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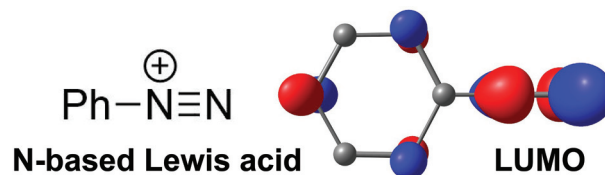
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Diazonium Salts as Nitrogen-Based Lewis Acids

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Abstract Aryldiazonium salts are widely used in many organic transformations with displacement of N_2 or through addition to the terminal nitrogen. Such aryldiazonium salts can be viewed as N-based Lewis acids that can react with Lewis bases to synthesize a wide variety of azo compounds. Additionally, diazonium salts are known to undergo single-electron transfer and release N_2 , forming an aryl radical, which results in different reactivity. Herein, we provide a concise overview of the reactivity of aryldiazonium salts undergoing classical donor-acceptor reactivity or single-electron transfer.

Key words diazonium salts, donor-acceptor adducts, N-based Lewis acids, phosphines, carbenes, radicals

Introduction

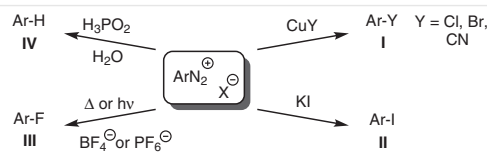
Diazonium salts¹ are organic compounds with the general formula $[\text{R}-\text{N}\equiv\text{N}]^+[\text{X}]^-$, in which R can be an alkyl or aryl group. The general chemistry of diazonium salts has been reviewed recently,² so in this short review we describe selected examples of reactions of aryldiazonium salts, with a focus on those retaining the azo ($\text{N}=\text{N}$) moiety. $[\text{X}]^-$ is typically an organic or inorganic anion such as a halide, $[\text{BF}_4]^-$ or $[\text{PF}_6]^-$. The reactivity of diazonium salts is often dominated by the loss of the N_2 moiety (Scheme 1).³ In the Sandmeyer reaction (I) the diazo group is replaced with a chlorine or bromine through the addition of the corresponding cuprous halide to a diazonium salt, forming an aryl halide.⁴ Formation of arylchlorides or arylbromides is also feasible using copper powder with HCl or HBr, referred to as the Gatterman reaction.⁵ Aryl cyanides can be formed *via* the Sandmeyer reaction with the use of CuCN , although here other metal complexes can be used.⁶ Aryl iodides can be prepared through the addition of hydroiodic acid or, more commonly, potassium iodide (II),⁷ and aryl fluorides are formed through thermal decomposition or photochemical induction of $[\text{BF}_4]^-$ or $[\text{PF}_6]^-$ with a diazonium salt in the Balz-Schiemann reaction (III).⁸ Mai showed that diazonium salts can be reduced by H_3PO_2 in water, forming the corresponding benzene analogue (IV).^{2,9}



Evi Habraken (left) was born in Valkenswaard (The Netherlands) in 1991. She completed her B.Sc. (2012) and her M.Sc. (2014) at the Eindhoven University of Technology, with also a research stay with P. G. Pringle at the University of Bristol (UK). She just finalized her Ph.D. thesis at the University of Amsterdam (UvA) under the supervision of Assoc. Prof. Chris Slootweg (UvA). Her work focused on the investigation of adduct formation and frustration of Lewis acids and base.

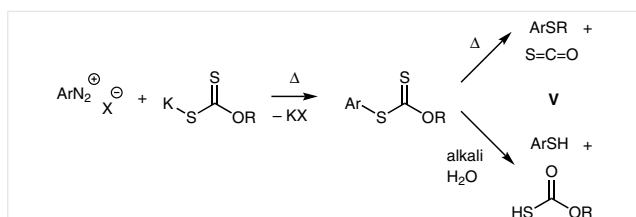
Andrew R. Jupp (middle) obtained his Ph.D. from the University of Oxford (2012–2016) under the supervision of Prof. Jose Goicoechea. He worked on phosphorus-containing analogues of the cyanate anion and urea, for which he was awarded the Reaxys Ph.D. Prize in Hong Kong in 2015. He subsequently carried out a Banting Postdoctoral Fellowship with Prof. Doug Stephan at the University of Toronto (2016–2018), working on the synthesis and reactivity of main-group Lewis acids and bases. He is currently a NWO-VENI laureate at the Van 't Hoff Institute of Molecular Sciences, University of Amsterdam, working with Assoc. Prof. Chris Slootweg on the activation of typically unreactive small molecules.

Chris Slootweg (right) was born in Haarlem (The Netherlands) in 1978 and received his undergraduate education from Vrije Universiteit Amsterdam in 2001. After earning his Ph.D. in 2005, he pursued postdoctoral studies at the ETH Zürich. In 2006, he returned to VU to initiate his independent career. He was promoted to Associate Professor in 2014, and moved to the University of Amsterdam in 2016. The mission of his laboratory is to educate students at the intersection of fundamental physical organic chemistry, main group chemistry and circular chemistry.



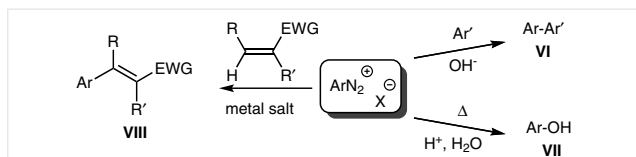
Scheme 1 Overview reactions of displacement of the N_2 group of diazonium salts. (I) Sandmeyer reaction; (II) replacement with iodide; (III) Balz-Schiemann reaction; (IV) reduction.

Thiols and thioethers can be formed in two steps from diazonium salts (Scheme 2). Addition of potassium xanthate and gentle warming promotes loss of N₂ and forms the intermediate shown. Subsequent pyrolysis forms the ArSR product, whereas alkaline hydrolysis yields the thiophenol derivative. This reaction is called the Leuckart thiophenol reaction (V).^{3,10}



Scheme 2 Representation of the Leuckart thiophenol reaction. The temperature is dependent on R-group and solvent used.

