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Photocatalysis

# The Photocatalyzed Meerwein Arylation: Classic Reaction of Aryl Diazonium Salts in a New Light

*Durga Prasad Hari and Burkhard König**

arylation · catalysis · diazonium salts · radicals · visible light

*The use of diazonium salts for aryl radical generation and C–H arylation processes has been known since 1896 when Pschorr first used the reaction for intramolecular cyclizations. Meerwein developed it further in the early 1900s into a general arylation method. However, this reaction could not compete with the transition-metal-mediated formation of $C(sp^2)$–$C(sp^2)$ bonds. The replacement of the copper catalyst with iron and titanium compounds improved the situation, but the use of photocatalysis to induce the one-electron reduction and activation of the diazonium salts is even more advantageous. The first photocatalyzed Pschorr cyclization was published in 1984, and just last year a series of papers described applications of photocatalytic Meerwein arylations leading to aryl–alkene coupling products. In this Minireview we summarize the origins of this reaction and its scope and applications.*

Aryl diazonium salts have always attracted chemists because, in addition to their classical applications as reagents in aromatic substitutions, they are an important source of aryl radicals[1] and provide an alternative to aryl halides and triflates in transition-metal-mediated coupling reactions.[1g,2] Aryl diazonium salts combine several advantages as starting materials in organic synthesis and have been therefore used extensively in preparative chemistry: 1) They are easily prepared in large quantities from aniline derivatives; 2) their reactions take place at ambient conditions; 3) the leaving group $N_2$ does not interfere with the reaction mixture; and 4) the coupling reactions can proceed with high chemoselectivity. Reactions of diazonium salts include homolytic and heterolytic bond cleavage as well as the formation of aryne intermediates.[3] Aryl diazonium salts take up an electron from reducing reagents, leading to aryl radicals and the liberation of dinitrogen.[3a] The chemistry of aryl radicals forms the basis of a number of classic name reactions in organic chemistry: the Sandmeyer reaction, the Pschorr cyclization, the Gomberg–Bachmann reaction, and the Meerwein arylation.[1d,4] In 1896, Pschorr first reported the synthesis of phenanthrenes from the corresponding aryl diazonium salts and the extension of this reaction was reviewed by Leake and DeTar.[3a,5]

In 1939, Meerwein reported the arylation of olefins by aryl diazonium salts catalyzed by copper(II) salts.[6] The original arylation reaction was limited to alkenes with electron-withdrawing groups such as in coumarin, cinnamic acid, and acrylic acid, but its scope was later expanded to include electron-rich olefins (Scheme 1 a).[1f,7] An important application of the Meerwein arylation is the decarboxylative cross-coupling, but the reaction has not been used frequently in organic synthesis.[8]

Even though the original Meerwein arylation has disadvantages, such as limited substrate scope and many side products, examples giving aryl–alkene coupling serve as the foundation of $C(sp^2)$–$C(sp^2)$ cross-coupling reactions. Several research groups contributed excellent new and improved variants of the Meerwein arylation and the Pschorr cyclization and described their applications to the synthesis of complex organic molecules. In 1985, Zanardi and his coworkers described the synthesis of benzothiophenes from corresponding *o*-methylthioarenediazonium salts with alkynes through a radical annulation process in the presence of freshly prepared copper powder, NaI, or $FeSO_4$.[9] Recently, Heinrich et al. reported Meerwein-type arylation reactions using stoichiometric amounts of $TiCl_3$ or $FeSO_4$ as reducing agents (Scheme 1 b).[10] Shortly thereafter, Schiesser et al. reported a synthesis of benzoselenophene and benzothiophene analogues of eprosartan and milfasartan through a cyclization process involving the reaction of *o*-thioalkyl- or *o*-selenoalkylphenyl radicals with alkynes using iron(II) sulfate heptahydrate.[11]

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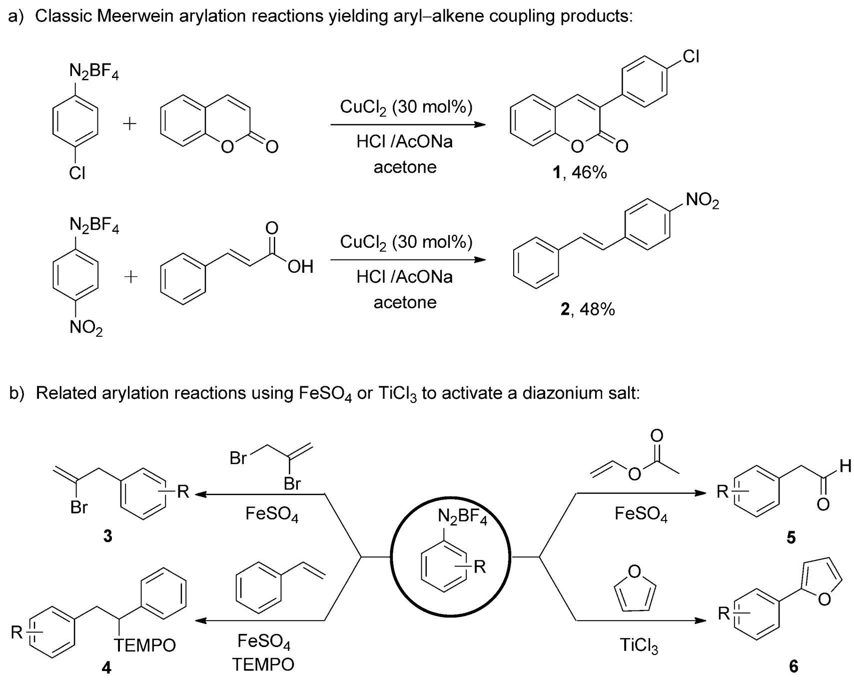
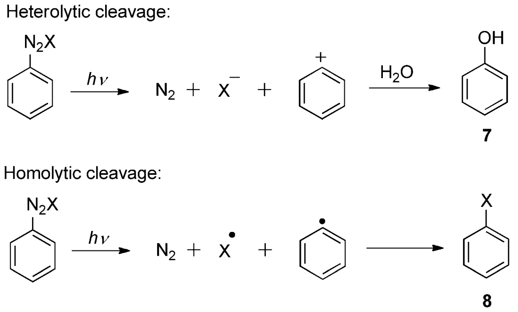
[*] M. Sc. D. P. Hari, Prof. Dr. B. König
Department of Chemistry and Pharmacy, Universität Regensburg
Universitätsstrasse 31, 93040 Regensburg (Germany)
E-mail: burkhard.koenig@chemie.uni-regensburg.de



**Scheme 1.** Meerwein-type arylation cross-coupling reactions and improved new variants of this cross-coupling reaction.

