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Digest paper

Recent advances in the field of nucleophilic aromatic substitution of hydrogen

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ABSTRACT

Recent advances in the filed of direct C–H functionalization of aromatics and heteroaromatics through nucleophilic displacement of hydrogen in an aromatic ring are discussed.

Contents

Introduction

One of the highlighted topics of current organic chemistry is direct C–H functionalization of aromatics without the incorporation of halogen or other functionalities, and thus corresponding to the principles of green chemistry.[1] A large number of methods for structural modification of aromatic and heteroaromatic compounds, including the wide-spread palladium-catalyzed cross-coupling reactions,[2–4] are based on the use of halogenated starting materials, although at times direct C–H functionalization can give better results. For instance, palladium-catalyzed amination of 2-chloro-5-ntropyridine results in the target amino compound in 25% yield, while the direct metal-free oxidative amination reaction of 3-nitropyridine provides a much better yield of the same compound (Scheme 1).[5]

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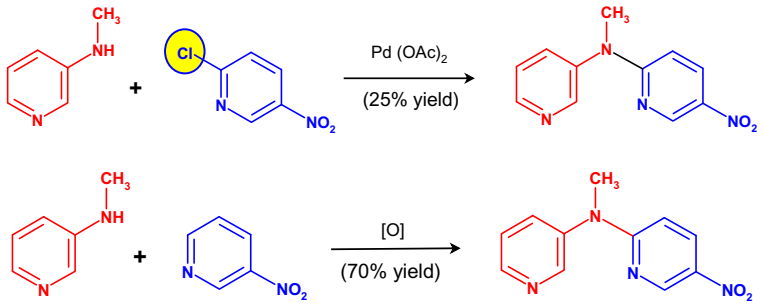
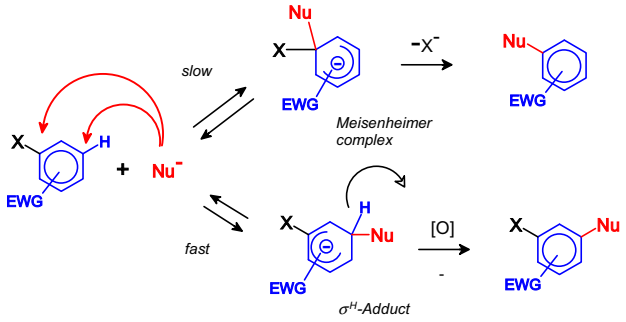
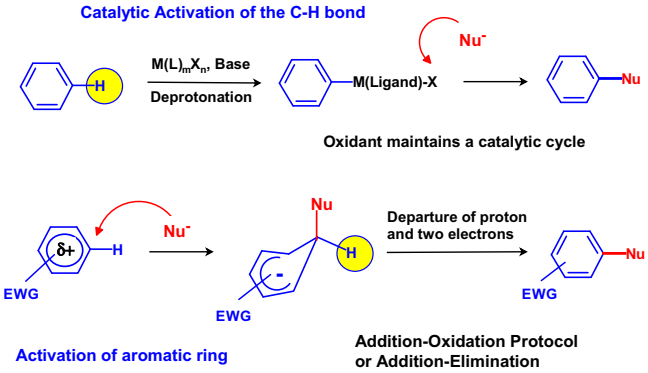


Scheme 1. Metal-catalyzed cross-coupling and metal free amination of nitropyridines.



Scheme 2. Nucleophilic attack at C–H versus C–X carbons.



Scheme 3. Catalytic and metal free C–H functionalization of aromatic compounds.

It is worth noting that the first approach requires incorporation of a chlorine atom into the pyridine ring, only to displace it later, and this certainly does not correspond to the principle of atom economy. On the other hand, it is well known that C–H carbons in electron-deficient aromatics are more vulnerable to nucleophilic attack than those of C–X bonds of compounds bearing a substituent X (Scheme 2).[6–12] Therefore, the σ^H-adducts, rather than the Meisenheimer complexes are expected to be formed, although appropriate conditions for elimination of hydrogen atom with pair of electrons have to be found (Scheme 2).[6–14] There are a large number of examples, where substitution of hydrogen proved to occur with retention of a leaving group X, even located in an activated position in nitroarenes or heteroaromatic compounds.[10–14]

Several years ago the American Chemical Society, the Green Chemistry Institute, and a number of pharmaceutical corporations appealed to chemists for development of more aspirational reactions, such as the direct C–H functionalization of aromatics.[15] American chemists Morton and Davis considered this field to be so important for the future, that they established the Center for selective C–H functionalization. They believe that the development of C–H functionalization techniques *can change the logic of organic synthesis*, and that C–H bonds have to be regarded as the favored functional groups.[16]

