

Photochemical Sandmeyer-type Halogenation of Arenediazonium Salts

Nardana Sivendran,^[a] Florian Belitz,^[a] Daniel Sowa Prendes,^[a] Ángel Manu Martínez,^[a] Rochus Schmid,^[a] and Lukas J. Goossen*^[a]

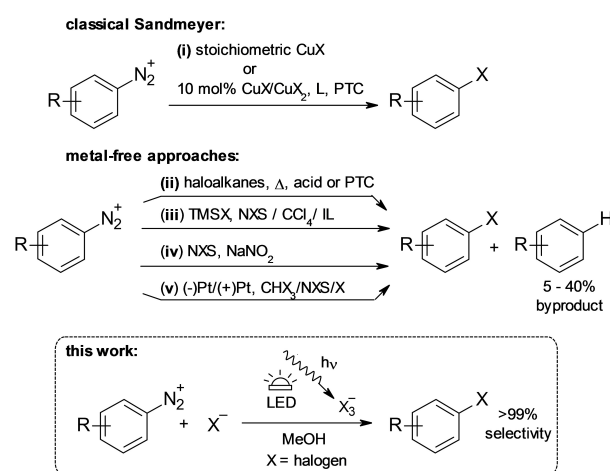
Abstract: Trihalide salts were found to efficiently promote photochemical dediazotizing halogenations of diazonium salts. In contrast to classical Sandmeyer reactions, no metal catalysts are required to achieve high yields and outstanding

selectivities for halogenation over competing hydridodediazotization. Convenient protocols are disclosed for synthetically meaningful brominations, iodinations, and chlorinations of diversely functionalized derivatives.

Introduction

Over the past 150 years, arenediazonium salts have become indispensable synthetic hubs in research labs as well as in the chemical industry.^[1] Their facile synthesis and high reactivity are exploited in a plethora of reliable synthetic transformations, in particular Sandmeyer reactions.^[2] These allow the conversion of arenediazonium salts into the corresponding aryl halides by reaction with Cu^I halides.^[3] Many variants have been developed, including dediazotizing C–B, C–Sn, C–P and C–CF₃ bond-forming reactions.^[4] The main drawback of classical protocols is that large quantities of copper are required to suppress background reactions, in particular hydridodediazotization. In the absence of copper, only strong nucleophiles such as I[−],^[5] SCN[−],^[6] or SCF₃[−]^[7] give high selectivities. Selective brominations and chlorinations require at least 10 mol% Cu even when employing activating ligands (L) or phase-transfer catalysts (PTC) (Scheme 1, (i)).^[8] Copper complexes have antimicrobial, anti-inflammatory and antitumor properties and can function as enzyme inhibitors or chemical nucleases.^[9] Their quantitative removal is a challenge that complicates applications in agrochemistry and drug discovery.^[10]

Numerous attempts have been made to overcome the necessity of metal mediators. In this context, toxicologically and ecologically questionable polyhalogenated alkanes, for example BrCCl₃, CHBr₃, CCl₄, or CHCl₃, have been utilized as halogen sources (ii). However, the practicality of the corresponding



Scheme 1. Dediazotizing halogenations of arenediazonium salts.

protocols is limited by strictly inert conditions,^[11] high reaction temperatures,^[12] or the use of PTC.^[13] Still, hydridodediazotization could not be fully suppressed.^[14] Trimethylsilyl halides (TMSX) as halogen sources also enable metal-free Sandmeyer-type reactions (iii). Keumi et al. firstly employed TMSX as halogen source in combination with *N*-halosuccinimides as activators,^[15] Lee et al. followed using this type of halogen source in toxic CCl₄,^[16] and Laali et al. employed the toxic ionic liquid (IL) [BMIM][PF₆] as solvent.^[17] Again, hydridodediazotization and other side reactions could not be avoided. Batra et al. demonstrated that anilines are converted to the respective haloarenes in the presence of *N*-halosuccinimides and excess amount of NaNO₂ via a diazonium salt intermediate in DMF (iv).^[18] Control experiments revealed that this halogenation is actually mediated by a NO₂X species. Mo et al. used electrochemistry to promote halogenations of diazonium salts with NBS, CH₂I₂, or LiCl (v).^[19] Due to competing protonation, polyhalogenation, and grafting of the electrodes,^[20] only moderate yields were obtained.

