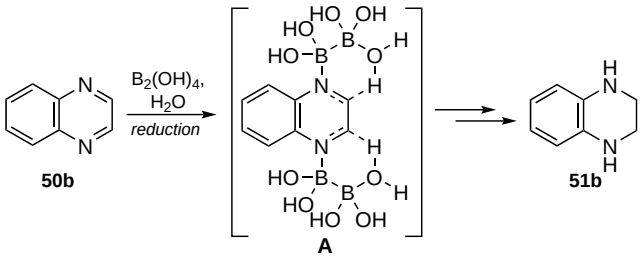


6a **50a** **51a** (64%)

reduce the nitro groups and also participate in the pyrazine ring hydrogenation in the intermediate compound **50**.

Presumably, the role of boron-containing compounds in the hydrogenation of quinoxalines **50** is to coordinate quinoxalines and water molecules to form type **A** transition states, in which water acts as a source of hydrogen atoms to convert the pyrazine ring into a piperazine ring (Scheme 59).[86]

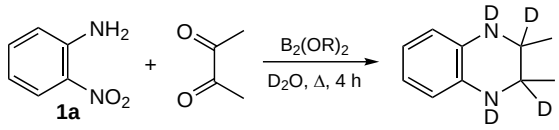
Scheme 59



50b **A** **51b**

The role of water as a source of hydrogen atoms in these reactions was proved by control experiments with deuterated water as a solvent (Scheme 60).[86]

Scheme 60

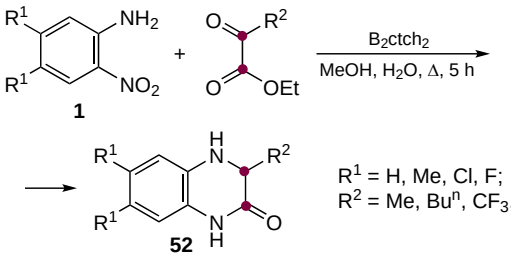


1a

R = H, ctch

When α-keto esters were allowed to react with *ortho*-nitroanilines **1** in the presence of B_2ctch_2, the reduction of nitro groups, condensation of the intermediate diaminobenzenes **3** with α-keto esters, and hydrogenation of intermediate quinoxaline-2-ones afforded 3.4-dihydroquinoxalin-2-ones **52** (Scheme 61).[87]

Scheme 61



1 **52** (70–97%, 10 examples)

R^1 = H, Me, Cl, F;
R^2 = Me, Bu^n, CF_3, Ar

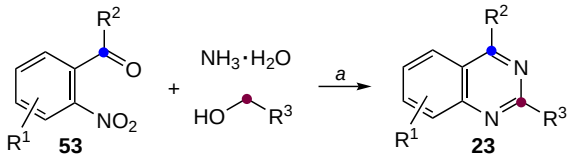
Thus, quinoxalines, 1.2.3.4-tetrahydroquinoxalines, and 3.4-dihydroquinoxalin-2-ones were synthesized by the reactions of *ortho*-nitroanilines and *ortho*-dinitrobenzenes with vicinal diols, α-keto alcohols, and α-dicarbonyl compounds under various reaction conditions.

9. *ortho*-Nitroacetophenones and *ortho*-nitrobenzyl alcohols in the synthesis of quinazolines

The construction of the quinazoline system from *ortho*-nitroacetophenones and *ortho*-nitrobenzyl alcohols requires compounds that would supply nitrogen and carbon atoms. As in the previous cases of building up heterocyclic structures, the carbon atom may come from alcohols (if a transition metal catalyst is present) or aldehydes (in the presence of a reducing agent). The required nitrogen atom can be provided by ammonia or another nitrogen-containing component. In this approach to construction of the quinazoline system, three components should participate in the reaction, and this is most often implemented in practice.

Quinazolines **23** were obtained in three-component reactions involving *ortho*-nitroacetophenones **53**, ammonia, and alcohols (Scheme 62).[88]

Scheme 62



(*a*) Au–NP/TiO_2 (0.8 mol.%), PhMe, H_2O, N_2, 130–150°C, 20 h;
R^1 = H, Me, Hal; R^2 = Alk, Ar; R^3 = Alk, Cy, Ar

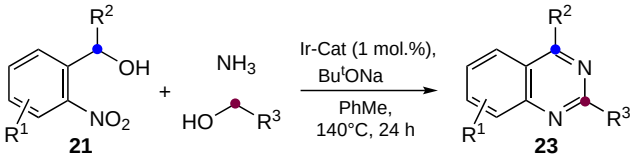
In this process, the alcohol is converted to an aldehyde under the action of gold catalyst, while acetophenones **53** are converted to the corresponding imine derivatives **A** under the action of ammonia. Hydrogen released upon the alcohol reduction is combined with the gold particles and reduces the nitro group in intermediate **A** to amino group in imine **B**. The intermediate **B** reacts with aldehyde, being converted to diimine **C**, which cyclizes to give quinazoline **23** (Scheme 63).

In the three-component reactions of *ortho*-nitrobenzyl alcohols **21**, aliphatic alcohols, and ammonia (Scheme 64), iridium catalyst triggers the conversion of benzyl alcohols to acetophenone derivatives or conversion of aliphatic alcohols to aldehydes, thus releasing hydrogen needed for nitro group reduction and for the subsequent reactions towards quinazolines **23**.[89]

Quinazolines were also obtained in the catalyzed reaction involving *ortho*-nitroacetophenone, ammonium formate, and aldehydes (Scheme 65); in this case, ammonium formate acts as a source of ammonia and reduces the nitro group (see the lower part in Scheme 65).[39]

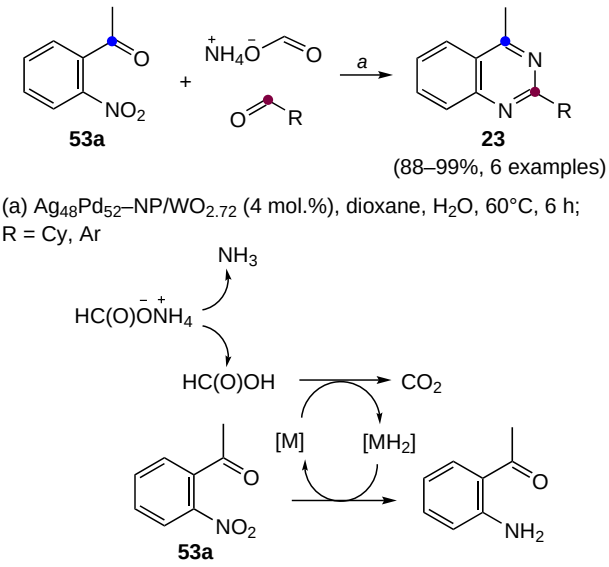
Glycine derivatives were used in reactions with *ortho*-nitrobenzyl alcohols **21** as compounds that simultaneously supply C and N atoms for the formation of quinazolines **23** (Scheme 66).[90] Similarly to what is depicted in Scheme 9, amino acid is converted to aldehyde under the action of the catalyst,

Scheme 64



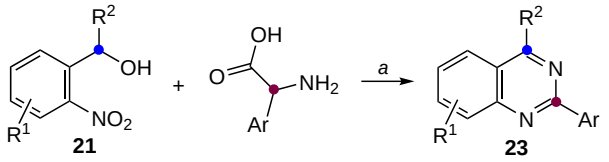
R^1 = H, Me, OMe, Hal;
R^2 = H, Me, Ph; R^3 = H, Alk, Ar

Scheme 65



(a) $Ag_{48}Pd_{52}$–NP/$WO_{2.72}$ (4 mol.%), dioxane, H_2O, 60°C, 6 h;
R = Cy, Ar

Scheme 66

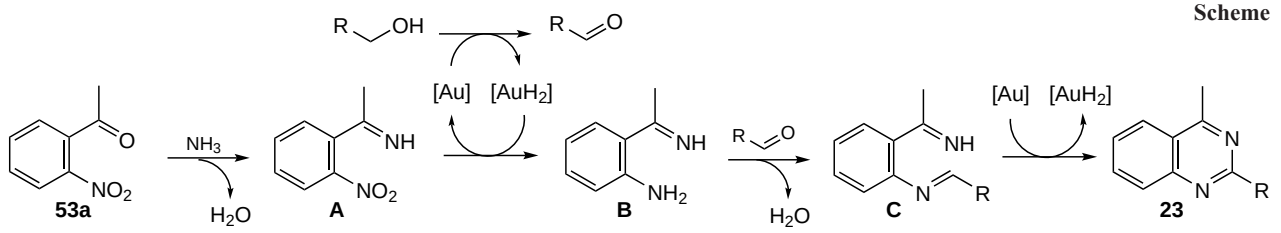


(*a*) $(NH_2)_2C{=}O$, Fe–Mo–Se (2 mol.%), TEDA, 120°C, 6–8 h;
R^1 = H, Me, OMe; R^2 = H, Me, Ph; TEDA is triethylenediamine

thus releasing CO_2 and NH_3, the catalyst converts benzyl alcohol **21** to acetophenone, thus generating hydrogen, which is needed to reduce the nitro group. This is followed by the reaction of acetophenone, ammonia, and aldehyde, the same as described in many above examples.

Thus, *ortho*-nitroacetophenones and *ortho*-nitrobenzyl alcohols can be converted to quinazolines *via* catalytic reactions in the presence of carbon atom sources (most often, alcohols or aldehydes) and nitrogen atom sources, represented by ammonia or ammonium-generating compounds.

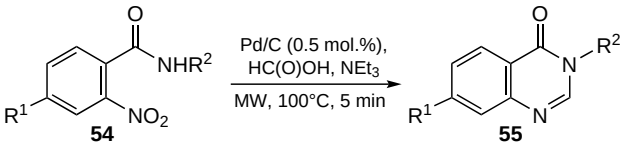
Scheme 63



10. *ortho*-Nitrobenzamides, *ortho*-nitrobenzonitriles, *ortho*-nitrobenzaldehydes, and *ortho*-nitrobenzyl alcohols in the synthesis of quinazolin-4-ones

Scheme 6 in Section 2 shows the conversion of *ortho*-nitroanilines **1** to benzimidazoles **2** under the action of formic acid in the presence of a palladium catalyst. Under the same conditions, *ortho*-nitrobenzamides **54** are converted to quinazolin-4-ones **55** (Scheme 67).[20] Formic acid acts as a reducing agent and a reactant supplying a carbon atom to the nascent quinazoline system.