In the Gomberg–Bachmann reaction (VI; Scheme 3) an aryl group is coupled to the diazonium salt in basic media,¹¹ and this can be carried out in an intramolecular fashion in the Pschorr cyclization. Addition of a hydroxyl group and thus formation of phenols proceeds upon heating a highly acidic aqueous solution of the diazonium salt, liberating an H⁺ (VII).⁷ In the Meerwein arylation (VIII) an electron-poor alkene is coupled to the diazonium salt with use of a metal salt, commonly a copper(II) salt.¹² The scope of the alkene as substrate has been extended to include a variety of olefins and even to electron-rich olefins.³



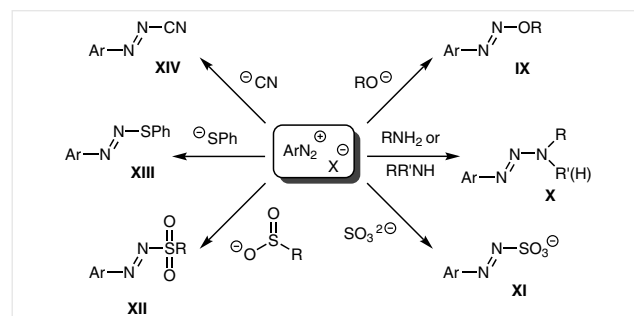
Scheme 3 Overview reactions of displacement of N₂ group of diazonium salts. (VI) Ar', OH⁻; (VII) H₂O, acidic condition, Δ; (VIII) electron-poor alkene + catalyst.

2 Azo Compounds

2.1 Retention of the Azo Moiety

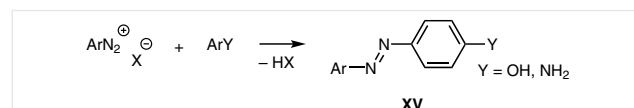
As well as displacement of the N₂ group, diazonium salts are able to react with nucleophiles that add to the terminal nitrogen (Scheme 4).³ Such reactions have been known for several decades and they result in the formation of (di)azo compounds; for example arenediazoethers from alkoxide ions (IX),¹³ or triazenes from primary and secondary aliphatic and aromatic (or heterocyclic) amines with release of H⁺ (X).³ Arenediazosulfonates are formed from sulfite ions (XI);³ first the *Z*-isomer forms, which is slowly transformed into the *E*-isomer. Note, the *Z*-isomer is highly reactive and can rapidly decompose into the starting mate-

rials. Diazonium salts with anions of sulfinic acids ([RSO(O)]⁻) in a slightly acidic aqueous medium form arenediazosulfones (XII).¹⁴ Unstable arenediazothioethers (XIII) are formed via the addition of thiolates, which decompose (explosively) to N₂ and the corresponding sulfide.¹⁵ Lastly, with cyanide ions arenediazocyanides (XIV) are formed; here too, first the *Z*-isomer forms in a reversible manner, which slowly converts into the stable *E*-isomer.¹⁶



Scheme 4 Overview reactions of addition of nucleophiles that react as Lewis base to diazonium salts. (IX) alkoxide ions; (X) various primary and secondary amines; (XI) sulfite ion; (XII) anions of sulfinic acids; (XIII) thiolates; (XIV) cyanide ion.

Perhaps a more common and well-known reaction of a nucleophile that adds to the terminal nitrogen is through electrophilic aromatic substitution (XV; Scheme 5). In this case the *para*-position of the phenyl group of aniline or phenol, containing strongly activating substituents, adds to the N₂ moiety of the diazonium salt.³

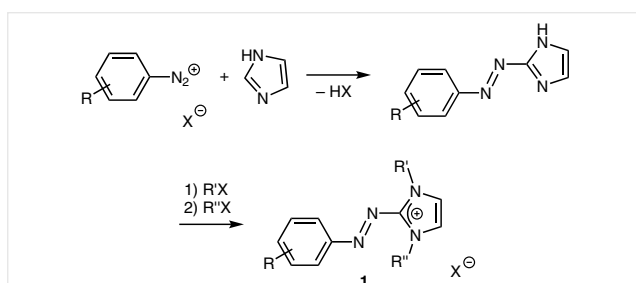


Scheme 5 Electrophilic aromatic substitution of an amine or phenol to a diazonium salt.

2.2 Coupling of Imidazoles to Diazonium Salts

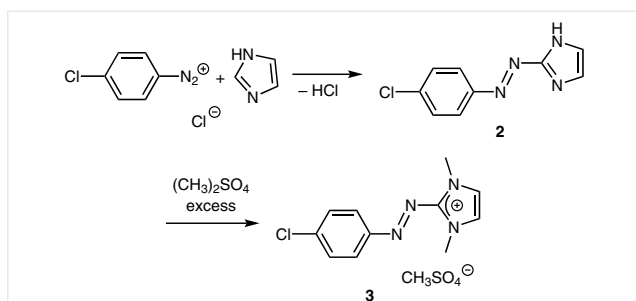
As the diazonium salt reacts as an electrophile, thermodynamically it can also be viewed as an N-based Lewis acid that can therefore react with Lewis bases. Compounds IX, XI, XII, XIII and XIV are examples of such reactivity, which is unusual reactivity for typical nitrogen-based molecules that contain a lone pair and are thus seen as Lewis bases. However, recent papers by Gandelman and Stephan demonstrated that nitrogen-based compounds can be tuned as useful Lewis acids.¹⁷ Generally, cationic azo dyes containing imidazolium groups are produced *via* the coupling of an aromatic diazonium compound with an imidazole, which acts as nucleophile, followed by alkylation (1; Scheme 6).^{18–21} This coupling is similar to the coupling of a diazonium salt to aniline or phenol (Scheme 5). Coupling followed by al-

kylation was already patented in the end of the 1950s; Klingsberg and Lewis reported this reactivity as the quaternization of *N*-alkylated imidazolium azo dyes.^{18a} The alkylation can be carried out in a stepwise manner, the first alkylation can be performed by dissolving the azoimidazolium salt in an alkaline solution and adding an alkylating agent. As the product is insoluble it precipitates out of the reaction mixture and is pure enough to be used directly in the second alkylation step. The second alkylation conveniently proceeds with alkyl halide, sulfate or arylsulfonate in an organic solvent. Through this route, the two groups on the imidazolium nitrogen centers can differ from each other.