Despite all these efforts, there is still no generally applicable, metal-free protocol that facilitates dediazotizing halogenations

[a] N. Sivendran, F. Belitz, D. Sowa Prendes, Dr. Á. Manu Martínez, Prof. Dr. R. Schmid, Prof. Dr. L. J. Goossen
Department of Chemistry and Biochemistry
Ruhr-Universität Bochum
Universitätsstr. 150, 44801 Bochum (Germany)
E-mail: lukas.goossen@rub.de

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of diazonium salts with the high selectivity of a copper-mediated Sandmeyer reaction.^[21] This is a severe limitation, since the quantitative separation of halogenated products from structurally similar, non-halogenated byproducts is laborious.

We reasoned that the photochemical excitation of diazonium halides in the presence of a non-metallic mediator might open up a concerted pathway that allows the selective halogenation of diazonium salts without background reactions such as hydridodediazotizations (Scheme 1, bottom).^[22]

Results and Discussion

The model reaction we chose to probe this hypothesis is the bromination of 4-fluorobenzenediazonium tetrafluoroborate (**1a**). Substrate **1a** is particularly susceptible to hydridodediazotization and thus well suited to identify conditions that would discriminate effectively between the target and side reactions (Table 1).

In acetonitrile solution, neither the bromination (**2a**) nor the hydridodediazotization product (**3a**) were observed after 1 h at 15 °C (Entry 1), confirming that non-photochemical, non-catalytic background reactions do not occur at low temperatures. Upon irradiation with a 3 W royal blue LED ($\lambda = 447$ nm), the corresponding aryl bromide **2a** formed rapidly, yet non-selectively over **3a** (Entry 2).

The reaction rate and selectivity strongly depend on the solvent system (Entries 3–6), and the highest yields of aryl bromide **2a** were obtained in methanol. However, all attempts

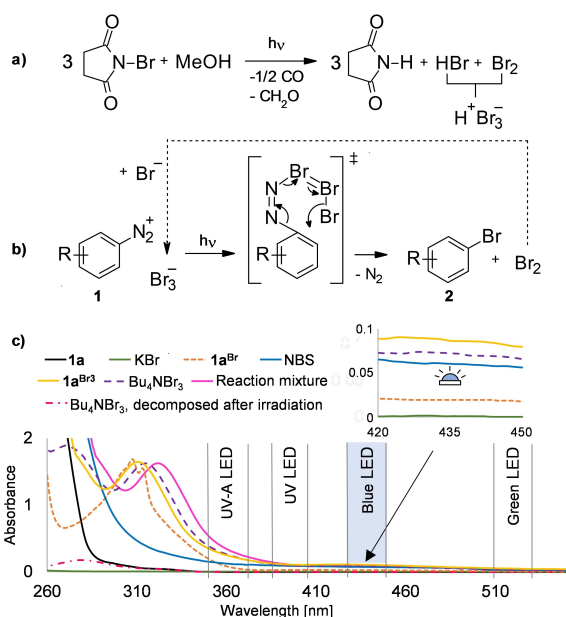
failed to increase the selectivity towards bromination by adding photosensitizers or photoredox catalysts.^[23] The commonly used photosensitizers Ru(bpy)₃(PF₆)₂, 9-mesityl-10-methylacridinium perchlorate (Mes-Acr) or 2,4,6-triphenylpyrylium tetrafluoroborate (TPP) did not improve the selectivity in favour of **2a** (Entries 7–9). We interpreted these findings in a way that the photochemical excitation of diazonium halides predominantly leads to formation of diazo radicals, which undergo non-selective dediazotization.

In contrast, the addition of the electrophilic reagent *N*-bromosuccinimide (NBS) increased the yield of **2a** to 98% (Entry 10). It has been reported that irradiation of methanolic NBS leads to the formation of formaldehyde and CO along with HBr and Br₂.^[24] This process was confirmed by trapping the formaldehyde with Tollens' reagent, and the bromine with phenylacetylene (Figure S5–7). We reasoned that NBS does not react with the diazonium salt directly, but undergoes photochemical reduction with formation of HBr and Br₂, which should rapidly form HBr₃[−] (Scheme 2a). Thus, we hypothesized that tribromide must be the actual bromination photocatalyst in our process. Indeed, the addition of 20 mol% of commercially available Bu₄NBr₃ promoted the photochemical bromination of **1a** with KBr in near-quantitative yields (Entries 12, 13). Acidifying the reaction medium with *p*-TsOH fully suppressed the formation of hydridodediazotization byproducts (Entry 14). At 25 °C, the reaction is complete already within 30 minutes (Entries 15, 16). The reaction also gives near-quantitative yields when using stoichiometric amounts of Bu₄NBr₃ or NBS instead of KBr (Entries 17, 11).