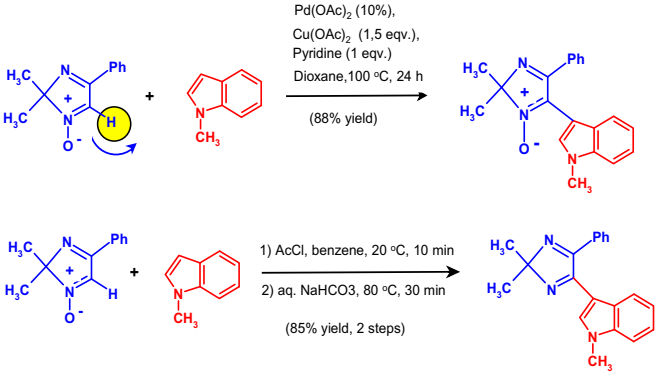
Actually, the direct functionalization of the C–H bond in aromatic compounds is now *a highlighted topic for many journals*. There are many aspects of C–H functionalization, including various pathways for the displacement of hydrogen through both catalytic and metal-free reactions. Within the scope of this Digest review, we intend to outline predominantly the publications of the last decade on metal-free C–H functionalization of aromatic compounds, proceeding through nucleophilic displacement of hydrogen.[7–14]

Nucleophilic C–H functionalization of arenes

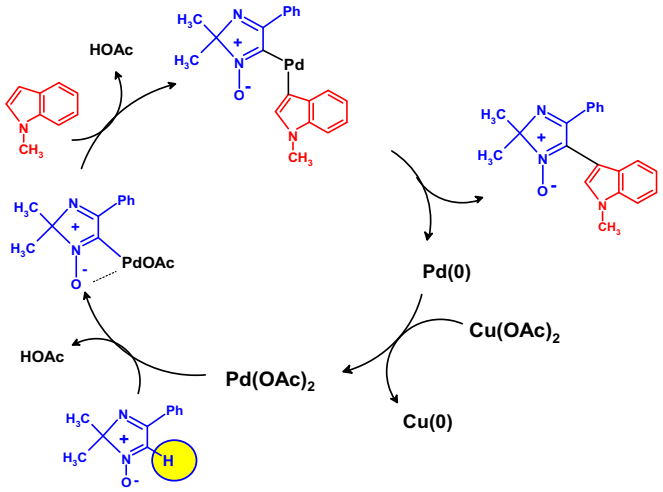
There are two principal approaches for incorporating fragments of nucleophilic reagents into aromatic or related systems by displacement of the hydrogen of the C(sp^2)–H bond. The first is based on catalytic activation of the C(sp^2)–H bond. It involves the step of deprotonation followed by the formation of organometallic intermediates, which then react with nucleophiles to give the final products. The second approach involves a direct nucleophilic attack on an activated electron-deficient system, leading to the intermediate σ^H-adduct, followed by departure of a proton through oxidative or eliminative pathways (Scheme 3).[7,17,18]

Both approaches to functionalize the C(sp^2)–H bond involve elimination of a proton, and an oxidant is needed for departure of the hydrogen. However, the sequence of steps and mechanisms of these C–H transformations are completely different, as illustrated by the recently published example taken from the chemistry of imidazole (Scheme 4).[17]

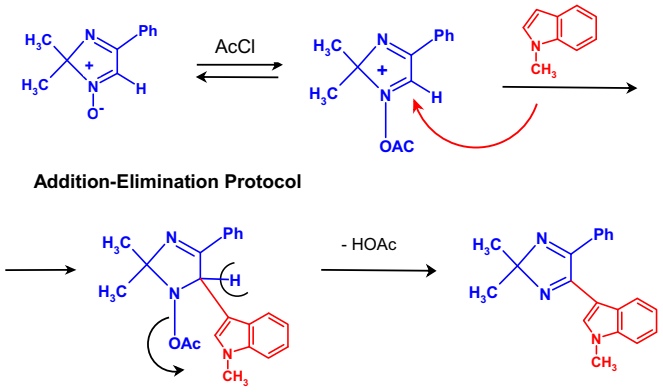
The first reaction is catalyzed by palladium acetate. It takes place in the presence of pyridine, as a base, and copper acetate, as oxidant, and results in the formation of indolyl-substituted imidazoles with the retention of the *N*-oxide moiety (Schemes 4 and 5).[17]



Scheme 4. C–H Functionalization of imidazoles.



Scheme 5. Catalytic cycle for palladium-catalyzed C–H functionalization of imidazoles.



Scheme 6. Nucleophilic displacement of hydrogen in imidazoles.