In the classical protocols the generation of aryl radicals from diazonium salts requires a catalytic or stoichiometric amount of a redox-active transition-metal salt. Visible light can provide the required redox energy as well and has been considered as an ideal reagent for organic synthesis because it is abundant, inexpensive, and innocuous. The photochemistry of diazonium salts has been studied starting in the early 19th century when it was noticed that benzenediazonium nitrate turns red on exposure to sunlight.[12] The principle of photodecomposition of diazonium salts by loss of nitrogen on exposure to light has been utilized in industrial techniques such as processes for printing on silk or cotton, diazo copying, and photolithography, but photochemical reactions of diazonium salts and related systems have been explored only since 1959.[3a,12] Typical aryl diazonium salts ($ArN_2^+X^-$) absorb in the ultraviolet spectral region. Direct photolysis of diazonium salts in aqueous solution leads to phenol (**7**) as the main product of heterolytic bond cleavage (Scheme 2). In addition to the photolytic hydro-dediazotization product, the replacement of the diazo group by anions $X^-$ is observed in a homolytic cleavage reaction and the Schiemann product **8** forms (Scheme 2).[13] The solvent, counterions, nucleophilic additives, and reducing agents are important factors that influence the cleavage of diazonium group in a homolytic or heterolytic fashion.[3a,14]

However, the inability of most aryl diazonium salts to absorb visible light has limited the number of photochemical applications of aryl diazonium salts in organic synthesis. Recently, many groups have utilized visible-light-absorbing photoredox catalysts to sensitize organic molecules by electron- or energy-transfer processes.[15] In this Minireview we will discuss the photoredox chemistry of aryl diazonium salts using visible light and cover pioneering examples from the 20th century as well as recent reports to summarize this rapidly developing area of research. So far, photoredox versions of the Meerwein arylation have led exclusively to the formation of cross-coupling products and the valuable alkene addition products that can be obtained under classic Meerwein arylation conditions have not been

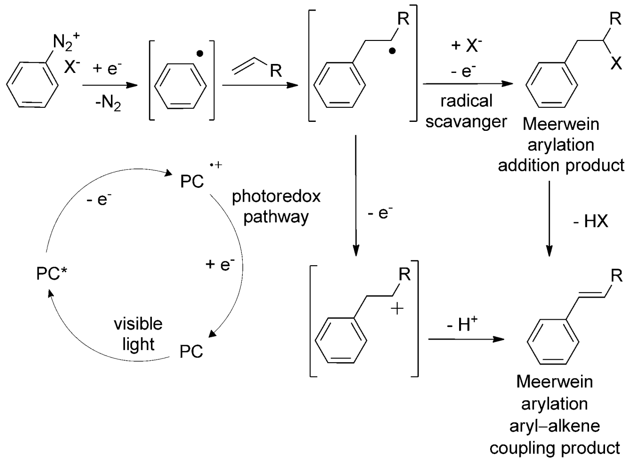


**Scheme 2.** Direct photolysis of diazonium salts.

*Durga Prasad Hari was born in Jarajapupeta, Vizianagaram, A.P (India). He received his Bachelor degree from the Silver Jubilee Government Degree College, Kurnool and his Master degree from IIT Madras. He is currently working under the supervision of Prof. Burkhard König for his PhD degree at University of Regensburg (Germany). His research interests focus on applications of photocatalysis in organic synthesis.*

*Burkhard König was born in Wiesbaden, Germany. He received his PhD in 1991 from the University of Hamburg under the guidance of Prof. A. de Meijere. He pursued postdoctoral studies with Prof. M. A. Bennett, Research School of Chemistry, Australian National University, Canberra, and Prof. B. M. Trost, Stanford University. In 1996 he obtained his Habilitation at the University of Braunschweig. He became full professor of organic chemistry at the University of Regensburg in 1999. His current research interests includes the development of synthetic receptors for the recognition of biological target structures and the application of photocatalysis in organic synthesis.*

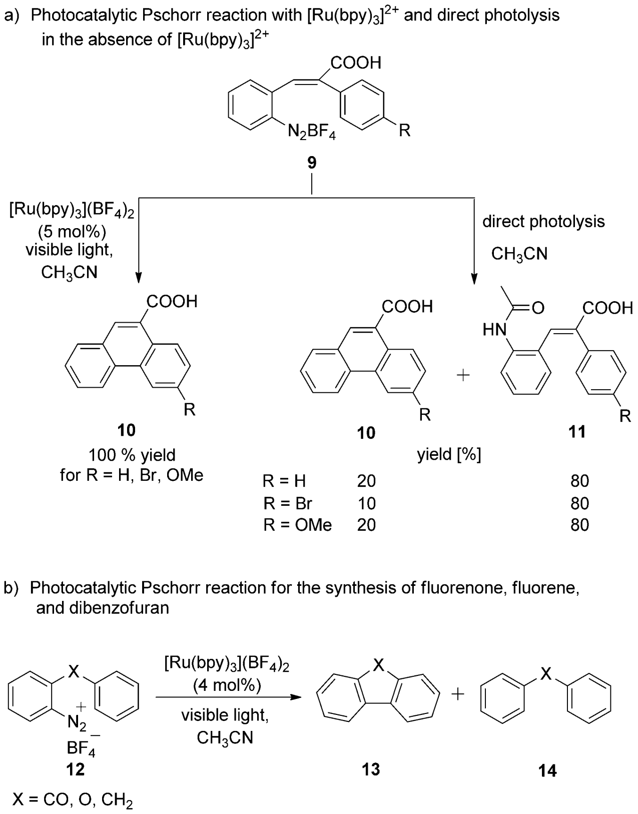
reported. Scheme 3 summarizes the different pathways: Electron transfer, either from the reducing agent or the photocatalysts to the diazonium cation yields the aryl radical, which adds to a double bond. The alkyl radical reacts with $X^-$ to give Meerwein alkene addition products that may eliminate HX, yielding the unsaturated cross-coupling products. Alternatively, oxidation of the alkyl radical regenerates the photoredox catalyst and yields a carbenium ion, which eliminates a proton to give the cross-coupled compounds.