Table 1. Optimization of reaction conditions.^[a]

#	Br [−]	LED	solvent	additive	2a , %	3a , %
1	KBr	–	MeCN	–	–	–
2	"	blue	"	–	32	4
3	"	"	MeOH	–	52	47
4	"	"	MeOH/ H ₂ O	–	–	3
5	"	"	Me ₂ CO	–	7	30
6	"	"	DMAc	–	10	89
7	"	"	MeOH	[Ru]	52	47
8	"	"	"	Mes-Acr	–	> 99
9	"	"	"	TPP	26	73
10	"	"	"	NBS	98	2
11 ^[b]	NBS	"	"	–	> 99	–
12	KBr	"	"	Bu ₄ NBr ₃	> 99	< 1
13 ^[c]	"	"	"	Bu ₄ NBr ₃	93	6
14	"	"	"	Bu ₄ NBr ₃ / <i>p</i> -TsOH	> 99	–
15 ^[d]	"	"	"	"	> 99	–
16 ^[d,e]	"	"	"	"	> 99	–
17	Bu ₄ NBr ₃	"	"	–	> 99	< 1
18	KBr	UV	"	Bu ₄ NBr ₃ / <i>p</i> -TsOH	89	11
19	"	green	"	"	0	5

[a] Conditions: 0.3 mmol of **1a**, 1.5 equiv. of Br[−] source, 0.2 equiv. of additive, 2.5 mol% of acid, 1 mL solvent, 15 °C, 1 h. Yields were determined by ¹⁹F NMR using α,α,α -trifluorotoluene as internal standard; [b] 2.0 equiv. of NBS; [c] 0.1 equiv. of Bu₄NBr₃; [d] 25 °C; [e] 0.5 h.



Scheme 2. Mechanistic blueprint of the targeted reaction and UV/Vis spectra.

The mechanism outlined in Scheme 2 illustrates the rationale that guided method development. Our strategy to achieve selectivity in favour of bromination was to identify a wavelength at which light is absorbed selectively by the tribromide. An overlay of the UV/Vis spectra of diluted solutions (Scheme 2c) shows that the diazonium tetrafluoroborate **1a** (solid black line) and KBr (solid green line) do not absorb blue LED light ($\lambda = 447$ nm), diazonium bromide **1a^{Br}** absorbs only weakly (dotted orange line), and NBS (solid blue line) and Bu_4NBr_3 (dashed purple line) more strongly. The strongest absorption in this region is observed for pre-formed diazonium tribromide **1a^{Br3}** (solid yellow line). This tribromide absorption dominates the UV/Vis spectrum of the reaction mixture (solid pink line).

The spectral shift from Bu_4NBr_3 to **1a^{Br3}** might be indicative of the formation of an adduct between the diazonium cation and the Br_3^- anion (Scheme 2b). A publication of the crystal structure of phenyldiazonium tribromide^[25] interprets the short $\text{ArNN}-\text{Br}_3$ distance as evidence for a partially covalent bond. The internal nitrogen atom is in close proximity to the middle bromine atom of a neighbouring Br_3^- unit in the crystal lattice. In solution, both interactions should be directed towards the same Br_3^- unit within a single ion pair. Calculations of the solvated ion pair have been performed with the TURBOMOLE V7.3 suite of programs using the hybrid functional B3LYP including D3 dispersion corrections (Becke-Johnson damping) and cc-pVDZ basis sets on all atoms.^[26] We found that the most stable conformer in a methanol solvent field features an $\text{ArNN}-\text{Br}_3$ distance of 3.26 Å (Figure 1). Electrostatic interactions draw the tribromide unit towards the internal nitrogen, causing the Br_3^- unit to fold back towards the arene ring. This brings the terminal bromine atom into close proximity to the *ipso* carbon atom of the arene. It is conceivable that photoexcitation induces a bending of the Br_3^- unit, giving rise to a six-membered

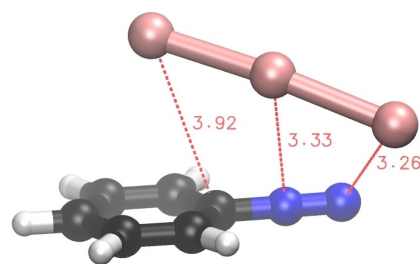


Figure 1. Calculated solution structure of $\text{PhN}_2^+\text{Br}_3^-$.

ring transition state (Scheme 2b). Extrusion of nitrogen and dibromine would then lead to a selective formation of aryl bromide **2**. The tribromide ion should then be regenerated by reaction of the released dibromine with fresh potassium bromide.