Scheme 67

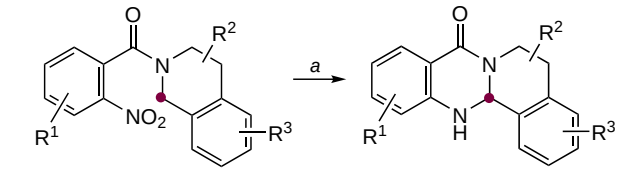


54 **55**

R^1 = H, OMe, F; R^2 = H, Alk, Ar, Het (63–95%, 14 examples)

By analogy with the reaction depicted in Scheme 17, *ortho*-nitrobenzamides with a 1.2.3.4-tetrahydroisoquinoline moiety as an amide component were converted to 1,2,3,4-fused tetrahydroisoquino-1.2-dihydroquinazoline systems *via* reduction and intramolecular cyclization (Scheme 68).[27] Substrates containing a pyrrolidine ring instead of the piperidine ring can also react in this way (the product yields are 75–94%).[27]

Scheme 68



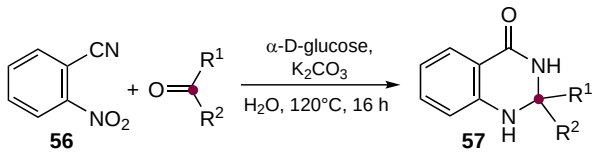
(38–92%, 20 examples)

(*a*) $PhNHC(S)NH_2$ (20 mol.%), LED (395 mm), $PhSiH_3$, dioxane, N_2, rt, 12–36 h;
R^1 = H, Me, OMe, Hal, C(O)OMe;
R^2 = H, Me C(O)OMe; R^3 = H, Me, OMe, OH, Hal

ortho-Nitrobenzonitriles are often used as the starting compounds in the synthesis of quinazolin-4-ones **55**. The nitrile group tends to be converted to amide group upon hydrolysis, which is a necessary step on the way from *ortho*-nitrobenzonitrile (**56**) to quinazolinones **54** *via* reactions with compounds that supply a carbon atom: alcohols,[91] aldehydes or ketones,[92–94] and aryl-substituted glycine derivatives.[21] While being oxidized to aldehydes under the action of transition metal catalysts, alcohols release hydrogen, which is spent for the reduction of the nitro group (this process is depicted, for example, in Scheme 2). When aldehydes or ketones serve as sources of the carbon atom, the system must contain a reducing agent together with the catalyst[92,93] or without a catalyst.[94] In the formation of 2,3-dihydroquinazolin-4(1*H*)-one **57** (Scheme 69), α-D-glucose acts as a reducing agent: in a basic medium, it generates hydrogen needed to reduce the nitro group (Scheme 70).

Sahoo and Pal[95] developed a one-pot process for the preparation of quinazolin-4-ones **55′** from *ortho*-nitrobenzaldehydes **13** and urea with subsequent addition of hydrazine hydrate and aliphatic or (hetero)aromatic aldehyde in the

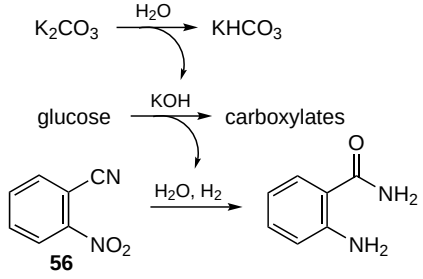
Scheme 69



56 **57**

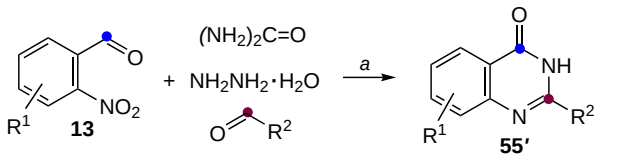
R^2 = H: R^1 = Bu^n, Ar;
R^1–R^2 = $(CH_2)_n$ (*n* = 4, 5) (18–90%, 18 examples)

Scheme 70



56

Scheme 71



13 **55′**

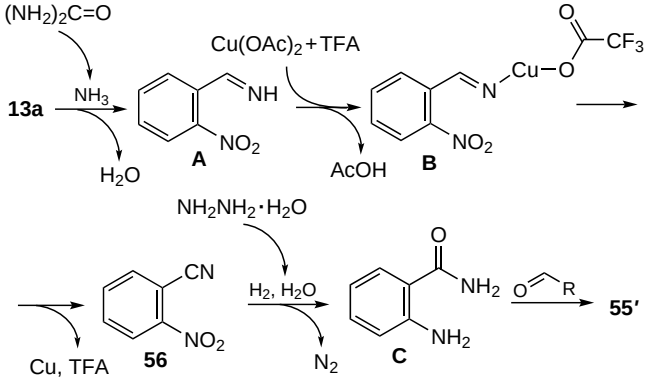
(47–88%, 22 examples)

(*a*) $Cu(OAc)_2$ (20 mol.%), TFA (20 mol.%), DMSO, 110°C, 6 h;
R^1 = H, NH_2, Hal, CF_3; R^2 = H, Me, Ar, Het

presence of the $CuOAc_2$–trifluoroacetic acid (TFA) catalytic system (Scheme 71).

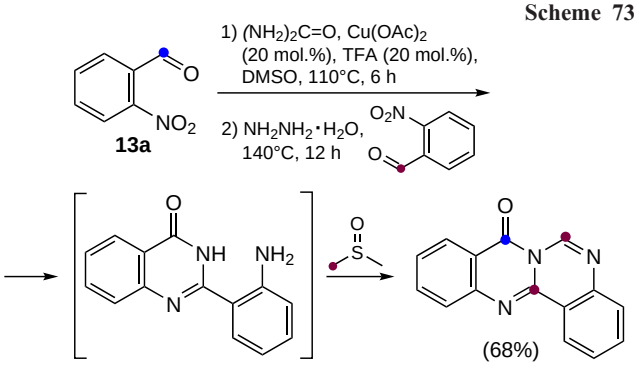
In this case, urea generates ammonia, which reacts with aldehyde **13a**, and thus compound **13a** is converted to imine **A**. Under the action of copper acetate and TFA, **A** is converted to salt **B**, which transforms to *ortho*-nitrobenzonitrile **56**. Here hydrazine is the reducing agent for the nitro group generating hydrogen, and, with participation of water, it converts *ortho*-aminobenzonitrile **56** to *ortho*-aminobenzamide **C**, which reacts with aldehydes to give product **55′** with R^1 = H, R^2 = R (Scheme 72).[95]

Scheme 72



When the substrate is used as the aldehyde component in the second step of the reaction of *ortho*-nitrobenzaldehyde **13a** under the same conditions, quinazolino[4.3-*b*]quinazolin-8-one is obtained. In the formation of the product, DMSO serves as not only a solvent, but a reagent providing a carbon atom for the

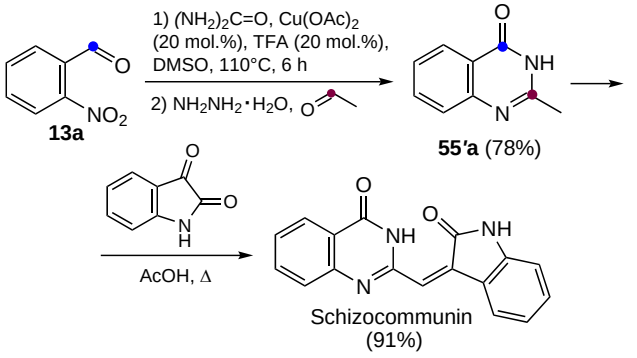
Scheme 73



construction of the heterocycle fused to quinazolinone (Scheme 73).[95]

In the case of acetaldehyde being introduced in the same reaction, the reaction gives 2-methylquinazolin-4-one (**55′a**), which reacts with isatin in refluxing acetic acid to give schizocommunin, a fungal natural alkaloid (Scheme 74).[95]

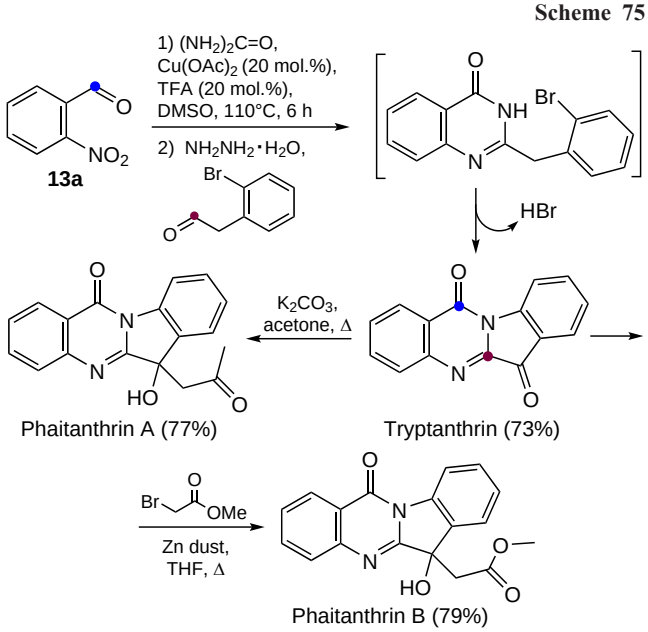
Scheme 74



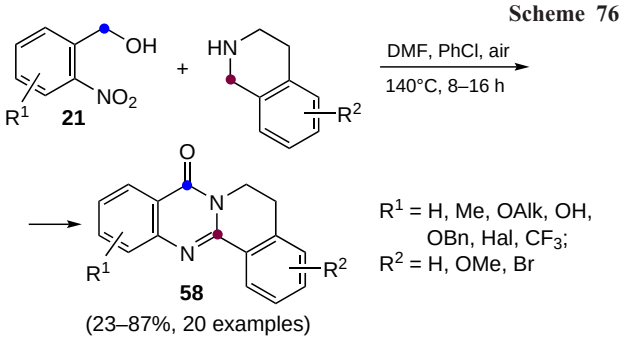
The use of 2-(2-bromophenyl)acetaldehyde as the aldehyde component made it possible to prepare a natural compound, tryptanthrin, which is converted to the natural compound phaitanthrin A when mixed with K_2CO or to phaitanthrin B upon the Reformatsky reaction with 2-bromoacetate B (Scheme 75).[95]