Scheme 6 Schematic representation of the coupling of an aromatic diazonium compound with an imidazole, followed by alkylation, R' can be similar to R'' (R', R'' = alkyl). X⁻ counter-ion.

Similar reactivity was described by Baumann and Dehnert (Scheme 7); they reacted *para*-chlorobenzenediazonium chloride with the imidazole at the 2-position of the ring, forming **2**, and subsequent addition of dimethyl sulfate resulted in cationic product **3**, which is alkylated at the 1- and 3-position of the imidazole.¹⁹ Along with the alkylation, the chloride counter-ion is exchanged for the methyl sulfate anion because the chloride is rather labile. Simov reported the one-pot process in water for obtaining such imidazolium cationic dyes and thus shortening the overall reaction time. Note, the coupling of the imidazole to the diazonium salt proceeds at pH values between 8.5 and 9.¹⁹

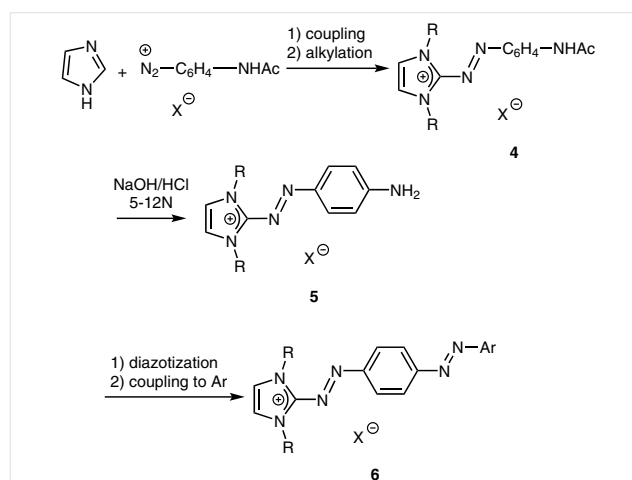


Scheme 7 Coupling and alkylation described by Baumann and Dehnert

This overall reaction was expanded and the alkylation can proceed with NaH and excess alkyl iodide (MeI, EtI or PhCH₂I) in anhydrous THF affording the desired compounds

with an iodide as counter-ion. Besides their use as dyes, these compounds are able to act as *N,N*-bidentate ligands to a metal center such as Cu(I) and Ag(I).²⁰

From a synthetic point of view, if after the initial coupling and alkylation, the azoimidazolium salt holds a suitably reactive group (e.g., NHAc in **4**, Scheme 8), then (after deprotection if necessary) a second diazotization and subsequent coupling to an aryl compound is feasible (**6**; Scheme 8).²¹ This order may be reversed, thus first the aryl couples to the diazonium salt and secondly the imidazole is coupled, followed by alkylation. This class of compounds is mostly used for dyeing keratin fibers such as hair.

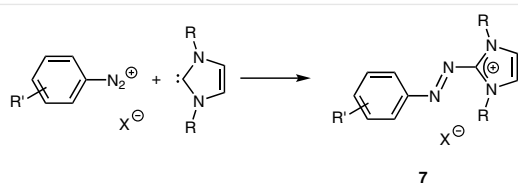


Scheme 8 Coupling of an imidazole to a diazonium salt, followed by alkylation. Reduction of the NHAc group to NH₂ and subsequent diazotization and coupling to an aryl compound

2.3 Coupling of *N*-Heterocyclic Carbenes to Diazonium Salts

Another way of accessing these azoimidazolium salts is by using carbenes as Lewis bases; specifically, *N*-heterocyclic carbenes (NHCs). This class of compound has made a significant impact as they are excellent σ -donor ligands for transition-metal complexes, they have been used in the stabilization of low-valent main group species, are used as organocatalysts, and are highly modular.²²

Through the direct coupling of *N*-aryl or *N*-alkyl NHCs to diazonium salts, these strongly colored cationic azoimidazolium dyes can be accessed in a straightforward manner and produced industrially (**7**; Scheme 9).²³ This reaction is well described in the patent literature, which states various R-groups on the nitrogen atoms or backbone of the NHC are feasible as well as variations in the diazonium salt. Examples in patents describe various syntheses that reveal the *in situ* formation of the carbene through the use of an organic or inorganic base, once it is added to the diazonium salt.²³ The imidazole derivative is added in slight excess (1.0 to 1.1 equiv) at 0 °C or room temperature and the azo compound is purified by column chromatography.^{23a}



Scheme 9 Direct coupling of an N-heterocyclic carbene with an aromatic diazonium compound (R = alkyl, aryl). X[−] counter-ion.

2.4 Coupling of Phosphines to Diazonium Salts

The analogous use of phosphines as Lewis bases in the addition to aryldiazonium salts is relatively underexplored, and only recently picked up interest. In 1953, Horner and Stöhr reacted triphenylphosphine with a variety of diazonium chlorides in an alcoholic solvent (methanol, ethanol or isopropanol) and obtained red azophosphonium chlorides **A** (R = H, Me, Cl, NO₂, CO₂H, OMe, OC(O)Me; Scheme 10).²⁴ Further reaction with water resulted in the formation of a triphenylaryl-hydrazyl phosphonium salt (**9**) and addition of hydrochloric acid resulted in the formation of aryl hydrazines (**10**) and triphenylphosphine oxide. Compound **8** is an unstable species, and Horner and Stöhr already noted that a second equivalent of triphenylphosphine is necessary to stabilize it. Compound **8** eliminates N₂ and decomposition results in substituted benzene (R-C₆H₅), N₂, HCl and triphenylphosphine oxide (Scheme 10, a). A few years later Horner and Hoffmann reported the ratio between the diazonium salt and PPh₃, as well as the use of anhydrous solvents, turned out to be of importance (Scheme 10, bottom), as different products could be formed, not all of which are stable.²⁵ It is noteworthy that the chemistry of the formation of compound **10** has only recently been described in the patent literature for its use in pharmacology.²⁶