In order to shed further light on the reaction pathway, we performed a series of mechanistic experiments (See the Supporting Information for details). The reaction between **1a** and KBr in the presence of Bu_4NBr_3 follows first-order kinetics. Its rate depends only on the concentration of **1a**. By plotting the time against the concentration of **1a** at various temperatures, the corresponding rate constants k were determined. By plotting $1/T$ against $\ln(k/T)$ following the linear form of the Eyring equation, a negative activation entropy of -159.75 J/molK was determined (Figure 2). This is indicative of a highly ordered transition state, and the value of ΔS^\ddagger is in the range of that calculated for six-membered transition states.^[27]

The photon flux through the reaction vial was determined by standard ferrioxalate actinometry as 2.41×10^{-7} einstein/s.^[28]

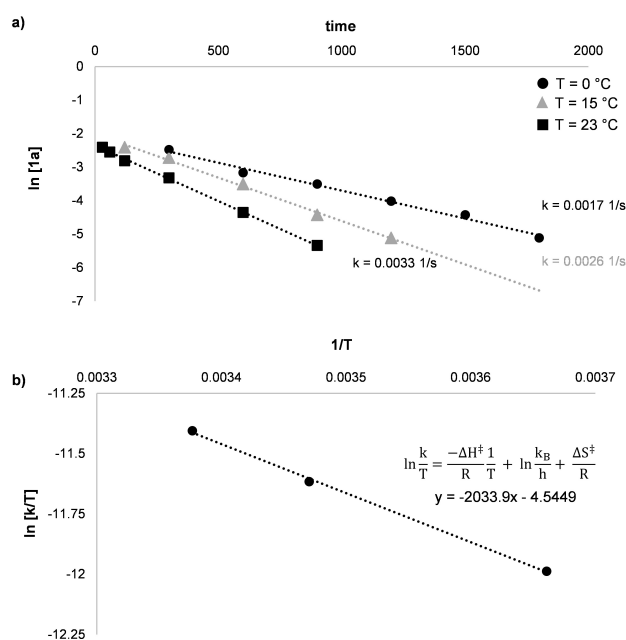
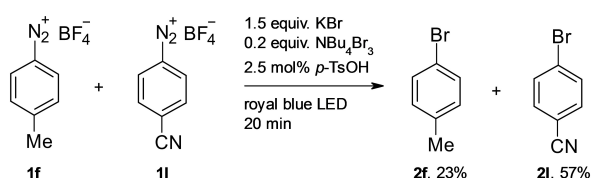


Figure 2. Determination of the reaction order and the activation entropy for the photochemical bromination of **1a**.

The UV/Vis spectrum of the reaction solution shows an absorption of 0.82 a.u. at 447 nm, meaning that 85% of the photons are absorbed. 1.5 h of irradiation, i.e. 6.65×10^{20} absorbed photons lead to the conversion of 1 mmol **1a**, corresponding to a quantum yield of 0.90. Thus, a radical chain process seems unlikely, especially since the reaction does not continue after stopping the irradiation. All of these experiments agree with the proposed mechanism.

In an intermolecular competition experiment at incomplete conversion, the electron-deficient **1l** reacted faster than the electron-rich **1f** (Scheme 3). This may be rationalized by preferential formation of the corresponding arenediazonium tribromide ion pair.

Irradiation of the reaction mixture with UV light ($\lambda = 395$ nm), which is also absorbed by the diazonium bromide (absorbance ratio **1a**^{Br} to $\text{Bu}_4\text{NBr}_3 = 1:3$), leads to a less selective reaction, whereas irradiation with green LED light is ineffective (Table 1, Entries 18, 19). Following irradiation of a methanolic Bu_4NBr_3 solution at 447 nm for 5 min, its absorbance decreases

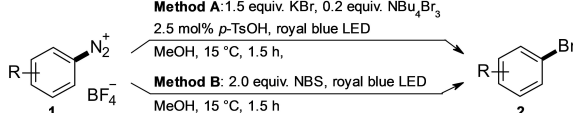


Scheme 3. Intermolecular competition experiment.

to near-zero (dashed red line). This shows that in the absence of the arenediazonium substrate, the reactive tribromide is irreversibly depleted. Thus, a protocol based on stoichiometric NBS as the bromide source should be particularly robust for less reactive diazonium salts. The photochemical reaction of NBS with methanol constantly replenishes the tribromide over the course of the reaction (see Entry 11). This reaction variant proceeds at the same rate with non-purified, commercial NBS and with freshly purified NBS. This indicates that an autocatalytic decomposition of NBS triggered by impurities in the bromination step is not involved (see the Supporting Information for details). When Br_2 was employed as the sole bromine source without added KBr, incomplete conversion and low yields were obtained, regardless of whether Br_2 was added in one portion or slowly over the course of the reaction. Thus, we can rule out Br_2 formed in situ as the actual brominating agent.