Phan's research group[96] synthesized 1,2,3,4-tetrahydroisoquino[1.2-*b*]quinazolin-4-ones **58** by the reactions of *ortho*-nitrobenzyl alcohols **21** with 1.2.3.4-tetrahydroisoquinolines on

Scheme 75



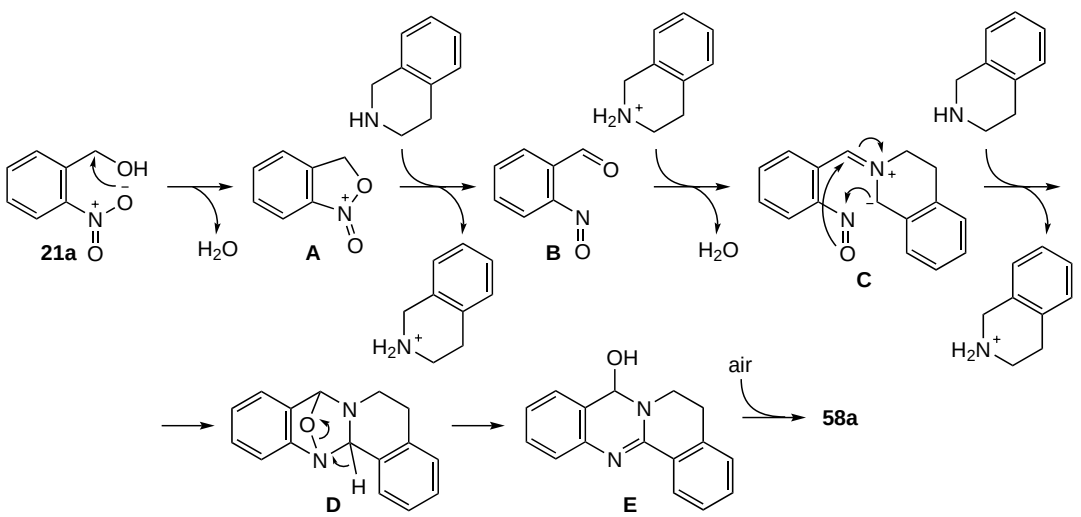
Scheme 76



heating in a mixture of DMF and chlorobenzene with air being passed through the reaction mixture (Scheme 76).

The mechanism of this reaction is depicted in Scheme 77 in relation to the unsubstituted *ortho*-nitrobenzyl alcohol **21a**. Substrate cyclization takes place to give intermediate **A**, followed by the formation of nitroso compounds **B** and **C** with tetrahydroisoquinoline acting as a base and a reactant, and cyclization of intermediate **C** to give **D** and then fused

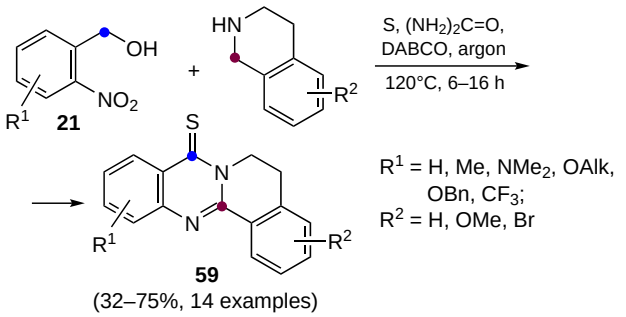
Scheme 77



quinolinoquinazoline system **E**, the hydroxyl group oxidation in which leads to product **58a**.

The addition of elemental sulfur, 1,4-diazabicyclo[2,2,2]-octane (DABCO), and urea to the reaction mixture under argon affords quinazoline-4-thiones fused to the tetrahydroquinoline system **59** (Scheme 78).[96] In this case, nitrosobenzaldehyde **B** (see the corresponding intermediate in Scheme 77) is reduced to *ortho*-aminobenzaldehyde by the S–DABCO complex, then an intermediate similar to heterocycle **E** (but devoid of the hydroxyl group in the quinazoline part) is formed over a few steps; under the action of the S–DABCO complex, this intermediate is converted to product **59**.

Scheme 78



(32–75%, 14 examples)

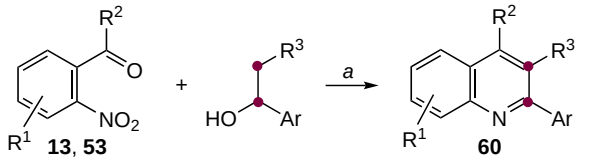
Thus, the formation of a quinazoline system from *ortho*-nitrobenzamides and *ortho*-nitrobenzonitriles requires, apart from a reducing agent, a source of a carbon atom, while for the formation of quinazolines from *ortho*-nitrobenzaldehydes and *ortho*-nitrobenzyl alcohols, sources of both carbon and nitrogen atoms are needed. It is noteworthy that the reaction of *ortho*-nitrobenzyl alcohols with 1,2,3,4-tetrahydroisoquinolines, leading to 1,2,3,4-tetrahydroisoquino[1,2-*b*]quinazolin-4-ones (see Scheme 76), proceeds without the addition of catalysts or reducing agents to the reaction medium, through the formation of intermediate nitroso compounds (see Scheme 77).

11. *ortho*-Nitrobenzaldehydes, *ortho*-nitroacetophenones, *ortho*-nitrobenzyl alcohols, and *ortho*-nitrobromobenzenes in the synthesis of quinolines and quinolinones

A conventional method for the synthesis of quinolines is the Friedländer reaction,[m] that is, the reaction of *ortho*-aminobenzaldehydes with aldehydes or ketones containing a methylene unit or methyl group adjacent to the carbonyl group in the presence of bases. In order to avoid side effects related, for example, to the self-condensation of *ortho*-aminobenzaldehydes, the reactions of *ortho*-nitrobenzaldehydes are performed with aldehydes[97] or alcohols,[12,98,99] capable of providing two carbon atoms for the formation of the pyridine ring in quinoline. In the transition metal-catalyzed reactions, the alcohol becomes the source of hydrogen, which reduces the nitro group being converted to aldehyde (see Scheme 2), and thus enables the subsequent Friedländer reaction. As the alcohol component in the synthesis of quinolines **60** by catalyzed reactions of *ortho*-nitrobenzaldehydes **13** and *ortho*-nitroacetophenones **53**, Li *et al*.[98] used 1-aryl-substituted ethyl or propyl alcohols, and the aryl moiety became the substituent in position 2 of quinolines (Scheme 79).

[m] See P.Friedländer. *Ber. Dtsch. Chem. Ges*., **15**, 2572 (1882).

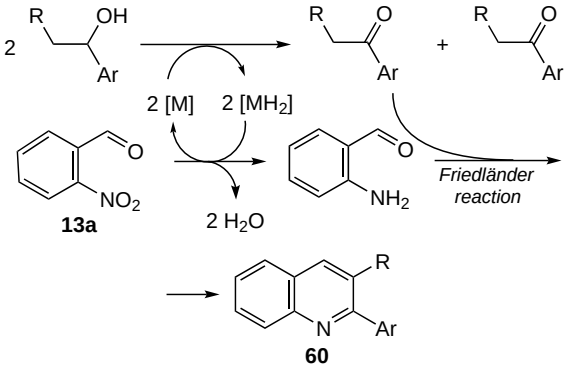
Scheme 79



(*a*) $Ru(PPh_3)_3Cl_2$ (5 mol.%), K_2CO_3, PhCl, Δ, 24 h; (46–83%, 14 examples)
R^1 = H, OMe, Cl, F; R^2 = H (**13**), Me (**53**); R^3 = H, Me

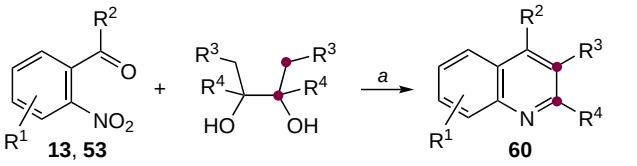
The reaction pathway is depicted in Scheme 80 in relation to *ortho*-nitrobenzaldehyde (**13a**). The pathway includes the reduction of the nitro group in substrate **13a** with hydrogen released from the alcohol under the action of the catalyst and the Friedländer reaction involving *ortho*-aminobenzaldehyde and the aldehyde formed from the alcohol.

Scheme 80



Sanz and co-workers[99] used butane-2.3-diol derivatives (Scheme 81) as the alcohol components in reactions of this type; the diols provided two carbon atoms for the pyridine ring of quinolines **60**, which were isolated after these reactions in moderate to high yields.

Scheme 81

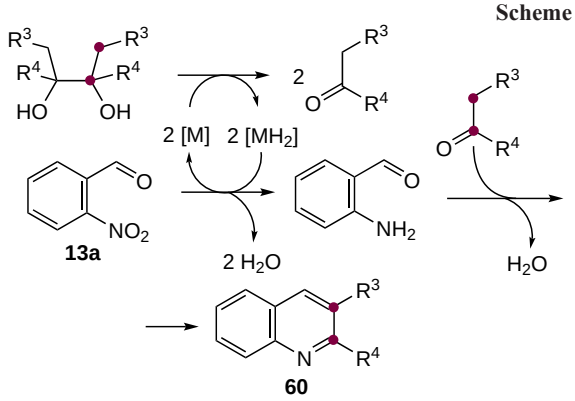


(44–89%, 31 examples)
(*a*) $MoO_2Cl_2(DMF)_2$ (5 mol.%), Me_2NH, MW, 26–60 min;
R^1 = H, Me, NMe_2, Hal, C(O)OMe, CF_3; R^2 = H, Me, CF_3;
R^3 = Alk, Ar, Het; R^4 = H, Me

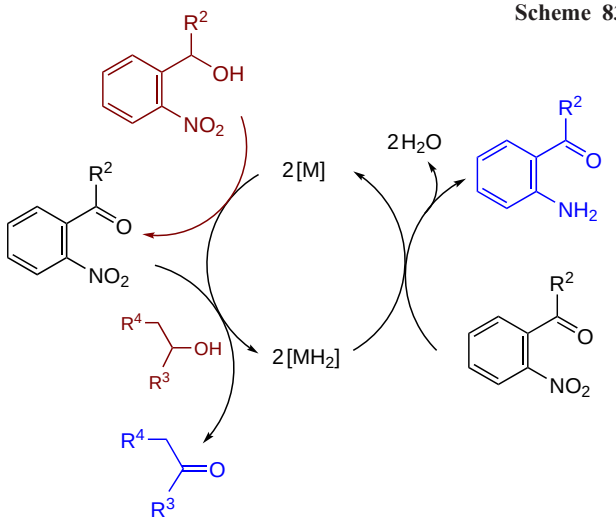
The transformation pathway of benzaldehyde **13a** to quinolines **60** induced by diols (Scheme 82) differs from that shown in Scheme 80 for monohydric alcohols only by the fact that an equimolar amount of diol is sufficient for generating hydrogen needed for the substrate reduction.