Further research into the properties of the phosphine was performed by the group of Sutton in 1974 where they reacted not only PPh₃ but also tri(*p*-methoxyphenyl)phosphine and methyldiphenylphosphine with a range of diazonium salts (**11**; Figure 1).²⁷ The diazonium tetrafluoroborate salts were dissolved in acetone and added to PPh₃ at 0 °C, yet only the electron-donating mesomeric substituents (NMe₂ and OMe) in the *para*-position resulted in the

formation of isolable compounds, otherwise decomposition led to [ArPPh₃][BF₄] with concomitant release of N₂. The benefit of the electron-donating groups leads to the formation of one large π -conjugated system, where the positive charge is not solely located on the phosphorus moiety but can also be found on the nitrogen or oxygen atom of the *para*-substituent, increasing the stability of the compound (Figure 1). A significant contribution of the delocalization of the positive charge can be observed in the crystal structure (Figure 1, X-ray structure). In the aryl ring C2–C3 and C5–C6 (C2–C3 1.342(8), C5–C6 1.351(8) Å) are shorter compared to the other four bonds (1.415(8) to 1.429(8) Å). Also, the N1–N2 bond is longer than the typical N=N bond (N1–N2 1.308(6), typical N=N bond 1.24 Å) and N3–C4 is shorter than the N3–C_{ethyl} bonds (N3–C4 1.336(7), N3–C_{ethyl1} 1.490(9), N3–C_{ethyl2} 1.473(8) Å), clearly showing the alternating long and short bonds throughout the crystal structure.²⁸ Sutton and co-workers also reported on the improved stability for tri(*p*-methoxyphenyl)phosphine ((MeO)₃P), whereas with methyldiphenylphosphine (MePh₂P) the compounds proved to be more unstable. This is attributed

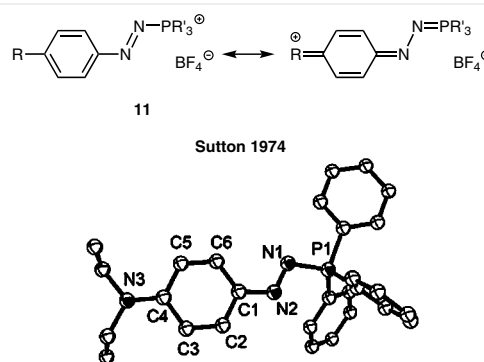
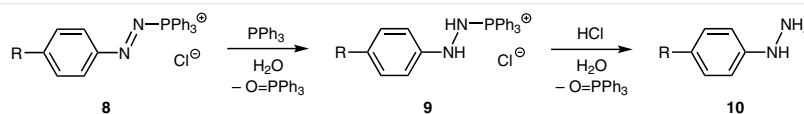
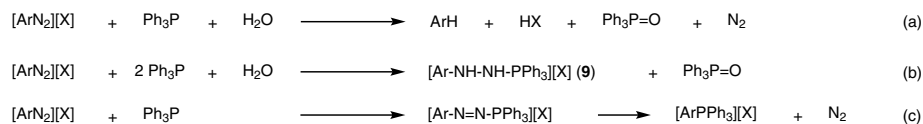


Figure 1 Example of azophosphonium salts developed by Sutton, (R = OMe, NEt₂; R' = PPh₃, PMePh₂, P(*p*-OMe-Ph)₃), including the resonance structure and X-ray crystal structure (R = NEt₂, displacement ellipsoids are set at 50% probability, hydrogen atoms and counter-ion omitted for clarity). Selected bond lengths [Å]: P1–N1 1.648(5), N1–N2 1.308(6), N2–C1 1.356(7), C1–C2 1.413(8), C2–C3 1.342(8), C3–C4 1.429(8), C4–C5 1.429(8), C5–C6 1.351(8), C4–N2 1.415(8), N3–C_{ethyl1} 1.490(9), N3–C_{ethyl2} 1.473(8).



Horner and Stöhr 1953



Scheme 10 Formation of triphenylaryl-hydrazyl phosphonium salt **9** and subsequently hydrazine **10** (top) and ratio between the components (bottom).

to the enhanced π -acceptor properties of phosphites relative to phosphines, leading to greater P–N multiple bonding character, and thus enhanced stability, in the former.²⁷

A few decades later in 1997, Wokaun and co-workers reacted tris(dimethylamino)phosphine with equimolar amounts of various diazonium tetrafluoroborate salts in acetonitrile ($R = \text{Cl}, \text{CN}, \text{SO}_2\text{NH}_2, \text{C}(\text{O})\text{OEt}$; Figure 2) affording the corresponding azophosphonium tetrafluoroborates **12** [$p\text{-R-PhN}_2(\text{P}(\text{NMe}_2)_3)[\text{BF}_4]$] in good yields (80–95%), which can be handled in air.²⁹ In 1999, Flower and co-workers obtained the azophosphonium salt **13** ($R = 6\text{-naphthalen-2-ol}$; Figure 2) in anhydrous THF, which they only characterized spectroscopically by ^{31}P NMR spectroscopy ($^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 40$ ppm).³⁰ Furthermore, Matsuda and co-workers obtained [$(p\text{-R-C}_6\text{H}_4\text{N}_2(\text{PR}_3))[\text{BF}_4]$] ($R = \text{H}, \text{CH}_3, \text{MeO}, \text{F}$) upon reaction of the corresponding diazonium salt with $(\text{PPh}_3)_4\text{Pd}$; they reported it as a side-product in their reaction.³¹

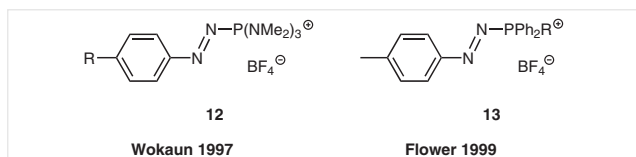
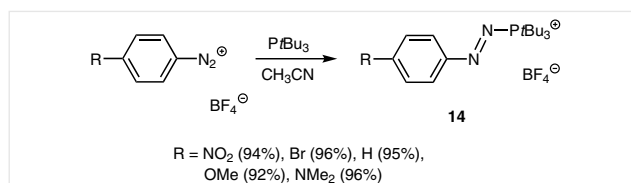