We next investigated the scope of the photochemical bromination, and were pleased to find that the most atom-efficient protocol, i.e. that using KBr with catalytic amounts of Bu_4NBr_3 , proved to be widely applicable both to electron-rich and electron-deficient substrates (Table 2, Method A). In the few cases in which method A gave incomplete conversion, method B, which is based on stoichiometric NBS, gave near-quantitative yields. Various substituents were tolerated in *para*- (**2a–2t**), *meta*-, and *ortho*-position (**2u–2aa**). Polysubstituted (**2ab–2af**) and heteroaromatic arenes (**2ag, 2ah**) also gave high yields. For substrates with insufficient solubility in methanol, the reaction was adapted to acetone-based systems,

Table 2. Scope of the photochemical Sandmeyer-type bromination.^[a]

Method A: 1.5 equiv. KBr, 0.2 equiv. NBu_4Br_3 , 2.5 mol% <i>p</i> -TsOH, royal blue LED, MeOH, 15 °C, 1.5 h.		Method B: 2.0 equiv. NBS, royal blue LED, MeOH, 15 °C, 1.5 h.	
			
para-substituted arenes:			
2a , 96% (A)	2b , 95% (A)	2c , 97% (A)	2d , 97% (A)
2e , 93% (A)	2f , 95% (A)	2g , 95% (A)	2h , 95% (B)
2i , 98% (B)	2j , 52% (A)	2k , 98% (A)	2l , 95% (A)
2m , 98% (A)	2n , 98% (B)	2o ^[b] , 97% (A)	2p , 98% (A)
2q , 97% (A)	meta/ortho-substituted arenes:		
2r , 97% (A)	2s , 71% (A)	2t , 65% (B)	2u , 95% (B)
2v , 93% (A)	2w , 94% (A)	2x , 95% (B)	2y , 94% (A)
poly-substituted (hetero)arenes:			
2ab , 94% (A)	2ac , 95% (A)	2ad , 95% (B)	2ae , 96% (B)
2af , 96% (B)	2ag , 95% (A)	2ah ^[c] , 88% (B)	2z , 94% (B)
2aa , 92% (B)			

[a] Method A: 0.75 mmol of **1**, 1.5 equiv. of KBr, 0.2 equiv. Bu_4NBr_3 , 2.5 mol% *p*-TsOH in 1.5 mL MeOH, irradiated for 1.5 h at 15 °C with royal blue LEDs (3 W); Method B: 1.0 mmol of **1**, 2.0 equiv. of NBS in 2 mL MeOH, irradiated for 2 h at 15 °C with royal blue LEDs (3 W). isolated yields. [b] 1 mL acetone/ H_2O . [c] 1 mL acetone/DMAc as solvent.

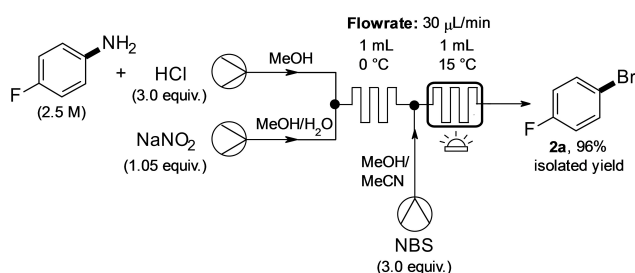
for example for **2o** or **2ah**. No trace of arene byproduct was detected for any substrate.

The reaction protocol was successfully scaled up to gram quantities for the example of **1a**. The bromination can also be carried out in one-pot starting directly from the aniline via an in situ diazotization with NaNO₂ in HCl. This was demonstrated by the synthesis of aryl bromide **2a** in 95% isolated yield (Scheme S1). Due to the explosive nature of some diazonium salts, handling of large quantities is avoided, especially in industrial applications. This can be achieved by synthesizing the diazonium salt in a flow reactor and directly converting it into the aryl bromide within a photochemical flow reactor (Scheme 4). Such a flow-through setup is advantageous anyway, as it simplifies the scale-up of the photochemical reaction step. Since KBr could not be fully solubilized, we used NBS as bromine source in this protocol.

We next investigated if the reaction concept also extends to other halogenations. Diazonium salts are known to react with KI with formation of aryl iodides via a radical pathway.^[5,29] However, control experiments showed that the iodination of 4-fluorobenzenediazonium tetrafluoroborate (**1a**) under the established, non-catalytic conditions leads to well above 5% hydridodediazotization byproduct (See Table S7).