The second reaction is free of metal catalysis. It occurs in the presence of acetyl chloride, proceeds faster, and results in compounds which have the same core structure as the indolyl-substituted imidazoles, but with the loss of the *N*-oxide group (Scheme 4).[17]

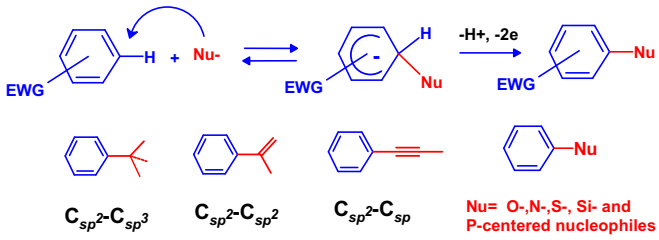
In the first case the C(sp^2)–H bond is activated through the formation of an organopalladium intermediate, accompanied by loss of a proton. The former reacts with the nucleophilic indole to give the second organopalladium intermediate and finally, the target imidazole *N*-oxide (Scheme 5).[17]

In the alternative approach the imidazole ring is activated for a nucleophilic attack through acylation of the *N*-oxide moiety, and the reaction proceeds according to the 'Addition–Elimination' protocol,[17] which is rather typical for nucleophilic substitution of hydrogen (S_N^H) (Scheme 6).[6,7]

There are many other examples, showing that metal-catalyzed and metal-free C–H functionalization reactions can be regarded as complementary to each other.[7] For instance, both approaches have been used successfully for amination of benzoxazole.[18]

Historical aspects of the S_N^H reactions

The first review article was published in 1976.[19] At that time an overwhelming majority of text-books on organic chemistry claimed that "*... as a rule, hydrogen in an aromatic ring is not displaced with nucleophiles*".[20] The next decades brought a great deal of data concerning nucleophilic C–H functionalization of aromatics



Scheme 7. General character and scope of the S_N^H reactions.

(the S_N^H reactions), enabling the distinguished chemist professor Terrier to name the field of nucleophilic aromatic substitution of hydrogen as "*...a fascinating subject of the last decade...*".[21]

Indeed, the data accumulated in the literature show that S_N^H reactions are of fundamental value and can be used to build a variety of carbon–carbon and carbon–heteroatom bonds.[6–14] This methodology involves a great variety of reactions: alkylation, alkenylation, alkynylation, arylation, amination, hydroxylation, alkoxylation, cyanation, halogenation, as well as carboranylation, ferrocenylation, and others (Scheme 7).[6–14]

Strong and weak points of the S_N^H methodology

In order to illustrate the synthetic opportunities of metal-catalyzed and metal-free C–H functionalizations, we have compared two approaches, the Negishi cross-coupling and the S_N^H reaction, used for the synthesis of the same chiral azinyl ferrocenes (Scheme 8).[22]

Two types of chiral ferrocenes, bearing asymmetric carbon or sulfur atoms, were taken as staring materials for the synthesis of *P,N*-containing ligands. The first approach was based on the Negishi reaction, proceeding through palladium-catalyzed cross-coupling of organozinc derivatives with halogenated azines, so first, these intermediates had to be obtained before their cross-coupling. The S_N^H approach proved to be a much shorter pathway, affording the same compounds in better yields, and under very mild conditions (strong points), although the presence of DDQ was needed as oxidant (a week point) (Scheme 8).[22]

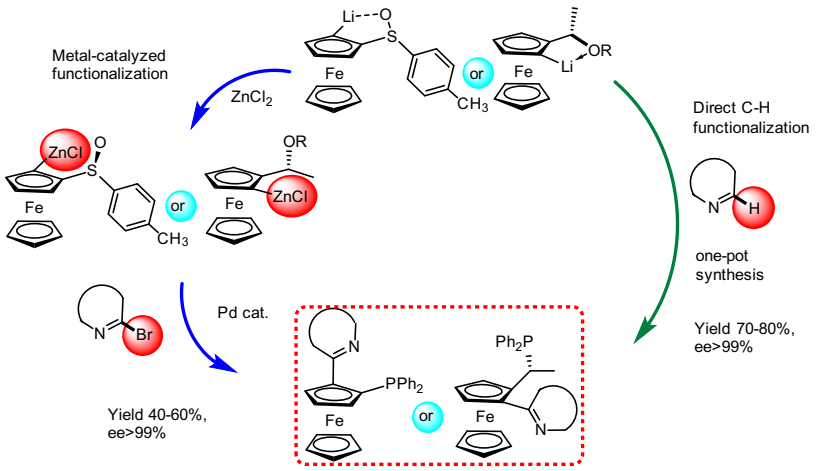
The story is the same for the use of S_N^H reactions in the series of cymantrenes.[23] Once again, we have to stress the crucial role of the oxidant, since the key problem of the S_N^H reactions is associated with *elimination of hydrogen with pair of electrons*. Therefore, an appropriate oxidant (or an auxiliary group) is needed to realize the S_N^H reaction through either oxidative or eliminative pathways (Scheme 9).[6–14,24] Electrochemical nucleophilic aromatic substitution of hydrogen also appears to be a valuable alternative to induce C–H functionalization processes through activation of an aromatic ring, or to facilitate the S_N^H process through selective anodic oxidation of intermediate adducts.[25–29]