If *ortho*-nitrobenzyl alcohols are used in reactions with alcohols providing carbon atoms for the quinoline system, the oxidation of both hydroxyl groups in both reactants (coloured red in Scheme 83) and reduction of the nitro groups take place under the action of the catalyst. The subsequent process includes the Friedländer reaction between the formed aldehyde or ketone and *ortho*-aminobenzaldehyde or *ortho*-aminoacetophenone (coloured blue).[100–105] The studies performed along this line are concerned, first of all, with the selection of catalysts aimed at increasing the yields of products and decreasing the process prime cost.

Scheme 82



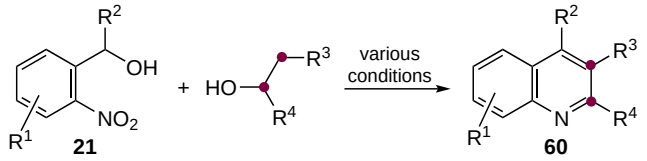
Scheme 83



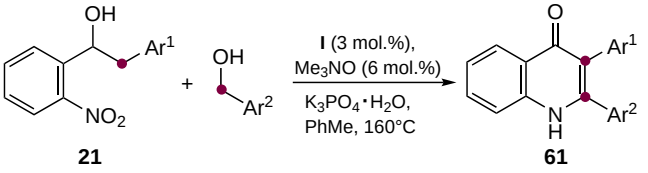
The reaction of *ortho*-nitrobenzyl alcohols with various aliphatic alcohols is presented in the general form in Scheme 84, while the conditions used in these reactions are summarized in Table 3.

ortho-Nitrobenzyl alcohols **21** containing an additional benzyl group adjacent to the CHOH moiety are converted to quinolin-4-ones **61** by reactions with benzyl alcohols catalyzed by the Knölker complex (**I**) in the presence of a base (Scheme 85).[105]

Scheme 84



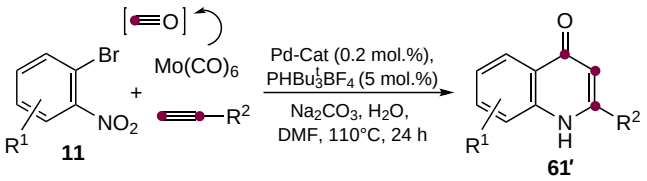
Scheme 85



(22–84%, 12 examples)

2-Substituted quinolin-4-ones **61′** were synthesized by palladium-catalyzed three-component reactions of *ortho*-nitrobromobenzenes **11**, acetylene derivatives, and $Mo(CO)_6$, which acts as a source of carbon monoxide (Scheme 86).[106] The CO molecule released from $Mo(CO)_6$ forms the C=O group in the product, while acetylene provides two carbon atoms for the construction of the quinoline system.

Scheme 86



R^1 = H, Me, OMe, Cl, F;
R^2 = Alk, Ar, 2-thienyl

(68–91%, 27 examples)

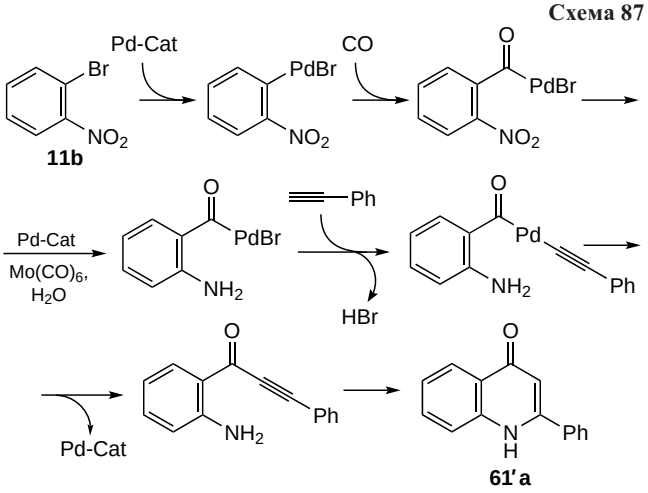
The mechanism of palladium-catalyzed conversion of *ortho*-nitrobromobenzene (**11b**) to product **61′a** is shown in Scheme 87. The palladium catalyst promotes the incorporation of the carbonyl group and acetylene moiety into the molecule. Apart from palladium and molybdenum complexes, water also takes place in the reduction of the nitro groups. The last step is the intramolecular addition of the amino group to the triple bond of the acetylene moiety giving the quinolinone system.

Table 3. Synthesis of quinolines from *ortho*-nitrobenzyl alcohols with aliphatic alcohols (see Scheme 84).

Line	Substituents				Catalyst	Reducing agent	Base	Solvent	Temperature, °C	Time, h	Number of examples	Yields (%)	Refs
	R^1	R^2	R^3	R^4									
1	H, OMe, Cl	H	H, Alk, Ph	H, Ar	$Ru_3(CO)_2$, dppf	–	Bu^tOK	TAA	150	18–20	25	40–79	100
2	H, OMe, Cl, F	H, Me, CF_3	H, Me, Ph	H, Pr^n, Ar	dppf	HC(O)OH	NPr^i_3	Toluene	150	24	18	39–79	101
3	H	H	H, Alk	Ar, 2-pyridyl	[Ir]	–	KOH	H_2O	100–120	24	7	69–92	102
4	H	H	Alk, Ar	H	$NiCl_2 \cdot DMF$, phen	–	Bu^tOK	*n*-Xylol	130	20	6	30–82	103
5	H, OMe	H	H	Ar, Het	Pd-NP, ZnO	–	–	–	130–150	24	28	63–89	104
6	H, Me, OMe, Hal	H, Me, Et, Cl, F, Ar	H, Alk	Ar, Het	Knolker complex (**I**), Me_3NO	–	–	Toluene	160	24–48	39	22–90	105

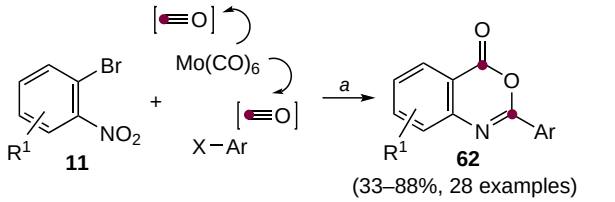
Note. The following abbreviations are used: dppf is 1,1′-bis(diphenylphosphino)ferrocene, TAA is *tert*-amyl alcohol.

Схема 87



The three-component reactions of *ortho*-nitrobromobenzenes **11**, aryl halides or aryl trifluoromethanesulfonates, and $Mo(CO)_6$ catalyzed by palladium in the presence of a phosphine ligand yield 2-aryl[*d*][1,3]oxazin-4-ones **62** (Scheme 88).[107] Two CO molecules participate in the construction of the oxazine moiety.

Scheme 88



(*a*) $Pd(OAc)_2$/xantphos (5 mol.%), $NEtPr^i_2$, dioxane, Δ, 24 h;
R^1 = H, Me, Br, F, C(O)OMe; CF_3; X = I, Br, OTf;
xanthene (9,9-dimethylxanthene-4,5-diyl)bis(diphenylphosphine),
Tf is trifluoromethansulfonyl

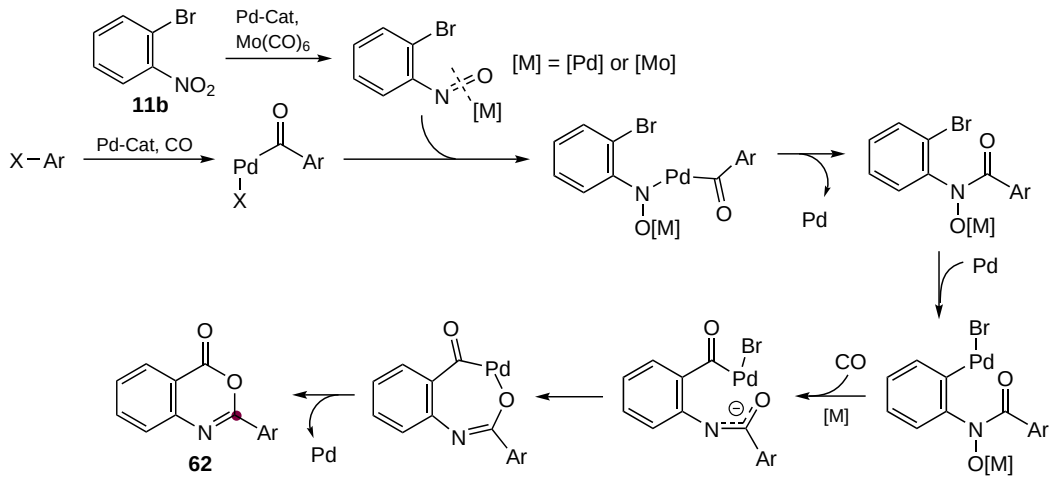
The mechanism of this transformation in the presence of a palladium catalyst is shown in Scheme 89. As in the previous case (see Scheme 87), $Mo(CO)_6$ not only acts as a CO source, but also participates in the reduction of the nitro group, together with the palladium catalyst.