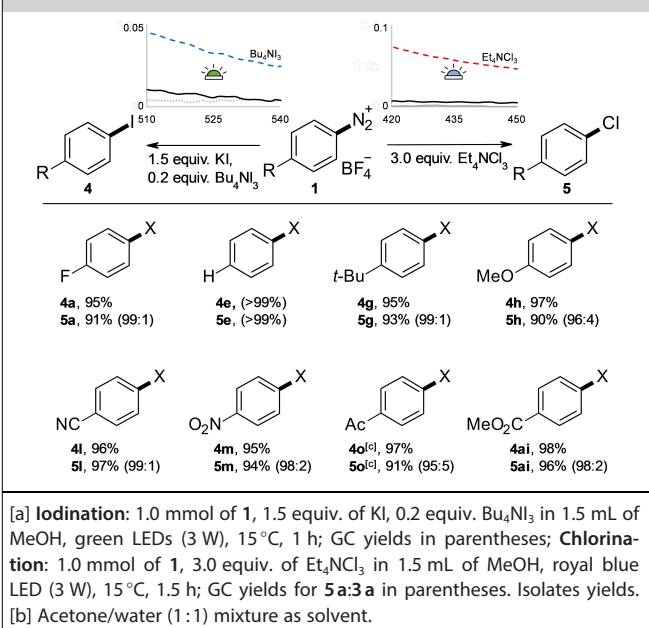
An overlay of the UV spectra (Figure S3) reveals that green light should be best suited to selectively photoexcite the triiodide Bu₄NI₃ but not the diazonium iodide **1a**¹. Indeed, when irradiating **1a** at 525 nm in the presence of 1.5 equiv. KI and 20 mol% Bu₄NI₃, at 15 °C, near-quantitative conversion to aryl iodide **4a** was achieved, without detectable traces of the arene. In contrast, irradiation with blue light gave as much as 14% arene byproduct. This was to be expected since this wavelength is also absorbed by the diazonium iodide, facilitating a less selective dediazotization pathway. Since iodine radicals are known to form even without photoexcitation,^[5,29] we tested if the iodination can also be performed without LED light. Indeed, when stirring **1a** with 1.5 equiv. KI in the presence of 20 mol% Bu₄NI₃, the reaction went to completion at ambient light when extending the reaction time to 1.5 h and raising the temperature to 25 °C. Details of the reaction optimization can be found in the Supporting Information (Table S7).

As can be seen from Table 3, various diazonium salts were successfully converted following the optimized protocol. Valuable aryl iodides were synthesized without detectable formation of hydridodediazotization byproducts.



Scheme 4. Diazotization and photochemical bromination in flow.

Table 3. Photochemical Sandmeyer-type iodination and chlorination of diazonium salts.^[a]



[a] **Iodination:** 1.0 mmol of **1**, 1.5 equiv. of KI, 0.2 equiv. Bu₄NI₃ in 1.5 mL of MeOH, green LEDs (3 W), 15 °C, 1 h; GC yields in parentheses; **Chlorination:** 1.0 mmol of **1**, 3.0 equiv. of Et₄NCl₃ in 1.5 mL of MeOH, royal blue LED (3 W), 15 °C, 1.5 h; GC yields for **5a:3a** in parentheses. Isolates yields. [b] Acetone/water (1:1) mixture as solvent.

Product	Yield (%)	GC Yield (%)	GC Selectivity (a:b)
4a	95%		
5a	91%		(99:1)
4e	>99%		
5e	>99%		
4g	95%		
5g	93%		(99:1)
4h	97%		
5h	90%		(96:4)
4i	96%		
5i	97%		(99:1)
4m	95%		
5m	94%		(98:2)
4o ^[c]	97%		
5o ^[c]	91%		(95:5)
4ai	98%		
5ai	96%		(98:2)

The chlorination of diazonium salts proved to be most challenging. The diazonium chloride **1a**^{Cl} absorbs light up to 370 nm, but commercially available *N*-chlorosuccinimide (NCS) only absorbs at wavelengths below 270 nm. Thus, it cannot be irradiated without also exciting **1a**^{Cl}. This was confirmed by experiments, in which hydridodediazotization was always detected (see the Supporting Information). In contrast, the absorption spectrum of Et₄NCl₃^[30] extends to blue light beyond 400 nm (Figure S4). This reagent is not commercially available but can easily be prepared by bubbling Cl₂ gas through a solution of Et₄NCl. When irradiating a mixture of freshly prepared Et₄NCl₃ and **1a** with blue LED light (λ = 447 nm), aryl chloride **5a** formed in near-quantitative yield along with 1% of the undesired arene **3a**. Unfortunately, the low stability of the trichloride did not permit its use in catalytic quantities. Once again, the choice of the correct wavelength was crucial, UV–A irradiation led to unsatisfactory 10:1, green light to 5:1 selectivity ratio for **5a** over **3a** at full conversion (Table S8). The scope of the photochemical chlorination was demonstrated by the representative examples in Table 3. The selectivities are excellent throughout, but in contrast to the bromination and iodination protocols, traces of hydridodediazotization products were still detectable.