Oxidative S_N^H reactions

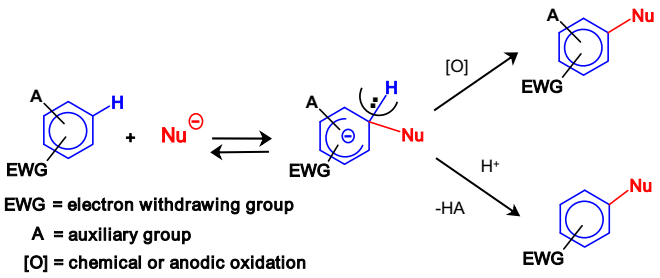
An external oxidant is usually needed to perform the S_N^H reactions. The most plausible mechanism for oxidative S_N^H reactions is through transfer of an electron from σ^H-adducts followed by loss of a proton and the second electron.[6,7,24]

Effective oxidative systems for amination and alkylamination of azaaromatics, enabling one to carry out S_N^H reactions under mild conditions have been suggested.[30–34] This has recently been exemplified by amination of triaza-pyrene (Scheme 10).[34]

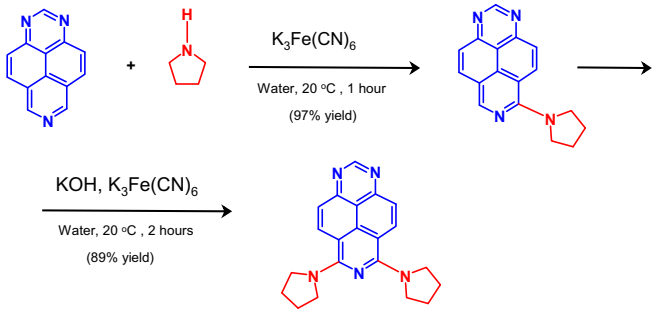
The starting electron-deficient substrate can be involved in the aromatization step. For instance, in the reaction with aromatic amines, occurring under argon atmosphere, the acridinium ion



Scheme 8. The Negishi cross-coupling versus the S_N^H reaction in the synthesis of chiral azinyl substituted ferrocenes.



Scheme 9. Principal modes of the S_N^H reactions.



Scheme 10. Amination of triazapyrene.

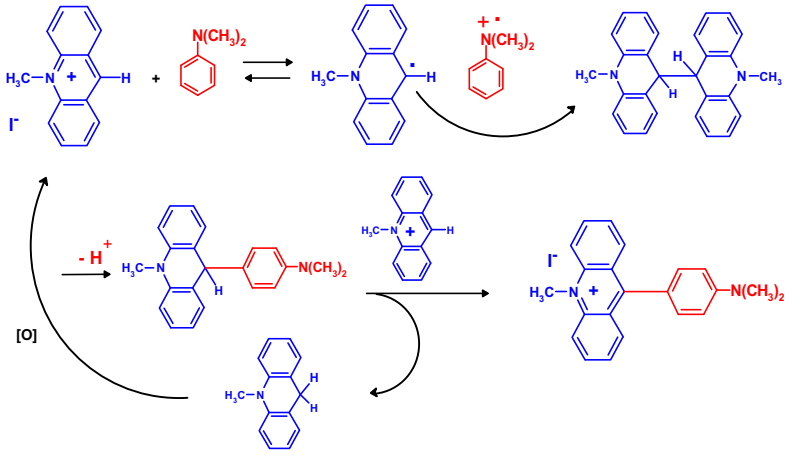
plays the role of oxidant, thus providing aromatization of the intermediate adduct. This mechanism has been confirmed by the ^{1}H NMR data, mathematic modeling and kinetic studies (Scheme 11).[6]

The arylation of acridinium salts and other oxidative S_N^H reactions can be accomplished very effectively with oxygen in air at room temperature, provided that titanium dioxide TiO_2 is used as photocatalyst.[35] When irradiated with UV light the system O_2/TiO_2 produces an electron/hole pair (e−/h+), and oxygen dissolved in a solution can be scavenged with exited electrons, thus affording the superoxide radicals, as very active oxidative species. Air is certainly attractive as oxidant from an ecological point of view, since the by-product is water, and it provides a better match with the atom economy and other principles of green chemistry (Scheme 12).[35]