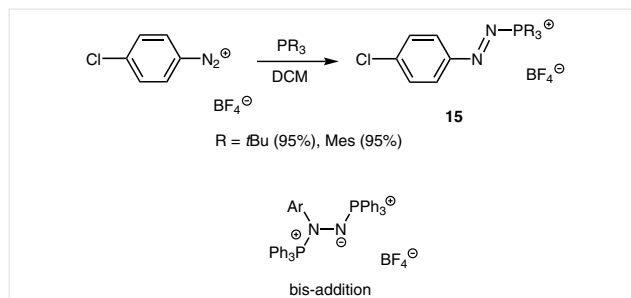
Figure 2 Examples of azophosphonium salts

We expanded this little knowledge about azophosphonium salts by addition of the bulky, electron-donating *tert*-butylphosphine to various aryldiazonium salts with *para*-substituents ranging from electron-withdrawing to electron-donating groups (**14**; Scheme 11).³² Addition of a slight excess of $t\text{Bu}_3\text{P}$ (1.1 equiv) to the *para*-substituted phenyldiazonium salts [$(p\text{-R-C}_6\text{H}_4\text{N}_2)[\text{BF}_4]$] ($R = \text{NO}_2, \text{Br}, \text{H}, \text{OMe}, \text{NMe}_2$) in acetonitrile at 0°C resulted in the formation of intensely colored compounds **14** ranging from purple to pink to red/brown ($R = \text{NO}_2$ to NMe_2 ; Scheme 11), respectively, which can be used as dyes. Removal of the solvent and subsequent addition of CH_2Cl_2 and *n*-pentane resulted in the precipitation of the desired solids, [$(p\text{-R-C}_6\text{H}_4\text{N}_2(\text{Pt-Bu}_3))[\text{BF}_4]$], which were obtained in high yields (92–96%). X-ray crystallography of the tetraphenylborate analogue confirmed the formation of [$(p\text{-H-C}_6\text{H}_4\text{N}_2(\text{Pt-Bu}_3))[\text{BPh}_4]$]. These azophosphonium salts are air-stable and experiments in D_2O and 2 M HCl, in which they dissolve poorly, revealed, over time, only hydrolysis of the tetrafluoroborate anion, leaving the azophosphonium cation intact. The high tunability of the diazonium salt directly relates to the color of the azophosphonium salt, which can be substantiated by UV/Vis spectroscopy, revealing two absorption bands from $\lambda_{\text{abs}} = 303\text{--}464$ nm ($\pi \rightarrow \pi^*$) and $\lambda_{\text{abs}} = 453\text{--}523$ nm ($n \rightarrow \pi^*$).



Scheme 11 Reaction of aryldiazonium salt [$(p\text{-R-C}_6\text{H}_4\text{N}_2)[\text{BF}_4]$] ($R = \text{NO}_2, \text{Br}, \text{H}, \text{OMe}, \text{NMe}_2$) with $t\text{Bu}_3\text{P}$; isolated yield in parentheses

Simultaneously, Stephan and co-workers reported the synthesis of new azophosphonium salts (Scheme 12) by reacting diazonium salt [$(p\text{-Cl-C}_6\text{H}_4\text{N}_2)[\text{BF}_4]$] with the bulky phosphines $t\text{Bu}_3\text{P}$ or Mes_3P in CH_2Cl_2 at room temperature, affording the azophosphonium salts **15** [$(p\text{-Cl-C}_6\text{H}_4\text{N}_2(\text{PR}_3))[\text{BF}_4]$] ($R = t\text{Bu}, \text{Mes}$), which are purple and red colored, respectively.³³ Further reaction of [$(p\text{-Cl-C}_6\text{H}_4\text{N}_2(\text{PMes}_3))[\text{BF}_4]$] with addition of 1 equivalent of $t\text{Bu}_3\text{P}$ resulted in the liberation of Mes_3P and showed clean addition of $t\text{Bu}_3\text{P}$, presumably because of the greater Lewis basicity of the latter. Note, addition of 1 equivalent of the less bulky Ph_3P leads to the unstable species [$(p\text{-R-C}_6\text{H}_4\text{N}_2(\text{PPh}_3))[\text{BF}_4]$] ($R = \text{H}$,³² Cl ³³) and, upon addition of 2 equivalents, bis-addition is observed, resulting in the addition of the phosphine to both nitrogen atoms in a pseudo-transoid disposition forming [$(p\text{-Cl-C}_6\text{H}_4\text{N}(\text{PPh}_3)\text{N}(\text{PPh}_3))[\text{BF}_4]$],³³ highlighting the necessity of bulky groups on the phosphine for controlled mono-addition.



Scheme 12 Top: reaction of aryldiazonium salt [$(p\text{-Cl-C}_6\text{H}_4\text{N}_2)[\text{BF}_4]$] with $t\text{Bu}_3\text{P}$ or Mes_3P , isolated yield in parentheses. Bottom: product of the bis-addition

The scope of azophosphonium salts was extended by our group by altering the aryl ring as well as the phosphine, demonstrating the readily tuneability of this synthetic protocol (Figure 3).³⁴ For the use of tri-*tert*-butylphosphine a wide range of stable adducts (**16**) can be synthesized in various shades of purple, pink and red ([$(p\text{-R-C}_6\text{H}_4\text{N}_2(\text{Pt-Bu}_3))[\text{BF}_4]$] ($R = \text{CN}, \text{CF}_3, \text{Cl}, \text{F}, \text{Ph}, \text{OC}(\text{O})\text{CH}_3, t\text{Bu}, \text{CH}_3, \text{OPh}, \text{OiPr}, \text{NH}_2$)). With the addition of trimesitylphosphine to selected aryldiazonium salts (**17** [$(p\text{-R-C}_6\text{H}_4\text{N}_2(\text{PMes}_3))[\text{BF}_4]$] ($R = \text{NO}_2, \text{Br}, \text{H}, \text{OMe}, \text{NMe}_2$)), a difference in color was ob-

served as lighter shades of color are formed. Compounds **17** have reduced thermodynamic stability owing to the less donating ability of PMe_3 compared with PtBu_3 .