*Scheme 3.* Reaction pathways of the Meerwein arylation addition, cross-coupling, and photoredox reactions.

In 1984, Cano-Yelo and Deronzier reported the photocatalyzed Pschorr reaction using $[Ru(bpy)_3]^{2+}$ as the photoredox catalyst under irradiation with blue light.[16] The Pschorr reaction typically involves the reduction of diazonium salts followed by an intramolecular cyclization. The authors synthesized phenanthrene carboxylic acid **10** quantitatively from the corresponding stilbene diazonium salt **9** in acetonitrile under visible-light irradiation (Scheme 4). It should be noted that the direct photolysis ($\lambda > 360$ nm) of diazonium salts in the absence of the photocatalyst provided the corresponding acetamide **11** as the major product and phenanthrene only as minor product (Scheme 4a).

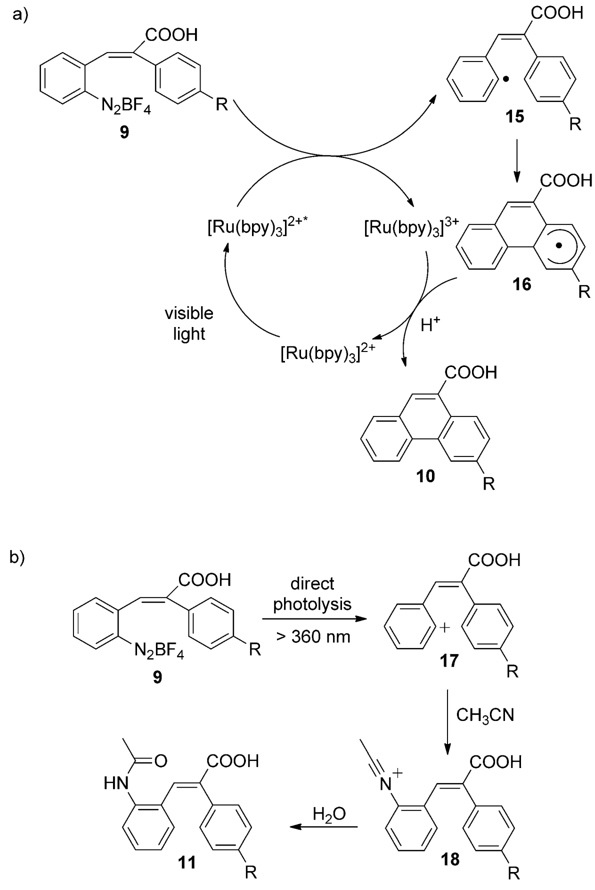
Following their success in the photocatalytic Pschorr reaction, Cano-Yelo and Deronzier further extended their methodology to synthesize fluorenone, fluorene, and dibenzofuran from the corresponding diazonium salts (Scheme 4b).[17] Visible-light irradiation ($\lambda > 410$ nm) of $[Ru(bpy)_3]^{2+}$ and aryl diazonium salt **12** in anhydrous $CH_3CN$ gave mainly the noncyclized product **14** (75–100 %) and only small amounts of the cyclized product **13** (0–25 %). The low reaction yield of cyclized products **13** in this reaction compared to that of stilbenediazonium salts in the previously reported Pschorr reaction was explained by the less rigid structure of **12** and smaller gain in aromatic stabilization energy of compound **13** compared to compound **10**. To accelerate the slow photoreaction, 0.5 equivalents of 4-methoxybenzyl alcohol and collidine were added to the reaction mixture. The product distribution did not improve, but the reaction times were significantly shorter.



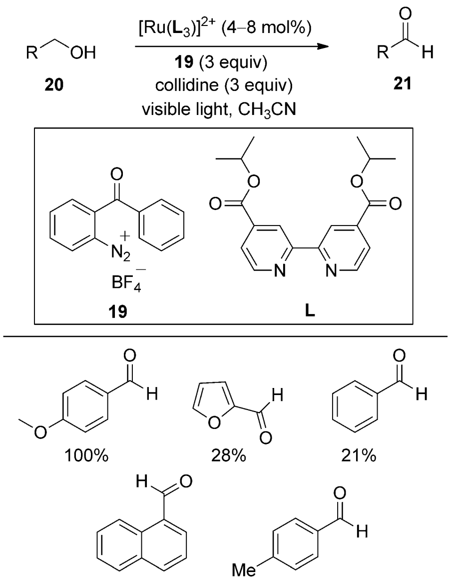
*Scheme 4.* Photocatalytic Pschorr reactions.

The proposed mechanism shown in Scheme 5 starts with the oxidative quenching of the excited state of $[Ru(bpy)_3]^{2+*}$ by the aryl diazonium salt **9**, generating aryl radical **15** and the strong oxidant $[Ru(bpy)_3]^{3+}$. Intramolecular cyclization of **15** furnishes radical **16**, which is then oxidized by $[Ru(bpy)_3]^{3+}$ and undergoes subsequent deprotonation to give compound **10** and regenerate the photocatalyst. Direct photolysis of aryldiazonium salt **9** produces the corresponding aryl cation **17**, which further reacts with the solvent $CH_3CN$ to give the aryl cation adduct **18**. The hydrolysis of the intermediate aryl cation **18** produces acetamide **11**. The authors also provided indirect proof of the electron-transfer mechanism by quenching experiments.[16,18] Irradiation of 4-bromobenzene diazonium salt and $[Ru(bpy)_3]^{2+}$ in anhydrous $CH_3CN$ generates $[Ru(bpy)_3]^{3+}$, which is verified by its characteristic absorption during photolysis. The back electron-transfer from the diazonium salt to $[Ru(bpy)_3]^{3+}$ is suppressed by the fast, irreversible decomposition of diazonium salt.