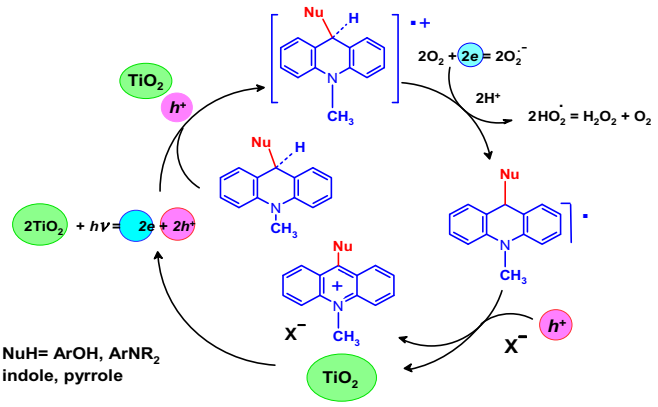
Eliminative S_N^H reactions

Another principal version of the S_N^H reactions is based on eliminative aromatization of intermediate adducts. In this case, two electrons have to be taken from adducts with the help of an auxiliary anionic group (Scheme 13).[6,7,10–14]

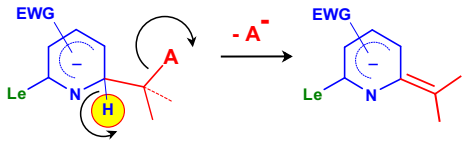
There are several modes of eliminative S_N^H reactions. The first mode is realized, when a nucleophile bears one auxiliary group. These reactions are regarded as *vicarious nucleophilic substitutions*,



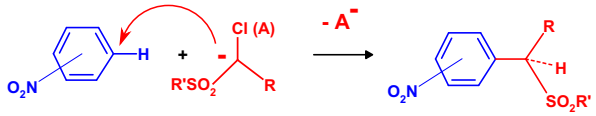
Scheme 11. Aminoarylation of acridinium salts.



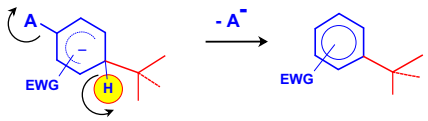
Scheme 12. Arylation of acridinium salts in the presence of TiO_2/air oxygen oxidative system.



Scheme 13. Elimination of an anionic auxiliary group from the intermediate σ^H-adduct.



Scheme 14. Vicarious nucleophilic substitution of hydrogen.



Scheme 15. *Tele*-substitution as one of the options of eliminative S_N^H reactions.

as suggested by Prof. Makosza (Scheme 14, for recent reviews see).[10–14]

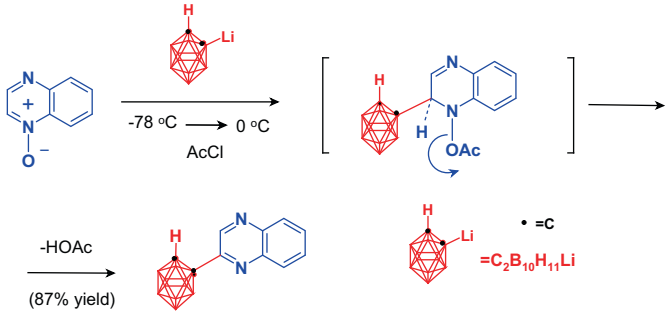
If an auxiliary group is present in substrate, we deal with *cine*- or *tele-substitutions* (Scheme 15).[6,7,10,11,36,37]

Departure of auxiliary *O*-acetyl group can be illustrated by the reaction of quinoxaline *N*-oxide with the lithium salt of carborane (Scheme 16).[38]

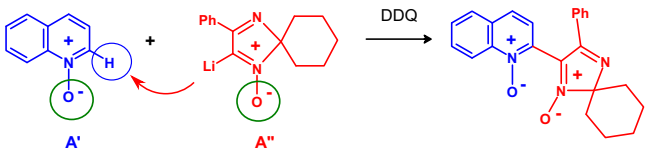
A more complicated situation occurs when two or more auxiliary groups are available in reagents. When the lithium salt of imidazole *N*-oxide reacts with quinoline *N*-oxide, the reaction outcome depends on the reaction conditions. In the presence of DDQ the oxidative version occurs, with retention of both *N*-oxide functions (Scheme 17).[39]

Without an exogenous oxidant, a more electrophilic quinoxaline is aromatized with elimination of its *N*-oxide function, while in a similar reaction of quinoline *N*-oxide the auxiliary OAc group is eliminated from the nucleophilic fragment (Scheme 18).[39]