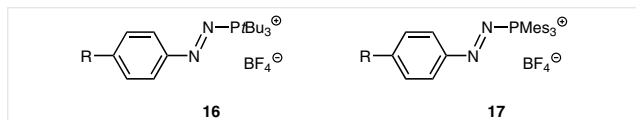
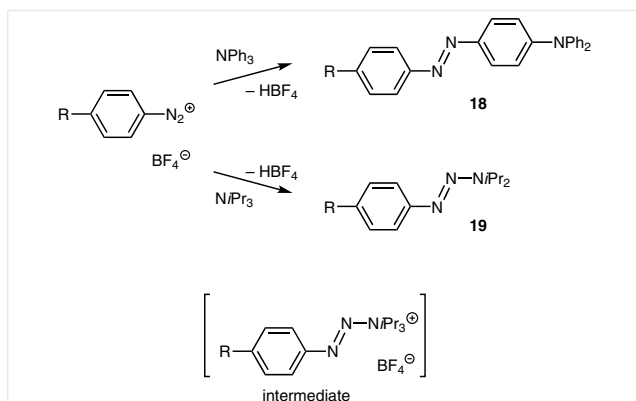


Figure 3 Azophosphonium salts with PtBu_3 and PMe_3 (PtBu_3 : $\text{R} = \text{CN}$, CF_3 , Cl , F , Ph , $\text{OC}(\text{O})\text{CH}_3$, $t\text{Bu}$, CH_3 , OPh , $\text{O}i\text{Pr}$, NH_2 ; PMe_3 : $\text{R} = \text{NO}_2$, Br , H , OMe , $\text{N}(\text{CH}_3)_2$).

2.5 Coupling of Tertiary Amines to Diazonium Salts

Notably, the use of tertiary amines as nucleophiles for the formation of azoammonium salts are still elusive as they can undergo electrophilic aromatic substitution with aromatic amines (**18**)³⁵ or undergo Hofmann elimination if β -hydrogen atoms are present (**19**), as found in triisopropylamine, and thus form a triazene.³⁶ Nevertheless, the formation of the triazene goes *via* the azoammonium intermediate (Scheme 13).



Scheme 13 Reaction of aryl diazonium salt with tertiary amines; top: electrophilic aromatic substitution, bottom: Hofmann elimination.

3 Use of Radicals with Diazonium Salts

For the aromatic amines, if the reactive *para* positions are blocked off, nucleophilic attack by the nitrogen could be envisioned, yet instead single-electron transfer occurs. Besides the reactivity of diazonium salts as a Lewis acid with a Lewis base, which is classical donor-acceptor reactivity, they can undergo single-electron transfer (SET) from a reducing agent. The diazonium ion is a useful oxidant that can undergo irreversible reduction in which it forms the intermediate diazenyl radical ($\text{ArN}=\text{N}^\cdot$), which is a rather labile species and readily releases dinitrogen forming the aryl radical Ar^\cdot (also referred to as dediazonation, Scheme 14).^{37,38}

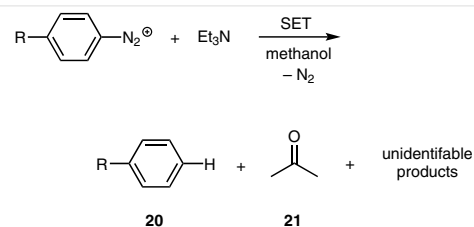


Scheme 14 Arenediazonium salt undergoing one-electron reduction, formation of the intermediate diazenyl radical before losing N_2 (counter-ion omitted)

There are various ways of generating such an aryl radical: through thermal decomposition, reduction at an electrode, photoinduction, radiolysis with γ -radiation, through reduction by metal cations, or through anion-induced dediazonation. Yet, the most essential element in all cases is that the redox potential of the reducing agent is strong enough to supply a single electron to the diazonium salt. Consequently, for the anion-induced case there is a fine line between coupling of the nucleophile (the anion) to the diazonium salt forming the azo-coupled product, or formation of the aryl radical via $\text{ArN}_2^+ + \text{Y}^- \rightarrow \text{ArN}_2 + \text{Y}^-$ (Y^- is a nucleophile and can be the solvent). The oxidation potential of the nucleophile and the solvent features plays an important role, still the azo-coupled product may cleave into the aryl radical photochemically or thermally.

3.1 Tertiary Nitrogen as Radical Species

Horner and Stöhr reported in 1953 the reaction of *p*-chloro- or *p*-nitrodiazonium salt with triethylamine in methanol and observed the release of N_2 (about 80% of product had released N_2 ; Scheme 15). Only a small amount of product could be isolated containing chloro- or nitrobenzene (**20**) and formaldehyde (**21**), suggesting it reacted via a radical pathway. The authors noted that when a drop of triethylamine was added to anhydrous diazonium salt it may explode.³⁷



Scheme 15 Reaction of aryl diazonium salt with triethylamine in methanol as solvent ($\text{R} = \text{Cl}$, NO_2) (counter-ion omitted)

We observed that reaction of $[\text{PhN}_2][\text{BF}_4]$ with tri-*p*-tolylamine leads to the formation of a blue color, which is evidence of the tri-*p*-tolylamine radical cation ($[\text{p-tol}_3\text{N}^{\cdot+}]$) and can be confirmed by EPR spectroscopy.^{39,32} This notion stands in contrast to the reaction of a diazonium salt with NPh_3 (Section 2.4), which undergoes two-electron chemistry. We illustrated that the more electron-rich tri-*p*-tolylamine is more prone to one-electron oxidation compared to triphenylamine as the oxidation potential is shifted to more negative potentials (*p*-tol₃N: $E_p^{\text{ox}} = 0.78\text{V}$ vs. Fc/Fc^+ , Ph_3N :

$E_p^{ox} = 0.97V$ vs. Fc/Fc^+ , Table 1) and is thus easier to oxidize by the diazonium salt.⁴⁰ Furthermore, the reaction pathway for *p*-tol₃N towards electrophilic aromatic substitution is blocked through the addition of methyl-groups to the *para* position. Investigation of the oxidation potential of triisopropylamine by our group revealed the potential is too high (1.20 V vs. Fc/Fc^+ , Table 1) to be reduced by phenyldiazonium tetrafluoroborate, making this classical donor-acceptor reactivity.