Later, Cano-Yelo and Deronzier reported the oxidation of carbinols to aldehydes using aryl diazonium salts as oxidative quenchers.[19] Blue-light irradiation of a mixture of carbinol **20**, the ruthenium complex, aryl diazonium salt **19**, and 2,4,6-trimethylpyridine (collidine) in anhydrous $CH_3CN$ provided the corresponding aldehyde **21** in moderate to good yields (Scheme 6). The aryl radical derived from **19** undergoes intramolecular cyclization to provide fluorenone (like in the Pschorr reaction) or it abstracts a hydrogen atom from the



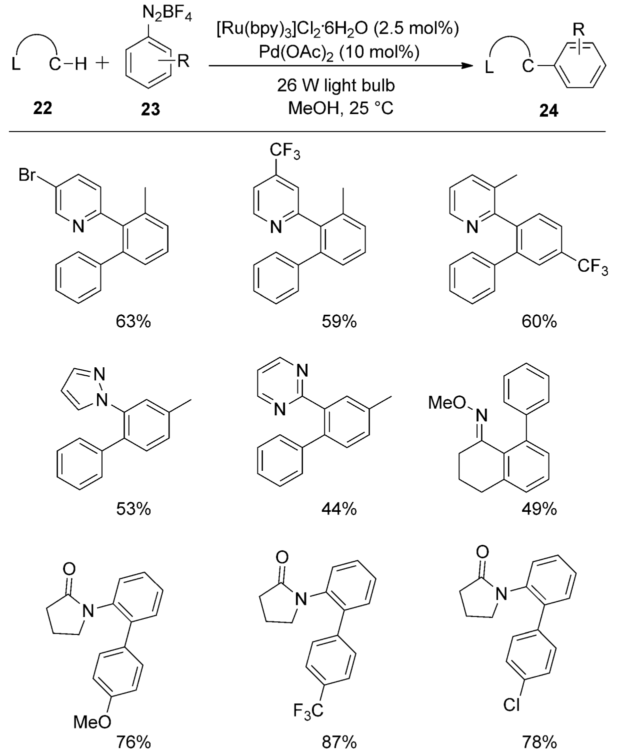
**Scheme 5.** Proposed mechanism for photocatalytic Pschorr reaction (a) and direct photolysis (b).



**Scheme 6.** Oxidation of carbinols to aldehydes by photoredox catalysis.

benzylic position of the carbinol giving benzophenone. Benzophenone and fluorenone were observed as byproducts in a ratio of 3:1. The reaction yields were improved by adding a base in the case of easily oxidizable carbinols, but lower yields were observed with less easily oxidized carbinols. The lower yields with carbinols having higher oxidation potentials are explained by the oxidation of the base by the ruthenium complex. The same authors reported the oxidation of α-phenylated primary and secondary alcohols to the corresponding carbonyl derivatives in the presence of aryl diazonium salts and a basic agent in MeCN and compared the results with electrochemical redox catalysis.[20] They propose a mechanism involving the oxidative quenching of the excited state of $[Ru(L_3)]^{2+*}$ by the aryl diazonium salt leading to $[Ru(L_3)]^{3+}$. A single-electron transfer from the carbinol to $[Ru(L_3)]^{3+}$ regenerates the catalytic cycle while producing the aldehyde. The photoreaction is significantly improved by adding collidine, because the oxidation of carbinol to the aldehyde requires two-electron and two-proton exchanges.

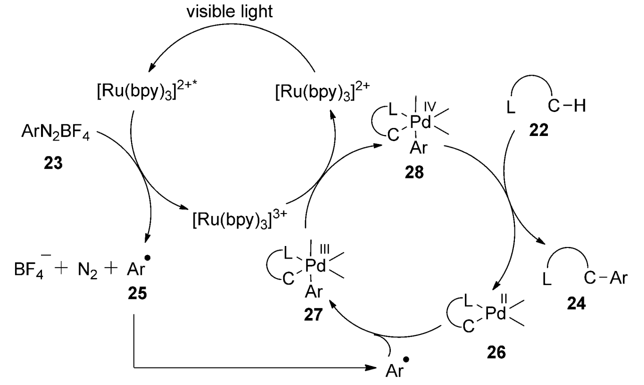
25 Years after the first application of photoredox catalysis with diazonium salts described by Cano-Yelo and Deronzier, Sanford and co-workers reported ligand-directed C–H arylation reactions with aryl diazonium salts in which palladium catalysis is combined with photoredox catalysis.[21] Blue-light irradiation of diazonium salt **23**, substrate **22**, $Pd(OAc)_2$, and $[Ru(bpy)_3Cl_2]\cdot 6H_2O$ in MeOH at room temperature afforded the corresponding products in good to excellent yields (Scheme 7). Since addition of the aryl radical to the Pd species is very fast, MeOH can be used as the solvent. Advantages of this strategy are the mild reaction conditions, the broad scope of aryl diazonium salts, and the tolerance to a wide range of functional groups. Amides, pyrazoles,



**Scheme 7.** Ligand-directed C–H arylation at room temperature by dual catalysis.

pyrimidines, and oxime ethers are suitable directing groups for this photoreaction.

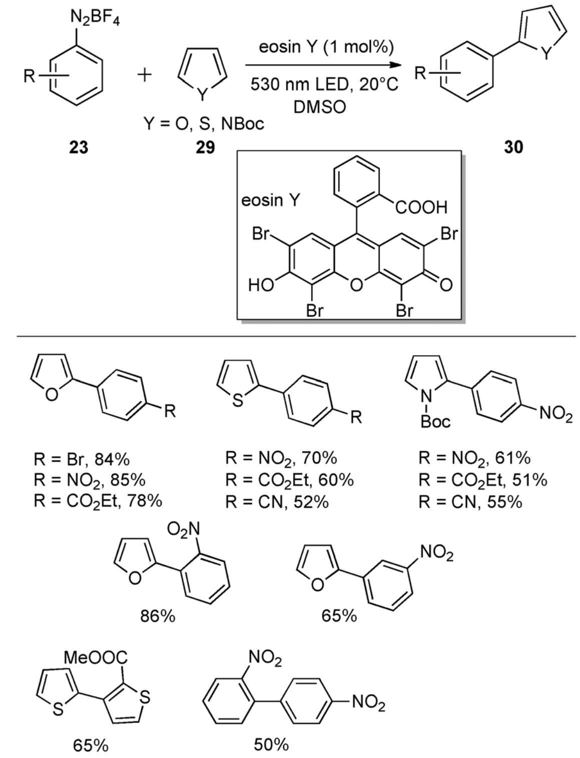
The proposed mechanism of the reaction starts with a single-electron transfer to aryl diazonium salt **23** from the excited state of $[Ru(bpy)_3]^{2+*}$, giving an aryl radical and $[Ru(bpy)_3]^{3+}$. Addition of the aryl radical **25** to the palladacycle **26**, which is generated by C–H activation of the substrate, affords the $Pd^{III}$ intermediate **27**. A single-electron transfer from $[Ru(bpy)_3]^{3+}$ to intermediate **27** regenerates the photocatalyst while producing the $Pd^{IV}$ intermediate **28**, which then undergoes reductive elimination to give the arylated product **24** and $Pd^{II}$ catalyst **26** (Scheme 8).