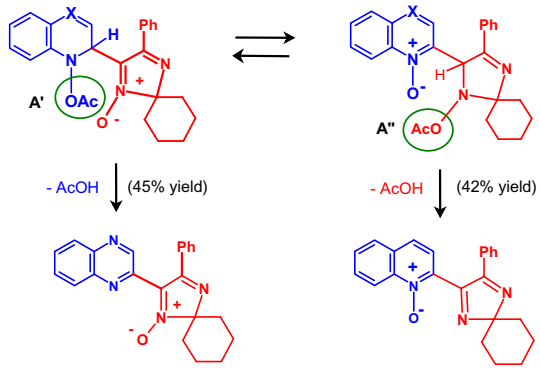
A new C–H functionalization protocol, based on the generation of nucleophilic species with two auxiliary groups in the course of



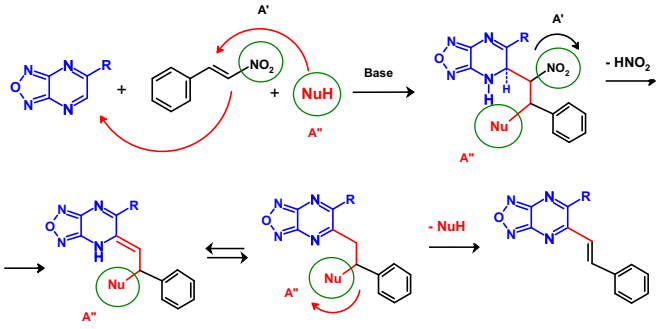
Scheme 16. Carboranylation of quinoxaline.



Scheme 17. Retention of both auxiliary groups in the oxidative version of C–H/C–H coupling of two heterocyclic *N*-oxides.

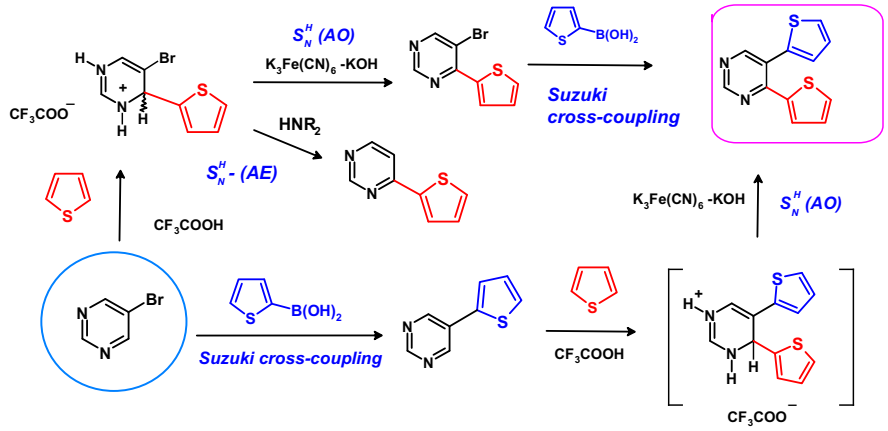


Scheme 18. Elimination of AcOH from intermediate adducts.



Scheme 19. Generation of nucleophilic species bearing two auxiliary groups and their elimination in the course of the C–H functionalization of the pyrazine ring.

the reaction, has recently been advanced (Scheme 19).[40] The process is initiated by the addition of morpholine at the C–C double bond of β-nitrostyrenes, and the subsequent addition of the carbanion generated to C-6 of furazano[3,4-*b*]pyrazines, followed by elimination of nitrous acid and morpholine.[40] It appears to be a general method for arylethenylation of aromatics, as shown by a similar C–H functionalization of other heterocyclic systems.[41]



Scheme 20. Combination of the metal free S_N^H and metal-catalyzed cross-coupling reactions of 5-bromopyrimidine.

Combination of the S_N^H and metal-catalyzed cross-coupling reactions

Metal-free S_N^H and metal-catalyzed cross-coupling reactions can be complementary to each other. It is nicely illustrated by transformations of 5-bromopyrimidine (Scheme 20).[42–44]

Actually, the Suzuki cross-coupling reaction can be used for modification of position 5 of the pyrimidine ring, which is less activated for nucleophilic attack, while the S_N^H methodology is effective for nucleophilic C–H functionalization of position 4. It is worth mentioning that various combinations of these two types of C–C coupling reactions, Addition–oxidation or addition–elimination, and also various sequences of steps can be used to obtain 4,5-disubstituted pyrimidines (Scheme 20).[42–44]

Some final remarks

Nucleophilic C–H modification of aromatic, heteroaromatic and related compounds can be realized through either metal-activation of C(sp^2)–H bonds or by means of nucleophilic substitution of hydrogen.