The tandem process involving *ortho*-nitrobenzaldehydes **13** and 2-cyanoacetic acid esters or amides, which includes the Knoevenagel condensation, reduction of the nitro group, hydrolysis of the cyano group, and cyclization, furnishes quinolines **60′** with an ester or amide group in position 3 and an amino group at the C(2) atom (Scheme 90).[108]

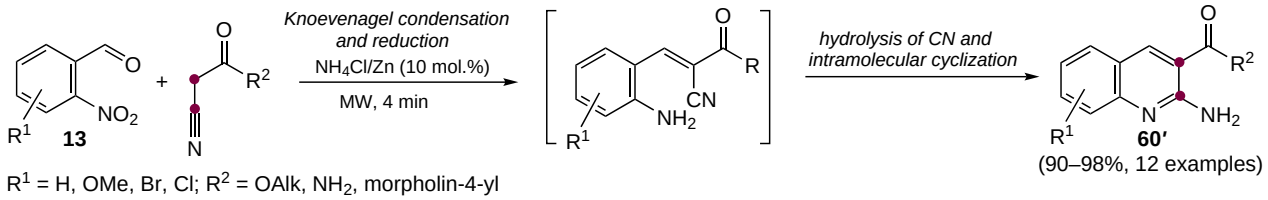
Wu and co-workers[109,110] prepared quinolin-2-one derivatives **63** by Pd-catalyzed three-component reactions shown in Scheme 91. In the first case [reaction (1)],[109] benzyl chlorides serve as sources of a carbon atom and an aryl substituent for the resulting quinoline system, while $Mo(CO)_6$ forms the C=O group. Meanwhile in the second case [reaction (2)],[110] the methylene carbon atom of 1-(allyloxy)-2-iodobenzenes forms the C(3) carbon atom of quinoline system **63′** (see Scheme 91).

Thus, for building the quinoline or quinolinone systems from *ortho*-nitrobenzaldehydes, *ortho*-nitroacetophenones, and *ortho*-nitrobenzyl alcohols, the reaction mixtures must contain, in addition to the reducing agents and catalysts, also sources of two carbon atoms. An example of using secondary benzyl alcohols with a methylene group (see Scheme 85) that is incorporated in the pyridine moiety of the resulting quinoline has been reported. In this case, an external source of only one carbon atom is needed. When *ortho*-nitrobromobenzenes are used in the reactions (see Scheme 86), reagents containing three carbon atoms are required to complete the quinoline system.

Scheme 89

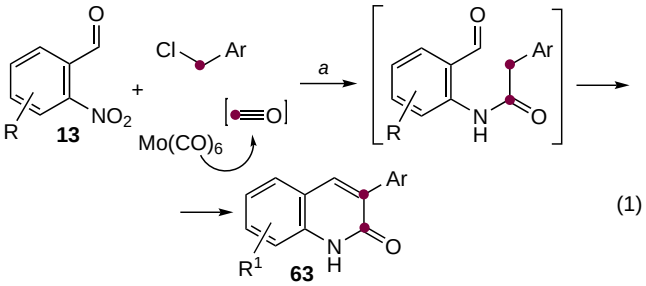


Scheme 90



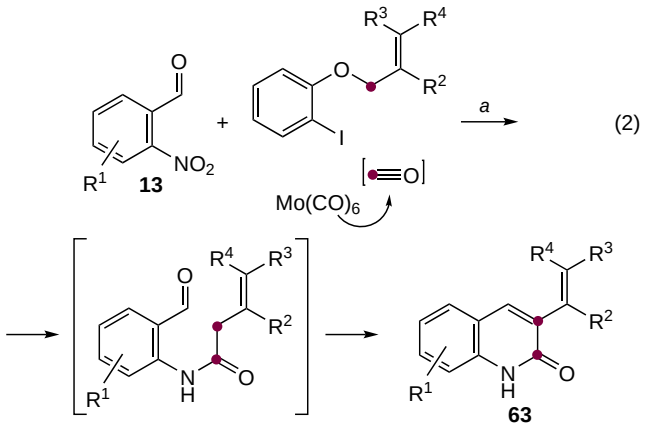
R^1 = H, OMe, Br, Cl; R^2 = OAlk, NH_2, morpholin-4-yl

Scheme 91



(55–99%, 28 examples)

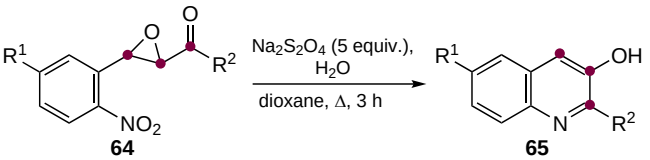
(*a*) $Pd(OAc)_2$/(2-$Ph_2PC_6H_4)_2O$ (5 mol.%), DBU, $MgSO_4$, Me_2O, 100°C, 30 h; R = H, Me, OMe, Cl, F, C(O)OMe



(62–99%, 14 examples)

(*a*) $Pd(OAc)_2$ (10 mol.%), $P(OPh)_3$ (20 mol.%), Cs_2CO_3, CH_2=CHC(O)OBu^t, MeCN, 100°C, 30 h;
R^1 = H, OMe, Cl, F, C(O)OMe; R^2, R^4 = H, Alk; R^3 = H, Alk, Ar

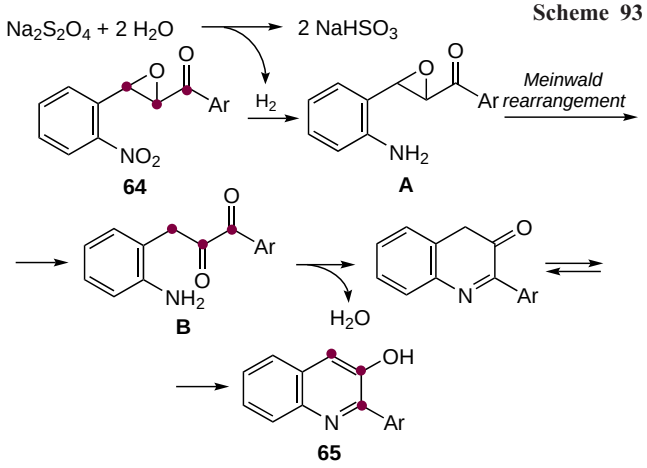
Scheme 92



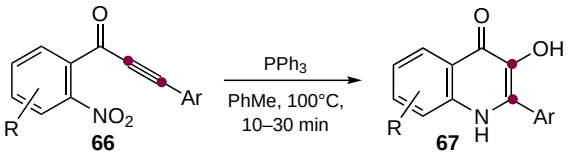
R^1 = H, Cl; R^2 = Me, Ar

(85–98%, 9 examples)

Scheme 93



Scheme 94



R = H, OMe, OBoc, OBn, F, CF_3

(58–90%, 13 examples)

12. 2-(*ortho*-Nitroaryl)oxiran-1-yl aryl(or methyl) ketones and 1-(*ortho*-nitroaryl)-3-arylprop-2-yn-1-ones in the synthesis of quinolines

This Section addresses the transformations in which all atoms needed to build the quinoline system are concentrated in one substrate molecule.

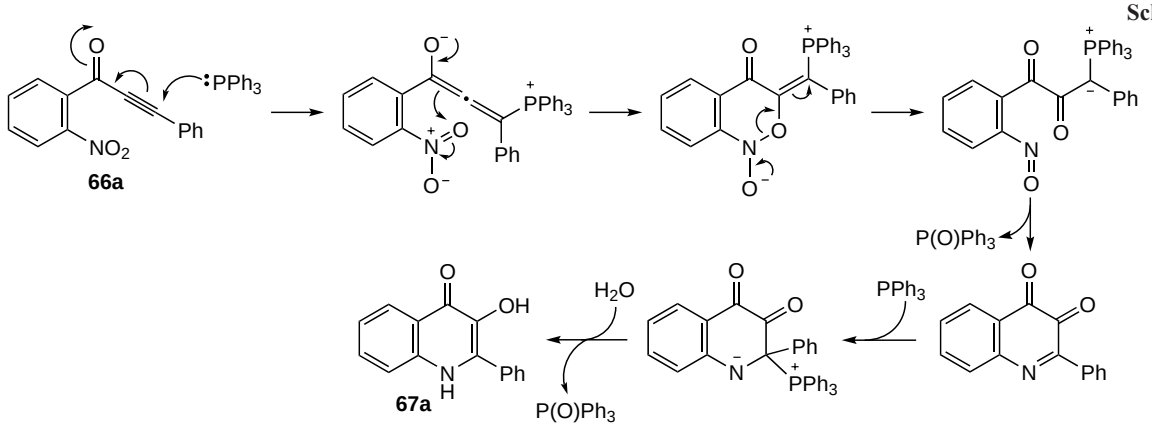
Professor V.A.Mamdov's research group[59,60,111–113] accomplished the transformation of [2-(*ortho*-nitroaryl)oxiran-1-yl] aryl (or methyl) ketones **64** (R^2=Ar or Me) induced by sodium dithionite in aqueous dioxane to give 3-hydroxy-2-aryl(or methyl)quinolines **65** (Scheme 92).

Scheme 93 shows the reaction pathway. Sodium dithionite and water generate hydrogen, which reduces the nitro group in oxirane derivative **64**; this is followed by the Meinwald rearrangement to convert oxirane derivative **A** to dicarbonyl derivative **B**, which undergoes intramolecular cyclization accompanied by the release of water to give product **65**.

Dutta and Ramasastry[114] converted 1-(*ortho*-nitroaryl)-3-arylprop-2-yn-1-ones **66** to 3-hydroxy-2-arylquinolin-4-ones **67** by treatment with triphenylphosphine (Scheme 94).

The reaction mechanism is presented in Scheme 95. Triphenylphosphine participates in all steps of this process, first, by adding to the substrate triple bond to form allene derivative and finally acting as a reducing agent for the nitro group.

Scheme 95

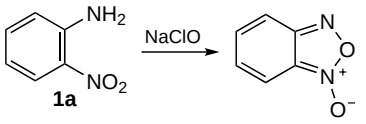


The reactions given in Schemes 92 and 94 demonstrate the potential of intramolecular cyclization of nitroarenes *ortho*-functionalized in different ways for the synthesis of quinoline systems.