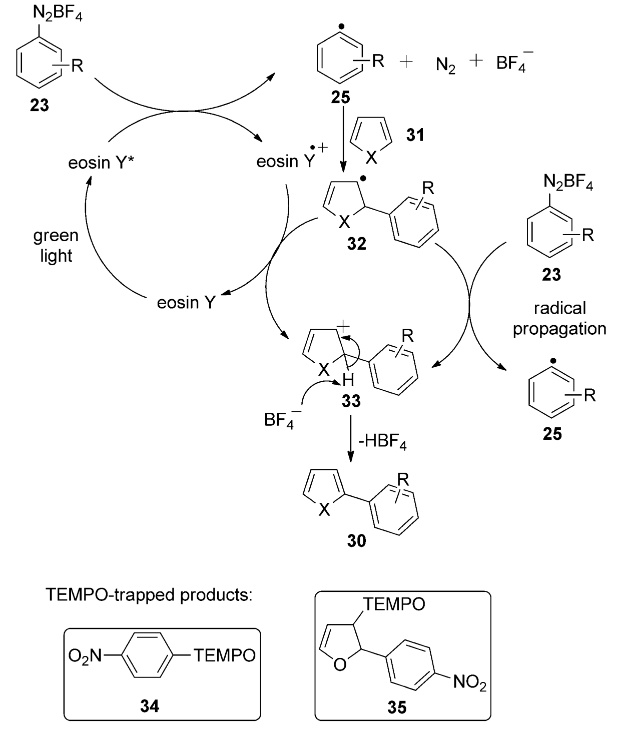
*Scheme 8.* Proposed mechanism for the arylation by Pd/Ru catalysis.

Our group recently developed a method for the direct C–H arylation of heteroarenes with aryl diazonium salts using the organic dye eosin Y as the photoredox catalyst with green-light irradiation.[22] In contrast to other C–H arylation methods, the reaction requires no metal catalyst, proceeds at ambient temperature, and has a high functional-group tolerance. Aryl diazonium salts bearing both electron-neutral or -withdrawing groups and a variety of heterocyclic compounds were shown to be efficient substrates for this photoreaction (Scheme 9). The methodology was applied to construct dithiophenes, which have applications in material chemistry. Control experiments in the absence of catalyst and light confirmed the photocatalytic nature of the reaction. In addition to heteroarenes, nitrobenzene was subjected to the photoreaction conditions and gave the expected cross-coupling product in 50% yield.

The suggested mechanism of the direct C–H arylation of heteroarenes is depicted in Scheme 10. First, green-light irradiation of eosin Y initiates a single-electron transfer to aryl diazonium salt **23** to produce aryl radical **25** and the cation radical of eosin Y. Then the aryl radical **25** adds to the heteroarene **31** to give the radical intermediate **32**, which is then further oxidized either by the eosin Y cation radical to produce the carbocation intermediate **33** and complete the catalytic cycle or it is oxidized by aryl diazonium salt **23** in a radical chain mechanism. Finally, the carbocation intermediate **33** is deprotonated yielding product **30**. The authors were able to trap the radical intermediates **25** and **32** with TEMPO, thus supporting the presence of radical intermediates during the photoreaction.



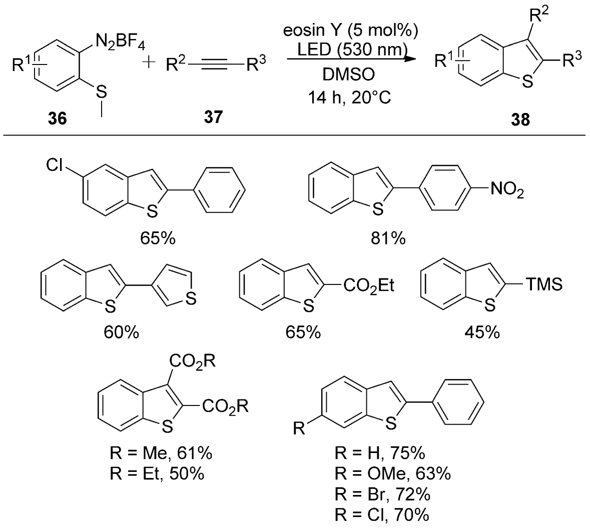
*Scheme 9.* Direct C–H arylation of heteroarenes with eosin Y as the photoredox catalyst.



*Scheme 10.* Suggested mechanism for photocatalytic C–H arylation of heteroarenes.

Next the photocatalyzed arylation reactions of heteroarenes were applied to synthesize privileged benzothiophene moieties, but unfortunately only poor yields and regioisomeric product mixtures were observed. The recently reported photocatalytic synthesis of benzothiophenes through a radical annulation process using eosin Y as the photoredox catalyst in green light overcomes the problem.[23]

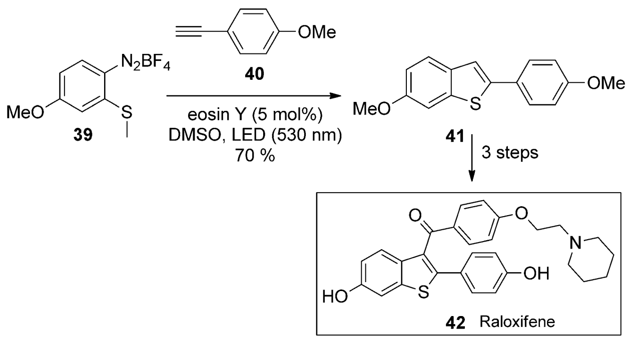
When a solution of *o*-methylthiobenzenediazonium salt **36** and alkyne **37** in anhydrous DMSO was subjected to irradiation at 530 nm for 14 h, only the desired regioisomer was obtained in moderate to good yields (Scheme 11). Diazonium salts containing either electron-donating or electron-neutral substituents are compatible with this photoreaction. The annulations reaction proceeds well with different alkynes.