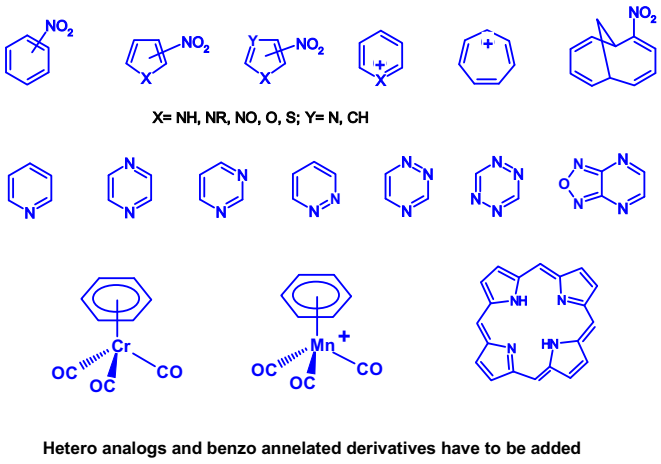
Advantages of the S_N^H methodology

As mentioned in Section *Strong and weak points of the S_N^H methodology*, the S_N^H approach provides a direct synthetic pathway to modify C(sp^2)–H bond in an activated aromatic ring. One of advantages of the S_N^H methodology is that it requires neither a preliminary functionalization, nor the use of transition metals (usually Pd), as catalysts. The latter is very important for the synthesis of drugs,[45] and/or organic dyes for solar cells,[46] in which even traces of transition metals are not permitted. This is why the direct metal-free C–H functionalization of aromatics is considered to be so aspirational for both academic and industrial chemists, by enabling them to avoid metal impurities in the target products.[6–14]

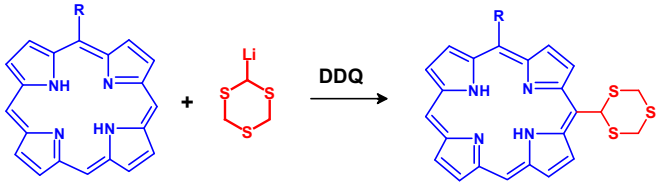
Scope and limitations of the S_N^H methodology

The S_N^H methodology has been applied to modify a variety of electron-deficient aromatic and heteroaromatic systems, as well as their benzo and hetero analogues (Scheme 21), by action of hundreds of C-, N-, O-, S-, Se-, Si-, and P-nucleophilic reagents of different nature.[6–14]

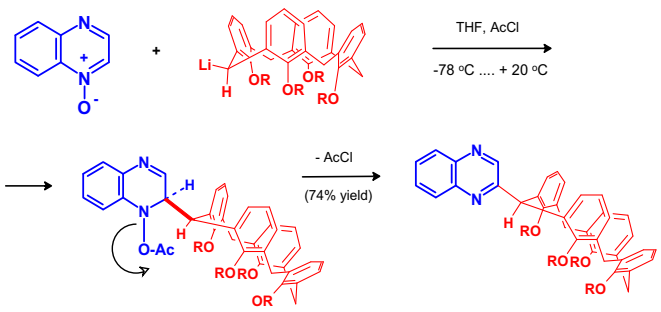
This methodology is an effective synthetic tool in medicinal[45] and supramolecular chemistry,[47–49] to modify metallabenzenes,[50] arene-metal complexes,[51,52] porphyrins (Scheme 22),[53,54] polymers[55] and free radical derivatives.[56]



Scheme 21. Aromatic systems entering the S_N^H reactions.



Scheme 22. Use of the S_N^H methodology to modify porphyrins.



Scheme 23. Use of the S_N^H methodology to modify calixarenes.

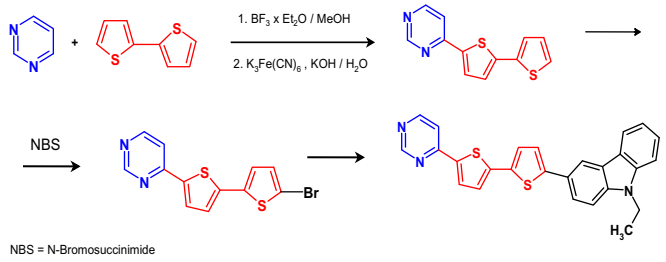
For instance, the S_N^H reactions have been used to modify both the upper rim and the *meso*-position of calixarenes.[7] A new example is shown in Scheme 23.[48,49]

The S_N^H reactions have found application in material science to obtain new heterocyclic ligands for metal complexes, and also compounds of the D–π–A type for dye-sensitized solar cells (Scheme 24).[46] Indeed, compounds of this family have rather promising photophysical properties.[57]