13. Miscellaneous examples of formation of heterocycles and other structures from *ortho*-functionalized nitroarenes

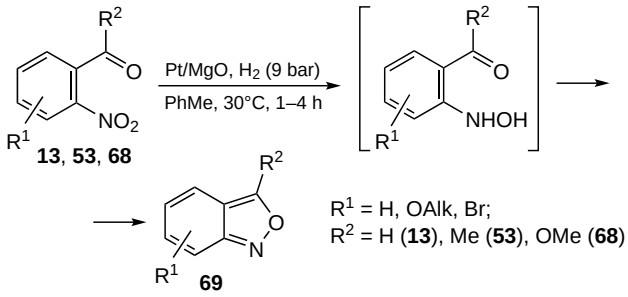
Treatment of *ortho*-nitroaniline (**1a**) with sodium hypochlorite induces cyclization of **1a** to benzofurazan oxide (Scheme 96), which is a widely used substrate for the synthesis of biologically active compounds and pharmaceutical substances.[115]

Scheme 96



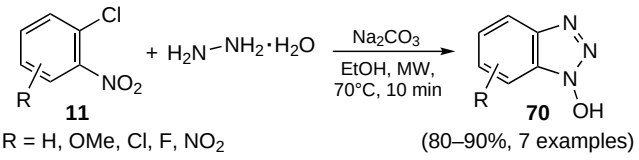
On treatment with H_2 in the presence of a platinum catalyst, *ortho*-nitrobenzaldehydes **13** (R^2 = H), *ortho*-nitroacetophenones **53** (R^2 = Me), and *ortho*-nitrobenzoates **68** (R^2 = OMe) are converted to benzisoxazoles **69** (Scheme 97).[116]

Scheme 97



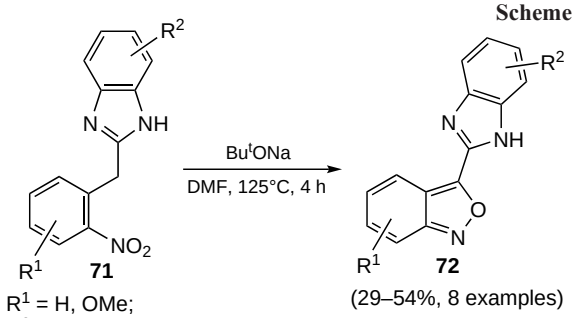
ortho-Nitrochlorobenzenes **11** react with hydrazine hydrate under the action of a base under microwave radiation to give 1-hydroxybenzotriazoles **70** (Scheme 98).[117]

Scheme 98



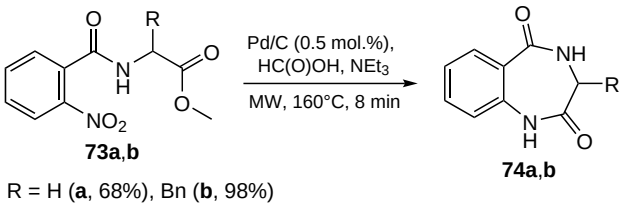
The intramolecular transformations of 2-(*ortho*-nitrobenzyl)-benzimidazole **71** that take place on heating the substrate in a mixture of Bu^tONa with DMF afford 3-(benzimidazol-2-yl)-benzisoxazoles **72** in moderate yields (Scheme 99).[118]

Scheme 99



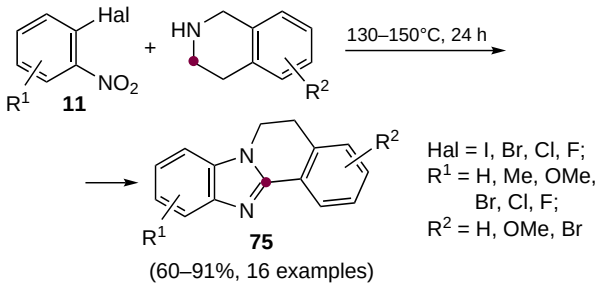
The palladium-catalyzed transformation of methyl 2-(*ortho*-nitrobenzamido)acetate **73a** and its benzyl derivative **73b** resulted in the formation of benzodiazepine-2.5-diones **74a**,**b** (Scheme 100).[20] The reaction proceeds in an azeotropic mixture of formic acid and triethylamine over a short period of time under microwave radiation, with product **74b** being isolated in almost quantitative yield.

Scheme 100



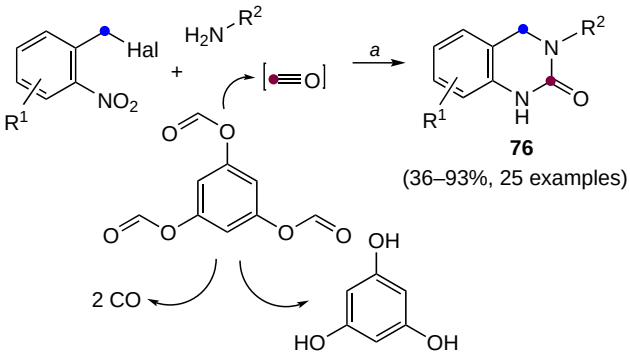
The reactions of *ortho*-nitrohalobenzenes **11** and 1,2,3,4-tetrahydroisoquinolines provide good yields of 5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinolines **75** (Scheme 101).[119]

Scheme 101



Selenium-catalyzed three-component reactions of *ortho*-nitrobenzyl chlorides (or bromides) with amines and benzene-1.3.5-triyl triformate in the presence of diisopropylethylamine as a base afford 3.4-dihydroquinazolin-2-ones **76** (Scheme 102). Benzene-1.3.5-triyl triformate serves as a source of CO, being decomposed to phloroglucinol.[120]

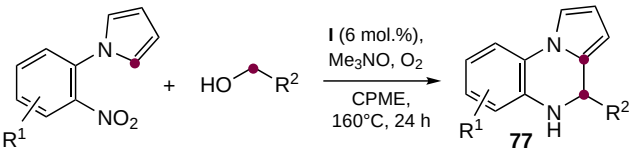
Scheme 102



A large series of pyrrolo[1.2-*a*]quinoxalines **77** were synthesized by reactions of *N*-(*ortho*-nitroaryl)pyrroles with alcohols catalyzed by the Knölker complex (**I**) in cyclopentyl methyl ether in the presence of trimethylamine oxide to activate the catalyst (Scheme 103).[121]

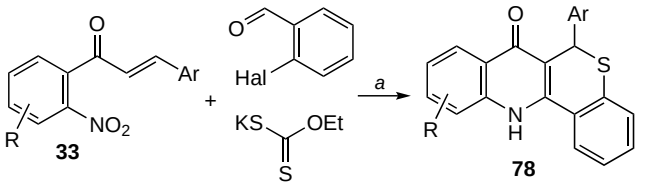
The copper acetate-catalyzed three-component reaction of *ortho*-nitrochalcones **33**, *ortho*-halobenzaldehydes, and potassium ethyl xanthate resulted in the synthesis of thiochromene[4.3-*b*]quinolinones **78** (Scheme 104).[122]

Scheme 103



R^1 = H, Me, OMe, Cl, CF_3;
R^2 = Alk, Ar, Het;
CPME is cyclopentyl methyl ether

Scheme 104



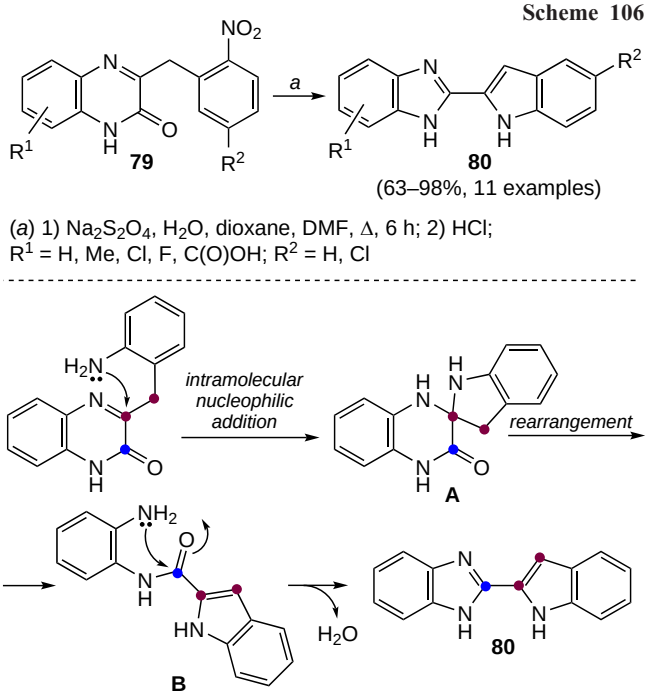
(*a*) 1) $Cu(OAc)_2$ (10 mol.%), NaOAc, DMSO, 100–130°C, 2 h; 2) KOH; Hal = I, Br; R = H, Me, OMe, OEt, SMe, Br, Cl, F

The putative reaction pathway is depicted in Scheme 105 in relation to the reaction of *ortho*-iodobenzaldehyde and chalcone **33a** giving product **78a** (R = H, Ar = Ph). In this process, potassium ethyl xanthate functions as a source of sulfur and participates in the nitro group reduction.

Professor V.A.Mamedov's research group[123,124] accomplished reactions to convert 3-(*ortho*-nitrobenzyl)-quinoxalin-2-ones **79** to 2-(indol-2-yl)benzimidazoles **80** (Scheme 106), 3-(*ortho*-nitrobenzyl)pyrido[2,3-*b*]pyrazin-2-one (**81**) to bis[2-(imidazo[3,4-*b*]pyridin-2-yl)indol-3-yl]-methane (**82**) (Scheme 107), and 3-(*ortho*-nitrobenzyl)-1,2,5-oxadiazolopyrazin-2-one (**83**) to fused oxadiazolopyrazino-quinoline system **84** (Scheme 108). All three reactions were conducted under the same conditions: by treating the substrates with an aqueous solution of sodium dithionite with heating in a mixture of dioxane and DMF followed by acidification.