Table 1 Reduction and Oxidation Potentials of Selected Lewis Acids and Lewis Bases

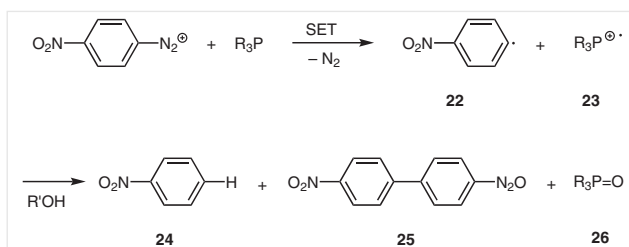
Substrate	E_p^{red} in V vs. Fc/Fc^+ ^[a]	E_p^{ox} in V vs. Fc/Fc^+ ^[a,b]
PhN_2^{+41}	-0.10	
NO^{+40}	0.87	
<i>p</i> -tol ₃ N ³¹		0.78
Ph_3N^{31}		0.97
<i>i</i> Pr ₃ N ³¹		1.20
<i>t</i> Bu ₃ P ³¹		0.90
Ph_3P^{31}		1.23

^a Fc^+ = at 0.40 V.

^b CH_3CN , 0.1 M [*n*Bu₄N][PF₆], glassy carbon working electrode, $\nu = 100$ mVs⁻¹.

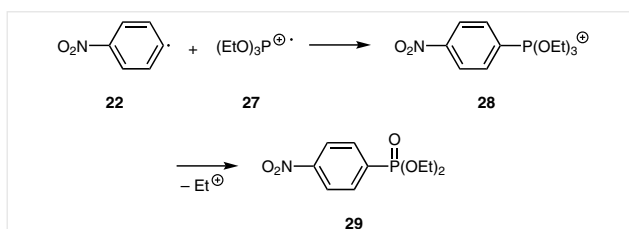
3.2 Tertiary Phosphines as Radical Species

Tertiary phosphines are also able to undergo single-electron transfer. In 1991, Ohno and co-workers reported on the reaction of *p*-nitrobenzenediazonium tetrafluoroborate ($[p\text{-NO}_2\text{-PhN}_2][BF_4]$) with triphenylphosphine (Ph_3P) or triethyl phosphite ($(EtO)_3P$) in an alcoholic solvent at room temperature in air in the dark (Scheme 16).⁴² First the aryl radical **22** and the phosphine radical cation **23** are formed, which subsequently react to give the benzene derivative **24** (major) with trace amounts of the coupled biaryl compound **25**. Evidence for a radical mechanism was provided with deuterium experiments and varying the ratio between the two starting materials. Deuterium experiments with CH_3OD and CD_3OD showed the hydrogen atom was abstracted from the methyl group of the alcohol solvent, and not from the OH group. Upon hydrogen abstraction, the solvent methanol, CH_2OH , gets oxidized by another equivalent of the diazonium salt, ultimately affording formaldehyde. Subsequently, the radical cation $R_3P^{\bullet+}$ (**23**) also reacts with the solvent, forming R_3POR' (the alcohol releases H^+ which adds to the counter-ion), which, upon release of R' , forms $R_3P=O$ (**26**). Further investigations on the mechanism, supported by EPR spectroscopy, were conducted under nitrogen or argon atmosphere because performing the reaction in air suppresses the formation of **24**.^{43–45}



Scheme 16 Reaction of *p*-nitrobenzenediazonium tetrafluoroborate with triphenylphosphine or triethyl phosphite ($R = Ph$ or OEt) in an alcoholic solvent. Major product **24** and traces of **25** observed. Counter-ion BF_4^- omitted for clarity.

For reaction with the phosphite $(EtO)_3P$ additionally a coupled product (**29**) of the aryl radical with the phosphine radical cation was observed. This was described as being formed by analogy with the Arbuzov reaction (Scheme 17).⁴²



Scheme 17 Coupled product of aryl radical and phosphine radical cation in the Arbuzov reaction

Follow-up chemistry by the same group showed expansion of the scope of the diazonium salt to $[p\text{-CH}_3\text{-PhN}_2][BF_4]$ and the phosphines with trimethylphosphite ($P(OMe)_3$), dimethyl phenylphosphonite ($PhP(OMe)_2$) and methyl diphenylphosphinite ($Ph_2P(OMe)$) to investigate the influence of the phenyl groups on the phosphine.⁴³ No phenyl groups on the phosphorus leads to the largest amount of coupled product **29**, as the electron pair is mostly centered on the phosphorus atom and not delocalized over the phenyl groups.

Comparing $[p\text{-NO}_2\text{-PhN}_2][BF_4]$ to $[p\text{-CH}_3\text{-PhN}_2][BF_4]$ or $[p\text{-CH}_3\text{O-PhN}_2][BF_4]$ revealed comparable yields to the reaction with the nitro-substituent, indicating little influence of the electron-donating or -withdrawing abilities of the *para* substituent.⁴⁴ Furthermore, changing the solvent methanol to a 1:1 mixture methanol/acetonitrile lowers the product formed through coupling with methanol (**24**) and increases the amount of coupled product **29**. Variation of the alcohol solvent (methanol, ethanol, cyclohexanol or propan-2-ol) influences the stability of the hydroxyalkyl radical and thus influences the ratio between the formed products, with increased formation of **24** for less stable hydroxyalkyl radicals.

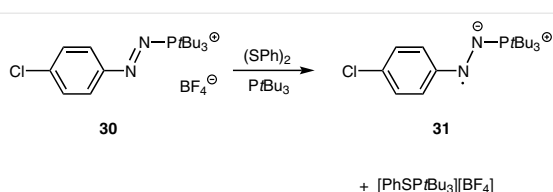
Additionally, we investigated the reactivity, one- or two-electron transfer, of triphenylphosphine and tri-*tert*-butylphosphine and confirmed that both undergo a two-electron Lewis acid-base coupling with the phenyldiazonium tetrafluoroborate.³² Investigations of the stronger oxidant nitrosium tetrafluoroborate ([NO][BF₄]; NO⁺: 0.87 V vs. Fc/Fc⁺, PhN₂⁺: -0.10 V vs. Fc/Fc⁺, Table 1), which is isoelectronic with the diazonium salt, resulted in single-electron transfer as small amounts of a radical species could be detected by EPR spectroscopy. We propose the nitrosylphosphine radical species *t*Bu₃P-NO[•], formed by the capture of the generated NO[•] with residual *t*Bu₃P (Scheme 18). The major product [*t*Bu₃PH][BF₄], detected by ³¹P NMR spectroscopy, is a result of quenching by subsequent reaction with acetonitrile of the reactive radical cation intermediate *t*Bu₃P^{•+}.