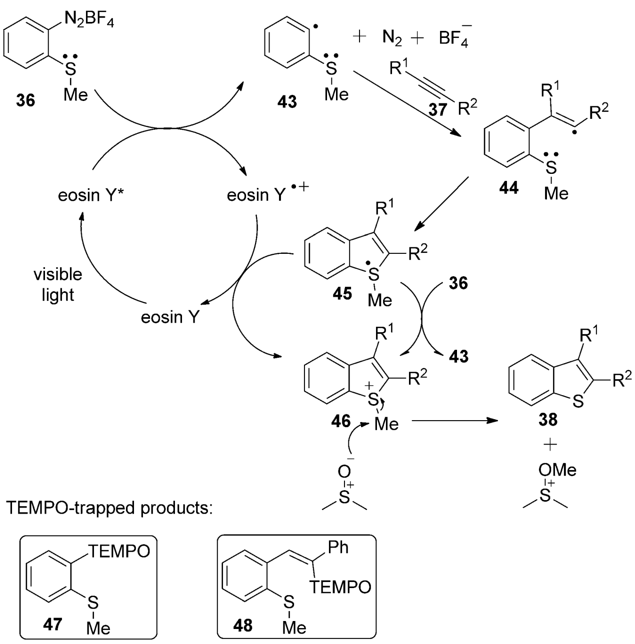
*Scheme 11.* Radical annulation for the synthesis of benzothiophenes by visible-light photocatalysis using eosin Y.

The photoannulation reaction was used to prepare the key intermediate **41** in the synthesis of the commercial drug Raloxifene (**42**). A solution of 4-methoxy-2-(methylthio)benzenediazonium salt (**39**) and 1-ethynyl-4-methoxybenzene (**40**) in anhydrous DMSO was subjected to the standard photoreaction conditions providing intermediate **41** in 70% yield (Scheme 12).

The proposed mechanism of the photoannulation reaction starts with a single-electron transfer (SET) from the excited state of eosin Y to *o*-methylthiobenzenediazonium salt **36** to generate aryl radical **43** and the radical cation of eosin Y. The highly reactive aryl radical **43** adds to alkyne **37** to produce a vinyl radical intermediate **44**, which then undergoes homolytic substitution at the sulfur atom to give the sulfuranyl radical intermediate **45**. Oxidation of intermediate **45** by the eosin Y cation radical regenerates the photocatalyst while affording the cation **46**. It should be noted that oxidation of the intermediate could also proceed with diazonium salts in a radical chain mechanism. Finally, cation **46** transfers a methyl group to the solvent DMSO by an $S_N2$ process to afford product **38**. TEMPO-trapped adducts **47** and **48** suggest the likely presence of radical intermediates in the reaction mechanism (Scheme 13).



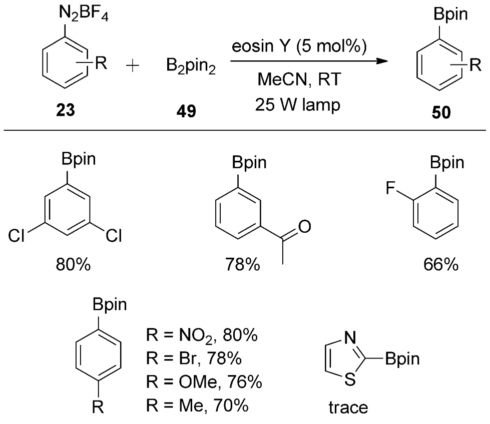
*Scheme 12.* Visible-light-catalyzed preparation of a key intermediate of synthesis of the antiulcer drug Raloxifene.



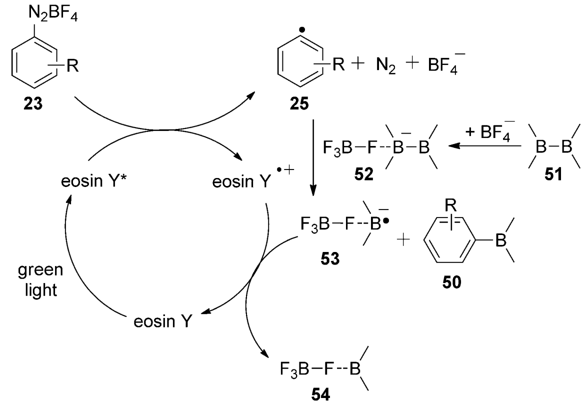
*Scheme 13.* Proposed mechanism for the photoannulation reaction.

All of the examples discussed so far address C–C bond-forming reactions utilizing the oxidative quenching of the photocatalyst. Very recently, Yan and co-workers reported C-borylation reactions through photoredox catalysis under visible-light irradiation with eosin Y.[24] The authors investigated the scope of the photoreaction by employing different diazonium salts. They found that aryl diazonium salts bearing various electron-donating and -withdrawing substituents smoothly gave the corresponding borylated products in moderate to good yields (Scheme 14). The borylation with heteroaromatic diazonium salts does not proceed as well as the reaction with aryl diazonium salts.

The authors proposed the reaction mechanism depicted in Scheme 15. After visible-light excitation of eosin Y a single-electron transfer to diazonium salt **23** gives aryl radical **25**. The aryl radical adds to complex **52**, which is formed in situ by the interaction between $B_2pin_2$ and the tetrafluoroborate anion, to afford the radical anion intermediate **53** and the