Conclusion

In conclusion, photochemical Sandmeyer-type halogenations of diazonium salts in the presence of trihalide salts have opened up straightforward synthetic entries to aryl bromides, iodides, and chlorides from easily accessible diazonium salts. The key benefits of this protocol over the classical Sandmeyer approach are the absence of transition metals and the extraordinarily

high selectivity for halogenation over the competing arene formation.

Experimental Section

Photochemical bromination: A 10 mL vial was charged with KBr (134 mg, 1.1 mmol, 1.5 equiv.), and Bu_4NBr_3 (72.3 mg, 0.15 mmol, 0.2 equiv., **Method A**), or *N*-bromosuccinimide (360 mg, 2.0 mmol, 2.0 equiv., **Method B**). The diazonium tetrafluoroborate (0.75 mmol), *p*-toluenesulfonic acid (26.9 mg, 25.1 μL , 2.5 mol%) and 1.5 mL methanol were added. The vial was closed with a septum cap, the reaction mixture placed over a 3 W royal blue LED (447.5 ± 5 nm) and stirred at 15 °C for 1.5 h. The resulting solution was diluted with 20 mL diethyl ether, washed two times with 20 mL of water and dried over MgSO_4 . After evaporation of the solvent, the aryl bromide was purified by filtration over a plug of silica using *n*-pentane.

Photochemical iodination: A 10 mL vial was charged with KI (189 mg, 1.5 mmol, 1.5 equiv.), Bu_4NI_3 (93.5 mg, 0.15 mmol, 0.2 equiv.), the diazonium tetrafluoroborate (1.00 mmol) and 1.5 mL methanol. The vial was closed with a septum cap, the reaction mixture placed over a 3 W green LED ($525 \text{ nm} \pm 5 \text{ nm}$) and stirred at 15 °C for 1 h. The resulting solution was diluted with 20 mL diethyl ether, washed two times with 20 mL of water and dried over MgSO_4 . After evaporation of the solvent, the aryl iodide was purified by filtration over a plug of silica using *n*-pentane.

Photochemical chlorination: A 10 mL vial was charged with Et_4NCl_3 (284 mg, 3.0 mmol, 3.0 equiv.), the diazonium tetrafluoroborate (1.00 mmol) and 1.5 mL methanol. The vial was closed with a septum cap, the reaction mixture placed over a 3 W royal blue LED (447.5 ± 5 nm) and stirred at 15 °C for 1.5 h. The resulting solution was diluted with 20 mL diethyl ether, washed two times with 20 mL of water and dried over MgSO_4 . After removing the solvent, the aryl chloride was purified via flash column chromatography (SiO_2 , *n*-pentane/diethyl ether 100:1).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