The bottom parts of Schemes 106–108 present the key steps of the reaction mechanisms. The conversion of *ortho*-nitrobenzylquinoxalinones **79** to indolylbenzimidazoles **80** is a one-pot reaction comprising the nitro group reduction and the intramolecular Mamedov rearrangement (see Scheme 106). This rearrangement occurs *via* the formation of spiro compound **A**,

Scheme 106



(*a*) 1) $Na_2S_2O_4$, H_2O, dioxane, DMF, Δ, 6 h; 2) HCl;
R^1 = H, Me, Cl, F, C(O)OH; R^2 = H, Cl

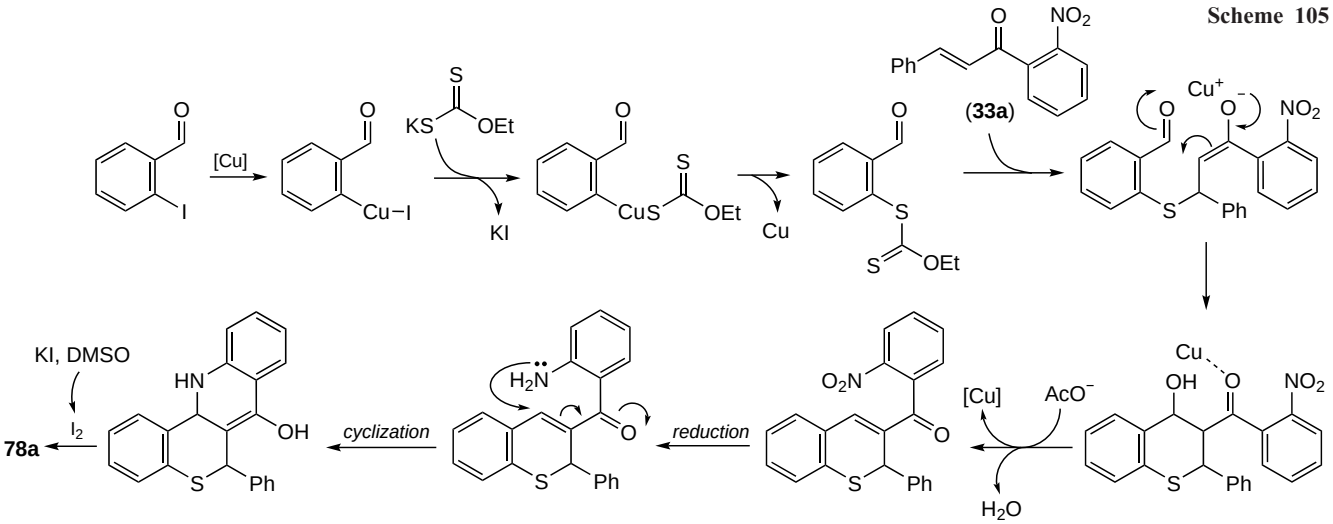
with the C(3) atom of the quinoxalinone system involved in the formation of the indole spiro moiety becoming the spirocyclic carbon atom. Compound **A** is converted to pyrazinone ring opening product **B**, the intramolecular condensation of which leads to imidazole **80**.

The transformation of *ortho*-nitrobenzylpyridopyrazinone **81** under the same conditions does not end with the Mamedov rearrangement giving 2-(indol-2-yl)imidazo[4,5-*b*]pyridine **C** (see Scheme 107), but is accompanied by formylation of position 3 of the indole ring in intermediate **C**. The subsequent coupling of formylated derivative **D** with the Mamedov rearrangement product **C** and reduction of the hydroxyl group in the bis(indolyl)-methanol **E** thus formed give compound **82**.

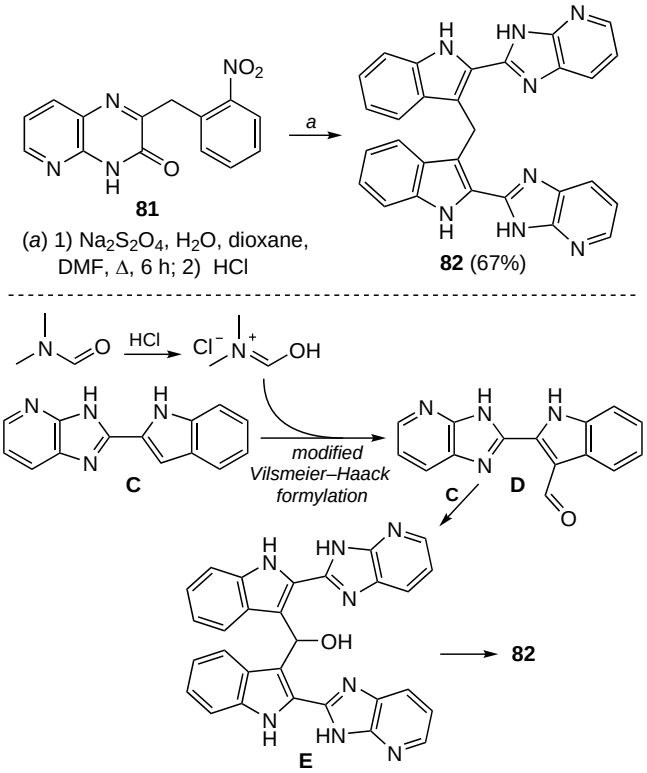
The conversion of compound **83** to product **84** occurs *via* nitro group reduction and intramolecular condensation giving a quinoline moiety (see Scheme 108).

The incomplete reduction reactions of the nitro group in 3-(*ortho*-nitroaryl)quinazolin-4-one **85** and cyclizations, resulting in the formation of benzimidazo[2,1-*b*]quinazolinones **86**, are induced by Zn powder in AcOH (Scheme 109).[125,126]

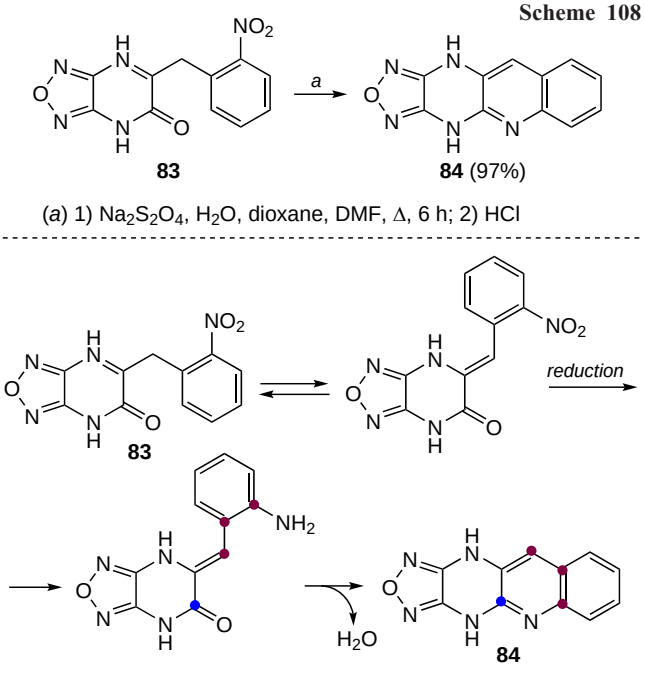
Scheme 105



Scheme 107



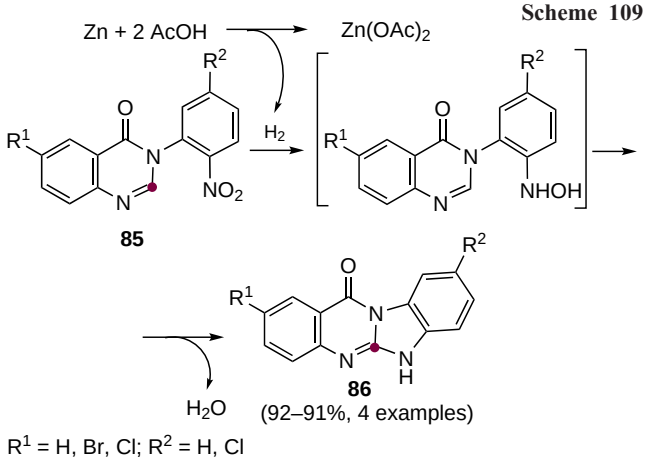
Scheme 108



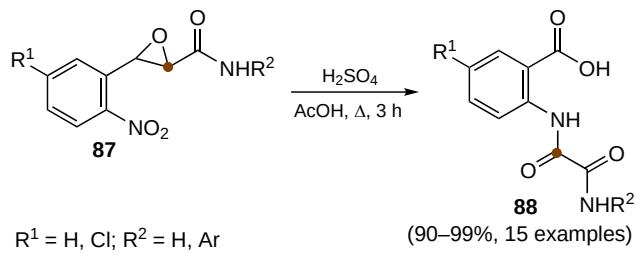
Professor Mamedov's research group [127–129] also discovered the rearrangement of 3-(*ortho*-nitroaryl)glycidic acid amides **87** to give *N*-(2-carboxyaryl)oxalamides **88** (Scheme 110; the carbon atom involved in the formation of the N–C bond in the initial molecule and in the product is marked with a brown circle), which is induced by sulfuric acid in refluxing acetic acid.

This rearrangement is accompanied by intramolecular oxirane ring opening by the nitro group giving a five-membered ring in structure **A**; opening of this ring yields nitroso compound **B**. This is followed by the formation of a new five-membered ring involving nitroso group oxygen (structure **C**). Stabilization

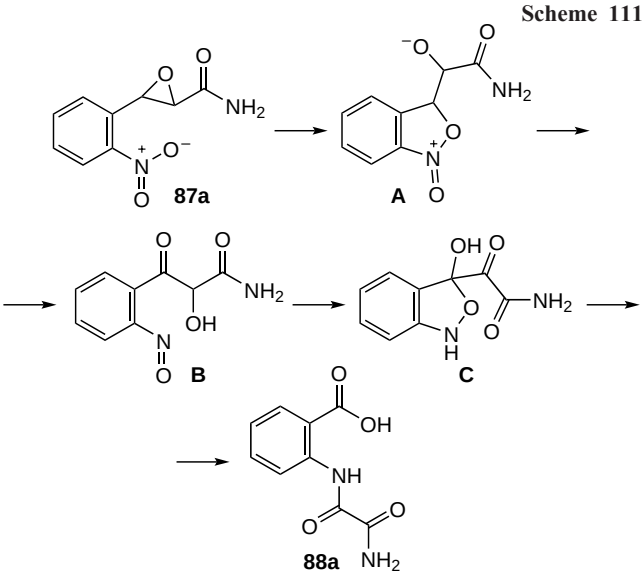
Scheme 109



Scheme 110



Scheme 111



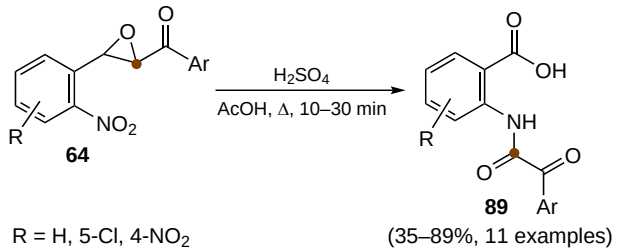
of intermediate **C** is accompanied by opening of the isoxazoline ring and migration of the $C(O)C(O)NH_2$ moiety to the *ortho*-nitrogen atom (Scheme 111).[130]

The above rearrangement does not lead directly to heterocycles, but the resulting oxalamides **88** can be considered as anthranilic acid derivatives. These compounds have been successfully used in the synthesis of a variety of quinazolines [125,126,128] by a modified Niementowski reaction.[n] Using this rearrangement, it is possible to obtain 2-(2-oxo-2-arylacetamido)benzoic acids **89** from [2-(*ortho*-nitroaryl)-oxiran-1-yl] aryl ketones **64** (Scheme 112).[127,131]

In the case of oxirane derivative **64a** (R = H, Ar = Ph), apart from the rearrangement product **89a**, 3-hydroxy-2-phenyl-

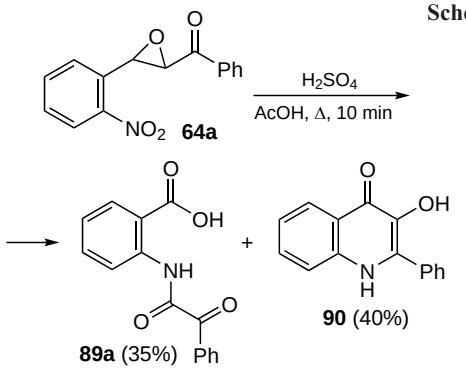
[n] See S.Niementowski. Ber. Dtsch. Chem. Ges., 27, 1394 (1894).