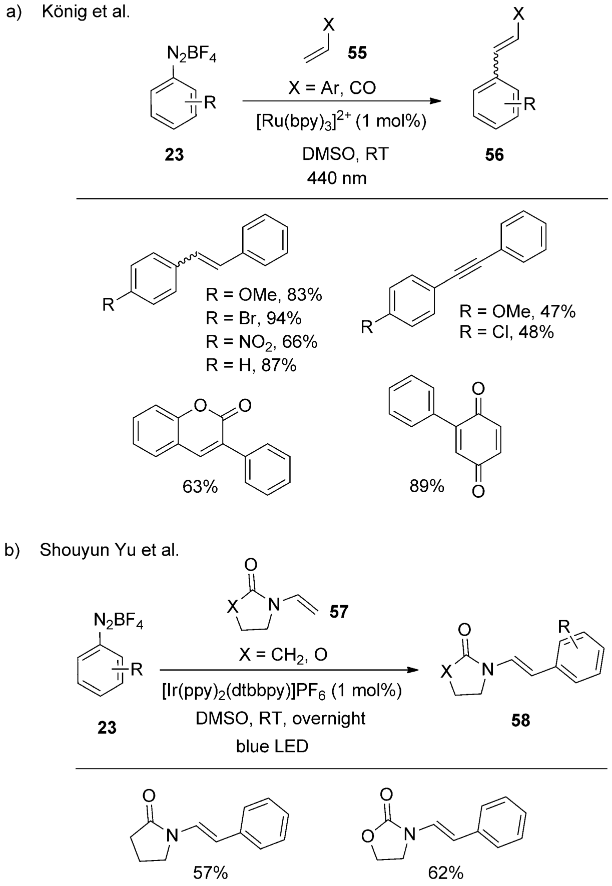
*Scheme 14.* Borylation of aryl diazonium salts by photoredox catalysis.



*Scheme 15.* Proposed mechanism for the borylation of aryl diazonium salts.

borylated product **50**. Oxidation of the reaction intermediate **53** by the eosin Y cation radical completes the catalytic cycle.

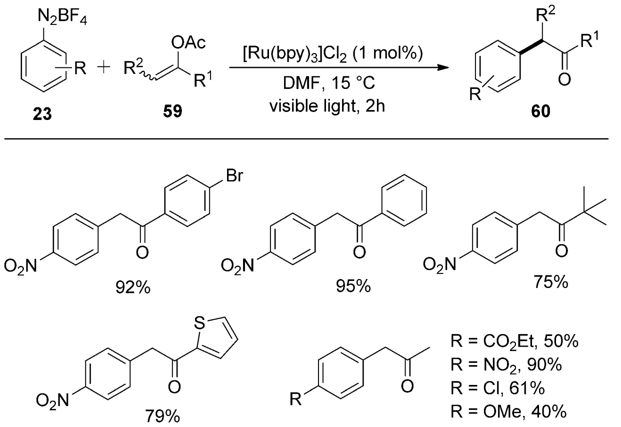
The Meerwein arylation protocol has been used to arylate various unsaturated compounds with metallic copper, iron(II) compounds, and iodine, but earlier reaction conditions suffered from low yields and side products. These drawbacks prevented the broader application of the Meerwein arylation reaction in organic synthesis. Improved reaction conditions, such as the use of chloride-based ionic liquids as promoting agents, allowed Meerwein arylations in satisfactory yields.[25] The recently reported photocatalytic version of the intermolecular Meerwein reaction for the arylation of alkenes, alkynes, and enones with aryl diazonium salts using $[Ru(bpy)_3]^{2+}$ or eosin Y as photoredox catalysts further improves the process.[26] The photocatalyst and light were found to be essential for the useful conversion to the arylated products. A solution of aryl diazonium salt **23**, unsaturated compound **55**, and the photocatalyst in anhydrous DMSO was irradiated by blue light for 2 h yielding the corresponding coupling products in good to excellent yields. Halogen-substituted diazonium salts have been employed in the photoreaction leaving the carbon–halogen bond intact and allowing further functionalization of the cross-coupling products by transition-metal-catalyzed or organometallic transformations. However, the reaction is limited to activated unsaturated compounds including coumarins, styrenes, quinones, and phenyl acetylenes (Scheme 16).



*Scheme 16.* Photo-Meerwein arylation of unsaturated compounds.

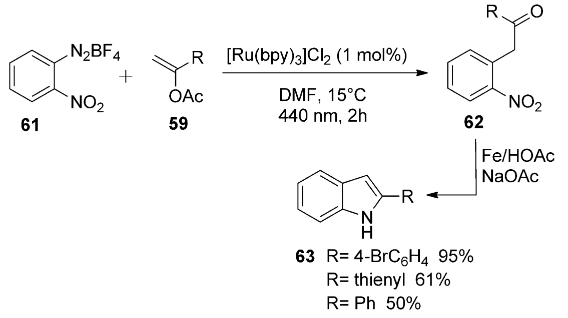
Shortly after this, the Yu group extended the Meerwein arylation to enamides and enecarbamates using aryl diazonium salts in blue light.[27] The photocatalyst $[Ir(ppy)_2(dtbbpy)]PF_6$ (1 mol %), aryl diazonium salt **23**, and substrate **57** were irradiated overnight by visible light with a 3 W blue LED strip to afford the corresponding product in moderate to good yields (Scheme 16). The mechanism of the photoreaction starts with the oxidative quenching of the photocatalyst by the aryl diazonium salt to form the aryl radical. This aryl radical adds to the unsaturated compound to give a radical intermediate, which then undergoes oxidation and deprotonation to yield the desired product.

α-Aryl carbonyl compounds are important substructures of pharmaceutical and biological active molecules. Typical synthetic routes include transition-metal- and base-catalyzed[28] steps, but an alternative approach is the use of photoredox catalysis with aryldiazonium salts as the radical source and enol acetates as coupling partners (Scheme 17).[29] Different photoredox catalysts and solvents were screened; the reaction proceeds best in DMF and DMSO with $[Ru(bpy)_3]Cl_2$ as the photocatalyst. The scope of the reaction was investigated for diazonium salts and enol acetates: Aryl



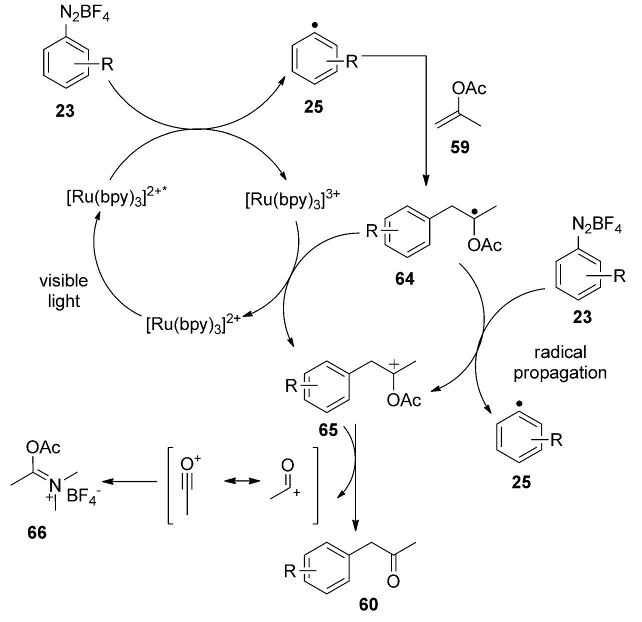
***Scheme 17.*** α-Arylation of enol acetates by photoredox catalysis.