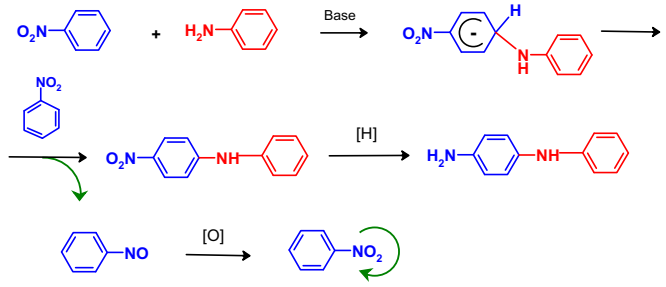
Contribution of the S_N^H methodology to Green Chemistry

The Nobel Prize winner professor Ryoji Noyori has claimed that in the 21st century chemists should pursue the principle of practical elegance, which means that a synthesis should be not only logical from technical point of view, but also ecologically benign.[58] We believe that at least a number of the S_N^H reactions do correspond nicely to this principle, as illustrated, for instance, by industrial synthesis of 4-amino-diphenylamine and other 4-nitroanilines (Scheme 25).[59,60]

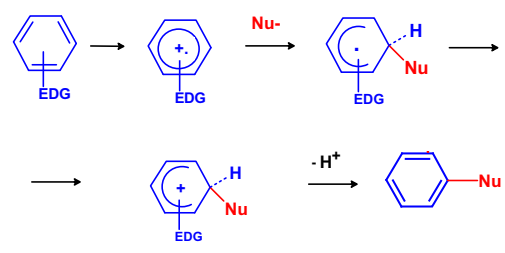
In this respect nucleophilic aromatic substitution of hydrogen has advantages over traditional synthetic approaches, including industrial chemistry. This is why the Flexsys America Co. was awarded with Green Chemistry Presidential Prize for development



Scheme 24. Use of the S_N^H methodology to obtain compounds for dye-sensitized solar cells.



Scheme 25. Industrial application of the S_N^H methodology.



Scheme 26. Electrochemically induced S_N^H reactions.

of a green synthetic route to 4-aminodiphenylamine based on the S_N^H methodology (Scheme 25).[59,60]

Conclusion

Nucleophilic aromatic substitution of hydrogen has been elucidating predominantly as C–H functionalization of π-deficient aromatic and heteroaromatic compounds.[6–14] However, the scope of the S_N^H reactions is not restricted by participation of electron-deficient aromatics. Neutral aromatic systems and arenes, bearing electron-donating groups, can also be activated for a nucleophilic attack through their anodic oxidation into radical-cation species, followed by addition of a nucleophile and elimination of proton (Scheme 26).[25–28]

This procedure can be regarded as an additional protocol for the S_N^H reactions, and this approach appears to be a promising area of organic synthesis.[25–28]

The data of the last two decades demonstrate that the S_N^H methodology appears to be a new chapter of aromatic chemistry, which is complementary to the advanced concept of metal-catalyzed cross-coupling reactions. The S_N^H reactions have a common character and undoubtedly belong to the key chemical processes, thus reflecting a fundamental property of aromatic compounds.[6–14]

In the scope of this digest review article, it is hardly possible to reflect all achievements in this rapidly growing field of organic chemistry. It is worth mentioning a number of recently published papers dedicated to novel applications of the S_N^H methodology for the synthesis of heterocycles,[61–63] including the reaction with Se-centered nucleophiles, leading to benzo[*b*]selenophenes,[63] and numerous S_N^H transformations of nitroarenes,[64–69] including those with P-centered diphenylphosphine anion,[68] and incorporation of dialkyl phosphoglycine fragments,[69] as well as new data on C–H functionalization of porphyrins,[70] and rather exotic sapphyrins.[71] Also it has recently been shown that even non-activated naphthalene can be involved in direct C–H functionalization by reacting with the complex of bromine with the chloride-anion in ionic liquids.[72]

We have omitted a detailed consideration of mechanistic aspects of the S_N^H reactions, which can involve electron-transfer acts and redox transformations between the following pairs 'aromatic substrate—nucleophile', 'nucleophile—oxidant', 'intermediate σ^H-adduct—oxidant', 'intermediate σ^H-adduct—starting aromatic substrate' and other reacting species, which are reflected partly in books[6,7] and review articles.[8–14,67] However, we believe that the examples presented above are convincing enough to show that the S_N^H methodology is gaining the interest of chemists (judging by a growing number of publications and research groups all over the world) as an efficient tool to build carbon–carbon and carbon–heteroatom chemical bonds between an aromatic ring and a variety of nucleophilic reagents, by using metal-free ecologically benign processes.

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