- [1] F. Mo, G. Dong, Y. Zhang, J. Wang, *Org. Biomol. Chem.* **2013**, *11*, 1582.
- [2] a) T. Sandmeyer, *Ber. Dtsch. Chem. Ges.* **1884**, *17*, 2650–2653; b) T. Sandmeyer, *Ber. Dtsch. Chem. Ges.* **1884**, *17*, 1633–1635; c) W. A. Cowdrey, D. S. Davies, *Q. Rev. Chem. Soc.* **1952**, *6*, 358.
- [3] a) H. H. Hodgson, *Chem. Rev.* **1947**, *40*, 251–277; b) D. C. Nonhebel, W. A. Waters, *Proc. R. Soc. London Ser. Math. Phys. Sci.* **1957**, *242*, 16–27.
- [4] a) F. Mo, D. Qiu, Y. Zhang, J. Wang, *Acc. Chem. Res.* **2018**, *11*; b) F. Mo, D. Qiu, L. Zhang, J. Wang, *Chem. Rev.* **2021**, *121*, 5741–5829; c) L. He, G. Qiu, Y. Gao, J. Wu, *Org. Biomol. Chem.* **2014**, *12*, 6965; d) X. Zhang, Y. Mei, Y. Li, J. Hu, D. Huang, Y. Bi, *Asian J. Org. Chem.* **2021**, *10*, 453–463.
- [5] S. S. Gholap, *Lett. Org. Chem.* **2018**, *15*, 594–599.
- [6] M. Barbero, I. Degani, N. Diulgheroff, S. Dughera, R. Fochi, *Synthesis* **2001**, *2001*, 0585–0590.
- [7] G. Bertoli, B. Exner, M. V. Evers, K. Tschulik, L. J. Gooßen, *J. Fluorine Chem.* **2018**, *210*, 132–136.
- [8] a) I. Beletskaya, A. Sigeev, A. Peregodov, P. Petrovskii, *Synthesis* **2007**, *2007*, 2534–2538; b) Y. M. Lee, M. E. Moon, V. Vajpayee, V. D. Filimonov, K.-W. Chi, *Tetrahedron* **2010**, *66*, 7418–7422; c) A. S. Sigeev, I. P. Beletskaya, P. V. Petrovskii, A. S. Peregodov, *Russ. J. Org. Chem.* **2012**, *48*, 1055–1058.
- [9] I. Iakovidis, I. Delimaris, S. M. Piperakis, *Mol. Biol. Int.* **2011**, *2011*, 1–13.
- [10] J. Magano, in *Transit. Met.-Catalyzed Couplings Process Chem.* (Eds.: J. Magano, J. R. Dunetz), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, **2013**, pp. 313–355.
- [11] S. H. Korzeniowski, G. W. Gokel, *Tetrahedron Lett.* **1977**, *18*, 3519–3522.
- [12] J. I. G. Cadogan, D. A. Roy, D. M. Smith, *J. Chem. Soc. C* **1966**, 1249.
- [13] R. A. Bartsch, I. W. Yang, *Tetrahedron Lett.* **1979**, *20*, 2503–2504.
- [14] D. A. Leas, Y. Dong, J. L. Vennerstrom, D. E. Stack, *Org. Lett.* **2017**, *19*, 2518–2521.
- [15] T. Keumi, T. Umeda, Y. Inoue, H. Kitajima, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 89–95.
- [16] J. G. Lee, H. T. Cha, *Tetrahedron Lett.* **1992**, *33*, 3167–3168.
- [17] A. Hubbard, T. Okazaki, K. K. Laali, *J. Org. Chem.* **2008**, *73*, 316–319.
- [18] S. Mukhopadhyay, S. Batra, *Chem. Eur. J.* **2018**, *24*, 14622–14626.
- [19] Q. Liu, B. Sun, Z. Liu, Y. Kao, B.-W. Dong, S.-D. Jiang, F. Li, G. Liu, Y. Yang, F. Mo, *Chem. Sci.* **2018**, *9*, 8731–8737.
- [20] D. Bélanger, J. Pinson, *Chem. Soc. Rev.* **2011**, *40*, 3995.
- [21] M. Barbero, I. Degani, S. Dughera, R. Fochi, *J. Org. Chem.* **1999**, *64*, 3448–3453.
- [22] a) M. S. Newman, W. S. Fones, *J. Am. Chem. Soc.* **1947**, *69*, 1221–1222; b) S. M. Loh, E. E. Turner, *J. Chem. Soc.* **1955**, 1274–1277; c) G. A. Olah, W. S. Tolgyesi, *J. Org. Chem.* **1961**, *26*, 2053–2055.
- [23] S. S. Babu, P. Muthuraja, P. Yadav, P. Gopinath, *Adv. Synth. Catal.* **2021**, *363*, 1782–1809.
- [24] E. Buckley, E. Whittle, *Trans. Faraday Soc.* **1959**, *55*, 1536–1542.
- [25] O. Andresen, C. Romming, *Acta Chem. Scand.* **1962**, *16*, 1882.
- [26] a) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165–169; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789; c) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; d) K. Eichkorn, O. Treutler, H. Oehm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283; e) T. H. Dunning, *J. Chem. Phys.* **1989**, *90*, 1007.
- [27] F. L. Wiseman, D. W. Scott, W. C. Cooper, J. Tamine, R. O'Connell, N. Mitchell, *RSC Adv.* **2017**, *7*, 28965–28978.
- [28] a) C. G. Hatchard, C. A. Parker, J. Bowen Edmund, *Proc. R. Soc. London Ser. Math. Phys. Sci.* **1956**, *235*, 518–536; b) H. J. Kuhn, S. E. Braslavsky, R. Schmidt, *Pure Appl. Chem.* **2004**, *76*, 2105–2146; c) M. Montalti, S. L. Murov, *Handbook of Photochemistry*, CRC/Taylor And Francis, **2006**.
- [29] C. Galli, *Chem. Rev.* **1988**, *88*, 765–792.
- [30] a) F. D. Chattaway, G. Hoyle, *J. Chem. Soc. Trans.* **1923**, *123*, 654–662; b) B. S. Ault, L. Andrews, *J. Chem. Phys.* **1976**, *64*, 4853–4859; c) T. Schlama, K. Gabriel, V. Gouverneur, C. Mioskowski, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2342–2344.

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