diazonium salts containing electron-withdrawing or neutral groups, and terminal enol acetates are suitable substrates. A synthetic application of the photoredox catalysis was demonstrated, the preparation of compound **62**, which is reduced by iron to give the corresponding substituted indoles **63** in good to excellent yields without isolation of intermediates (Scheme 18).[30]



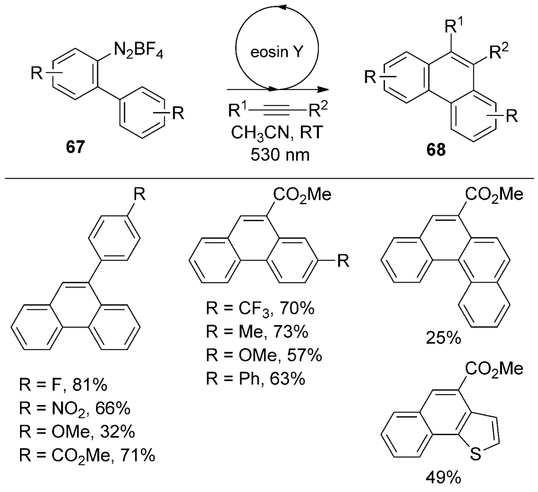
***Scheme 18.*** Synthesis of substituted indols precursors by photoredox catalysis.

Similar to the previously discussed mechanisms the oxidative quenching of $[Ru(bpy)_3]^{2+*}$ by aryl diazonium salt **23** gives aryl radical **25** and the strong oxidant $[Ru(bpy)_3]^{3+}$. The addition of the aryl radical to enol acetate **59** generates radical intermediate **64**. Re-oxidation of the intermediate **64** by $[Ru(bpy)_3]^{3+}$ forms the carbocation intermediate **65** and regenerates the catalyst $[Ru(bpy)_3]^{2+}$. The desired product **60** is obtained by transfer of an acyl cation from the intermediate carbocation **65** to a nucleophile present in the reaction mixture such as DMF giving the stable salt **66**, which is one of the likely intermediates in the first step of the Vilsmeier–Haack reaction. However, alternative pathways for the oxidation of the radical intermediate **64** by aryl diazonium salts cannot be excluded at this time (Scheme 19).



***Scheme 19.*** Proposed mechanism for α-arylation of enol acetates with aryl diazonium salts in visible light.

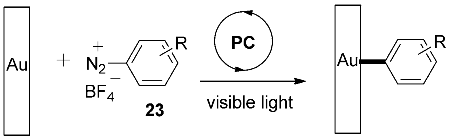
A common synthetic approach to phenanthrenes is the photocyclization of stilbenes by irradiation with UV light followed by oxidation. Zhou and co-workers recently reported the synthesis of phenanthrenes from diazonium salts and alkynes using visible light and the organic dye eosin Y as a photoredox catalyst.[31] Irradiation of a solution of biphenyl diazonium salt **67**, 10 equiv of alkyne, and 1 mol% eosin Y in $CH_3CN$ with green light for 12 h afforded the corresponding product **68** in good to excellent yields (Scheme 20). It is important to note that the addition of base to the reaction mixture causes a decrease in the yield, presumably due to the direct reaction between the base and the diazonium salt. The photoreaction proceeds smoothly with a series of diazonium salts and alkynes. A range of functional groups including ketones and nitro, methoxy, halogen, and ester groups do not interfere with this photoreaction. A SET from eosin Y* to the biphenyl diazonium salt produces a biaryl radical. The



***Scheme 20.*** Visible-light-induced synthesis of phenanthrenes.

generated radical adds to the alkyne to form a vinyl radical intermediate and intramolecular addition to the aromatic ring yields the cyclic radical intermediate, which then undergoes further oxidation and subsequent deprotonation to give the final product.

Functionalized surfaces have many applications from analytical and biochemical sensors to microelectronics and biomedical industrial applications. UV photochemical methods have been used for functionalizing surfaces, but these methods are mainly restricted to alkenes and arylazides. Recently, Pinson et al. described a photochemical method for modifying gold surfaces with diazonium salts by application of visible light and either $[Ru(bpy)_3]^{2+}$ or eosin Y as photosensitizers (Scheme 21).[32]



*Scheme 21.* Functionalization of surface with diazonium salts by photoredox catalysis.

In addition to diazonium salts, aryl sulfonyl chlorides and aryl iodonium salts can also be used as aryl radical sources in visible-light catalysis. Recently, Li and co-workers reported the synthesis of functionalized indenes from arylalkynes and arylsulfonyl chlorides through photoredox catalysis.[33] Sanford et al. developed a C–H arylation method with diaryliodonium reagents merging photoredox and transition-metal catalysis.[34]

Visible-light photoredox catalysis utilizing diazonium salts as aryl radical sources has become a powerful and efficient method to form carbon–carbon and carbon–heteroatom bonds. The oxidative quenching of photocatalysts by diazonium salts allows for inter- and intramolecular cyclization reactions with regioselective formation of products and the method has already been applied to the synthesis of biologically active compounds and drug intermediates. Although the photocatalytic versions of the classic Meerwein arylation protocol have given access so far only to cross-coupling products and not to alkene addition products, the method significantly improves applications in organic synthesis. Although excellent progress has been made in the area, many challenges and opportunities still remain.

Photocatalysis facilitates reactions at low temperatures, which may be beneficial for the development of stereoselective variants in particular if the scope is expanded to Meerwein alkene addition products. Aryl radical chemistry in combination with visible-light photocatalysis has not been broadly applied to carbonylation reactions, although two out of three industrial processes use aryl diazonium salts in carbonylation processes.[2b,35] While there is already good evidence for some of the radical intermediates, a more detailed mechanistic investigation is highly desirable to improve our understanding of the mechanisms and allow for a better design of new photocatalytic reactions of diazonium salts.

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