Scheme 18 Generation of the radical species of the nitrosium cation with tri-*tert*-butylphosphine

3.3 Azophosphonium Salt as Radical Species

Stephan and co-workers demonstrated that the formed azophosphonium salt could be used in follow-up chemistry forming a radical species (Scheme 19).³³ Dissolving the azophosphonium salt **30** with *t*Bu₃P in CH₂Cl₂ gave an immediate color change of the solution to dark-red/brown upon addition of diphenyl disulfide. EPR spectroscopy indicated the formation of a paramagnetic species **31** [(*p*-Cl-C₆H₄)N₂(Pt-Bu₃)], which could also be formed by reacting the azophosphonium salt directly with PhSNa, potassium metal or Cp₂-Co. The EPR spectrum of **31** and the character of the LUMO of **30** indicate the unpaired electron is delocalized across the PN₂Ar fragment.



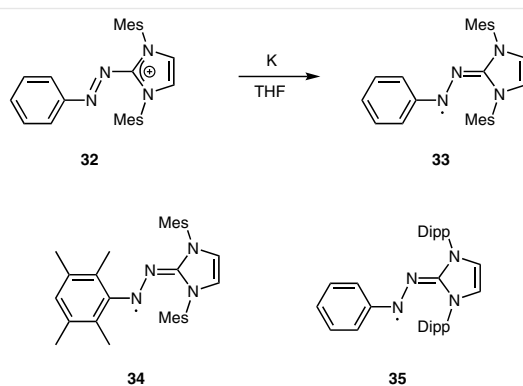
Scheme 19 Reaction of azophosphonium salt [(*p*-Cl-C₆H₄)N₂(Pt-Bu₃)] [BF₄] with (SPh)₂ and *t*Bu₃P. Note, an unidentifiable product was also formed.

Cyclic voltammetry revealed a reversible reduction potential of the compounds [(*p*-Cl-C₆H₄)N₂(PR₃)] [BF₄] (R = *t*Bu, Mes) at the potentials of -0.91 and -0.93 V vs. Fc/Fc⁺, respectively. K, Cp₂Co and PhSNa all revealed to be strong enough reductants to reduce the azophosphonium salts. This reduction is a reversible reaction; the radical species can be oxidized back with [Cp₂Fe][BF₄] to the azophosphonium tetrafluoroborate salt.

3.4 Azoimidazolium Salt as Radical Species

Like the azophosphonium salts, the azoimidazolium salts are able to form a radical species. Severin and co-workers investigated various azoimidazolium salts (Scheme 20) given that, upon irradiation of **32** with UV-light, the ¹H NMR signals were no longer observable, indicating a paramagnetic species.⁴⁵ Cyclic voltammetry of **32** in acetonitrile revealed a reversible one-electron reduction (*E*^o = -0.89 V vs. Fc/Fc⁺) and, synthetically, addition of potassium to the azoimidazolium salt in THF revealed the formation of a neutral radical (Scheme 20), which, upon oxidizing with I₂, proved to be reversible. The phenyl analogue **33**, with mesityl groups on the nitrogen, turned out to be remarkably stable under inert conditions and, even after exposure to air, only relatively slow decomposition was observed. Severin commented on the importance of the *N*-aryl substituents on the imidazole (Mes **33**, **34** or Dipp **35**) as the reduction of compounds containing *N*-methyl or *N*-isopropyl substituents were not successful. Computational studies and X-ray crystallography indicated 50% of the spin density is located on the N₂ moiety, with the largest value on the nitrogen linked to the aryl group; thus, the radical can be described as an aminyl radical.

Note the azoimidazolium salt precursors applied in this study were synthesized via a new route, addition of AlCl₃ to NHC-N₂O and the corresponding arene,⁴⁶ and not the coupling of a diazonium salt with a carbene.



Scheme 20 Top: reduction of the azoimidazolium salt to the neutral radical; Bottom: Two additional neutral radicals through reduction of corresponding azoimidazolium salts. Counter-ion omitted for clarity, Dipp = 2,6-diisopropylphenyl.

Stephan and co-workers reported on the analogy of their azophosphonium radical species to these azoimidazolium radical species, indicating both class of compounds have similar EPR spectra.^{33,45} Moreover, both azo compounds can be reversibly reduced to their corresponding aminyl radical species and both reductions can be performed with potassium as reducing agent.

4 Summary and Outlook

Diazonium salts are important intermediates and can undergo various reactions, some of which are well-established, like the Sandmeyer reaction or electrophilic aromatic substitution with aniline. Two mechanisms for reactivity are identified in this research, firstly donor-acceptor reactivity and thus adduct formation where the diazonium salts reacts like a Lewis acid, and secondly where the diazonium salts act as an oxidant and hence undergo single-electron transfer. Direct addition of Lewis bases towards aryldiazonium salts offers a facile approach to azo compounds that can find applications as dyes. Azoimidazolium salts have found widespread use in industry and are synthesized via two pathways: through the addition of an imidazole followed by alkylation or through the direct addition of an N-heterocyclic carbene. On the other hand, the synthesis of azophosphonium salts has only recently picked up interest, and we have shown that they have a readily tuneable synthesis. Nevertheless, the azoammonium salts remain elusive. Reaction of a diazonium salt with a tertiary amine or phosphine, which undergoes single-electron transfer, predominantly forms the corresponding substituted benzene through release of N_2 and by hydrogen abstraction of the solvent of the formed aryl radical $Ar\cdot$. Additionally, both azophosphonium salts and azoimidazolium salts have been shown to find applications as one-electron acceptors and form stable organic radicals. This overview shows great potential for the formation of a wide variety of azo compounds and their use in radical chemistry.

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