Scheme 112



R = H, 5-Cl, 4-NO_2 (35–89%, 11 examples)

Scheme 113



quinolin-4-one (**90**) was also isolated from the reaction mixture (Scheme 113); the mechanism of formation of this product is still unclear.[131]

The material presented in this Section leads to the following conclusions. Benzofurazan oxide (see Scheme 96), benzisoxazoles (see Schemes 97, 99), and benzotriazoles (see Scheme 98) extend the series of benzene-fused five-membered heterocyclic structures described in Sections 1–7. Sections 2 and 3 summarize the methods for the synthesis of benzimidazoles from *ortho*-nitroanilines and *ortho*-dinitrobenzenes that require an additional reagent to provide a carbon atom for the nascent imidazole ring. This Sections addresses examples of the synthesis of benzimidazole derivatives from *ortho*-halonitrobenzenes using sources of carbon and nitrogen atoms that belong to one reagent [see Scheme 101; a similar approach was applied in the synthesis of quinazolines from *ortho*-nitrobenzyl alcohols (see Scheme 68, Section 10)]. The pyrrole moiety of starting *N*-(*ortho*-nitroaryl)pyrroles provides a carbon atom to the nascent quinoxaline system, in addition to the external source of carbon (see Scheme 103).

In addition to the methods for the synthesis of quinazolines and quinazolin-4-ones described in Sections 9 and 10, a three-component method for the preparation of quinazolin-2-ones is presented here (see Scheme 102). The reduction and intramolecular cyclization of methyl 2-(*ortho*-nitrobenzamido) acetate yields benzodiazepine-2.5-dione (see Scheme 100). Meanwhile, when quinoxalin-2-one-3-methylene moiety occurs as a functional group in the *ortho*-position of nitroarenes (see structure **79** in Scheme 106), it participates, together with the nitro group, in the construction of 2-(indol-2-yl)benzimidazoles. This transformation goes through successive reduction–cyclization–ring transformation–cyclization steps (see the bottom part of Scheme 106). Similar reactions with their further development take place if the starting reactant contains a pyrido[2,3-*b*]pyrazin-2-one moiety, instead of the quinoxalinone moiety (see Scheme 107). If 1,2,5-oxadiazolo[3,4-*b*]pyrazin-2-one moiety is present in the substrate in place of the quinoxalinone ring (see structure **83** in Scheme 108), the reduction and cyclization steps afford quinoline annulated to oxadiazolopyrazinone.

In the case of nitroarenes with a quinozalin-4-on-3-yl moiety in the *ortho*-position, the reduction and cyclization sequence results in the formation of the fused benzimidazoquinozalinone system (see Scheme 109). An unusual case of intramolecular redox rearrangement of nitroarenes containing a 2-carboxyoxiran-1-yl moiety in the *ortho*-position to give anthranilic acid derivatives is depicted in Schemes 110, 112, and 113.

14. Conclusion

Thus, analysis of the recent literature concerning the behaviour of *ortho*-functionalized nitroarenes under various reaction conditions has demonstrated numerous options for using structures of this type to synthesize heterocyclic compounds. The most important aspects that can be pointed out in the given data will be useful for synthetic chemists to minimize the time and money expenditures when planning syntheses of specific heterocyclic structures. For example, while having *ortho*-nitroaniline at disposal and planning to convert it into benzimidazole, one should think about the source of the carbon atom, which can be represented by an alcohol or an aldehyde. In the presence of a transition metal catalyst, an alcohol provides the system with hydrogen, which reduces the nitro group in nitroaniline, while the alcohol is converted to aldehyde, which participates in the subsequent reactions. If an aldehyde is used as a carbon atom source, a reducing agent for the nitro group should be introduced into the system, while the catalyst is not required in this case. If it is planned to build a quinoxaline system from the same nitroaniline, it is necessary to use vicinal diols or α-diketones as sources of two carbon atoms, as well as a transition metal catalyst in the former case and a reducing agent in the latter case. Planning of quinazoline synthesis from *ortho*-nitrobenzaldehydes or *ortho*-nitroacetophenones requires a source of nitrogen atom (*e.g.*, ammonia), as well as the source of a carbon atom, an alcohol or an aldehyde, in the presence of a transition metal catalyst or a reducing agent. α-Amino acids may serve as sources of both carbon and nitrogen under certain conditions.

Some other aspects of the chemistry of *ortho*-functionalized nitroarenes deserve attention, *e.g.*, the use of carbon monoxide generated *in situ* from $Mo(CO)_6$ or the use of benzene-1.3.5-triyl triformate as a compound providing the C=O moiety for the design of quinolinone or 3.4-dihydroquinozalin-2-one structure (see Schemes 86, 88, 91, and 102). In addition, hydrazine hydrate can be used in the reaction as a reducing agent and a source of two nitrogen atoms for the formation of benzotriazoles from *ortho*-nitrochlorobenzenes (see Scheme 98).

Attention should be paid to the starting substrates that originally contain all atoms necessary for the formation of a heterocycle such as *ortho*-alkynylnitroarenes, *ortho*-nitrostyrene derivatives, and methyl 3-(*ortho*-nitrophenyl)glycidate in the synthesis of indoles (see reaction 1 in Scheme 39 and Schemes 40, 43); *N*-benzylidene-*ortho*-nitroanilines in the synthesis of benzimidazoles (see Scheme 41); *ortho*-nitro-1,1′-biphenyl in the synthesis of carbazole [see Scheme 43, reaction (1)]; [2-(*ortho*-nitroaryl)oxiran-1-yl] aryl (or methyl) ketones and 1-(*ortho*-nitroaryl)-3-arylprop-2-yn-1-ones in the synthesis of quinolines (see Schemes 92 and 94); 3-(*ortho*-nitrobenzyl)-1,2,5-oxadiazole[3,4-*b*]pyrazin-2-one and 3-(*ortho*-nitroaryl)quinazolinones in the synthesis of fused heterocycles (see Schemes 108 and 109), *etc*.

We cannot help mentioning the intramolecular transformations in 3-(*ortho*-nitrobenzyl)quinoxalinones, which are converted to bis-heterocyclic systems composed of indole and benzimidazole rings linked by a C–C bond (see Schemes 106, 107).

Finally, it is necessary to recall the reactions in which the nitro group is not reduced to amino group, but other processes take place. Examples are syntheses of benzothiazoles and benzoselenazoles from halonitroarenes (see Section 5), indazol-3-ones and indazoles from *ortho*-nitrobenzaldehydes and *ortho*-nitrobenzyl derivatives (see Section 6), oxalamide derivatives from amides of 3-(*ortho*-nitroaryl)glycidic acids (see Scheme 110), *etc*.

This review can be a guide to planning the synthesis of specific heterocyclic structures from available reactants. At the end of the review, we would like to quote Elias J. Corey, the inventor of the retrosynthetic analysis[o] and Nobel Prize winner in Chemistry in 1990:[132] 'The synthetic chemist is more than a logician and strategist; he is an explorer strongly influenced to speculate, imagine, and even to create. These added elements provide the touch of artistry which can hardly be included in a cataloguing of the basic principles of synthesis, but they are very real and extremely important.'

This review was written with a partial financial support of the Russian Science Foundation (Project No. 24-13-00098).

15. List of abbreviations and symbols

The following abbreviations and symbols are used in the review:

acac — acetylacetonate;
BINAP — 2.2′-bis(diphenylphosphino)-1.1′-binaphthyl;
Boc — *tert*-butoxycarbonyl;
Cat — catalyst;
Ch — choline;
CPME — cyclopentyl methyl ether;
ctch — catecholate;
Cy — cyclohexyl;
DABCO — 1.4-diazabicyclo[2,2,2]octane;
dba — dibenzylideneacetone;
DBU — 1.8-diazabicyclo[5,4,0]undec-7-ene;
DES — deep eutectic solvent;
DMAP — 4-(dimethylamino)pyridine;
dppf — 1,1′- bis(diphenylphosphino)ferrocene;
IL — ionic liquid;
LED — light emitting diode;
[M] — transition metal catalyst;
MW — microwave radiation;
NMM — *N*-methylmorpholine;
NMP — *N*-methylpyrrolidin-2-one;
NPs — nanoparticles;
phen — phenanthroline;
pin — pinacolate;
PMHS — polymethylhydroxysiloxane;
qncl — quinuclidine;
rt — room temperature;
TAA — *tert*-amyl alcohol;
TBD — 1,5,7-triazabicyclo[4,4,0]dec-5-ene;
TEDA — triethylenediamine;
Tf — trifluoromethanesulfonyl (triflyl);
TFA — trifluoroacetic acid;
tfa — trifluoroacetate;
tmphen — 3,4,7,8- tetramethyl-1,10-phenanthroline;
TPGS-750-M — DL-α-tocopherol methoxypolyethylene glycol succinate;
Ts — *p*-toluenesulfonyl (tosyl);
xantphos — (9,9-dimethylxanthene-4,5-diyl)bis(diphenylphosphine);
XPhos — 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl.

[o] Retrosynthetic analysis is a step-by-step simplification of the structure of a target molecule to simple and available starting compounds, which results in a set of chemical reactions that provide conversion of the selected reactants to the target product with minimized time and cost expenditures.

16. References

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