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Unprecedentedly Simple Method of Synthesis of Aryl Azides and 3-Hydroxytriazenes

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Fischer's approach towards the synthesis of aryl azides and triazinoles from diazonium salts and hydroxylammonium chloride (phenylhydraxylamine) was reinvestigated and optimized. The new methodology enables preparation of aryl azides and triazinoles in high yields in water at room temperature. The procedure is very simple, robust, easily scalable, reproducible, and "green".

Introduction

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Aryl azides have found broad utilization in many fields of organic and bioorganic chemistry.¹ Reactions of dipolar cycloaddition of organic azides with alkynes catalyzed by copper or ruthenium complexes lead to formation of 1,4- and 1,5- disubstituted 1,2,3-triazoles, respectively. These reactions are of high importance in modern synthetic organic chemistry,² introduction of molecular tags into biomolecules,³ in particular effective control of *in vivo* DNA synthesis using "click" reactions of 5-ethynyl-2'-deoxyuridine,⁴ as well as in surface modification⁵ and polymer science.⁶ Such a wide range of applications of aromatic azides determines the interest in the development of the efficient methods their synthesis.

Aromatic azides can be obtained using various methods (Scheme 1): nucleophilic substitution of halogen in activated aryls by azide anion;⁷ interaction of azides (NaN₃, Me₃Si-N₃, Tos-N₃) with Grigniar ArMgX or aryllithium ArLi compounds;⁸ diazotization of aryl hydrazines;⁹ interaction of aromatic amines with TfN₃ or 2-azido-1,3-dimethylimidazolium hexafluorophosphate;¹⁰ interaction of nitrosoarenes with hydrogen azide;¹¹ base induced decomposition of triazenes;¹²



However, the most general method of the synthesis of aromatic azides is based on the interaction of aryl diazonium salts with an appropriate source of the azide.^{1, 15} Although, this method is not free from disadvantages. Thus, diazonium salts are characterized by low thermal stability or even explosiveness.¹⁶ Recently, several approaches of safe synthesis of aryl azides using aryl diazonium salts stabilized by various anions, 15a, 17 and via in situ utilization of the obtained diazonium salts were reported.¹⁸ To exemplify, aryl diazonium tetrafluoroborates are highly thermally stable, have low sensitivity, and are commercially available. However, due to low solubility in water, aryl diazonium tetrafluoroborates are usually applied in mixed water/organic solvents.¹⁹ Obviously, it would be of interest to perform the reaction under more "green" conditions, avoiding utilization of organic solvents due to safety, health and environmental reasons.20



Scheme 1. Approaches towards the synthesis of aryl azides.

Another significant drawback of interaction of diazonium salts with azides is the toxicity of the conventional azide sources, such as sodium azide. While sodium azide is affordable, it's

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acute toxicity, especially in acidic media, makes it's utilization impractical in laboratory due to the risks of poisoning.²¹

It is also worth noting, that in the synthesis of aryl azides from diazonium salts the elimination of dinitrogen takes place. Despite of the fact that dinitrogen constitutes 75.5% of the atmosphere, and is not an industrial pollutant, conversion of unreactive atmospheric nitrogen into chemically active compounds consumes a lot of energy. Thus, the development of the methods of synthesis of aryl azides without the loss of nitrogen is actual for the development of energy effective, sustainable chemical processes.

As early as in 19 century Emil Fischer reported formation of phenyl azide in the reaction of phenyl diazonium salt with hydroxylamine.²² Later, Mai reported formation of phenyl azide upon interaction of benzaldoxyme with phenyl diazonium chloride.²³ Later, this approach was, to our opinion, undeservedly forgotten.

Last several years our group was active in the development of "green" chemical approaches that might be relevant both for the academia and for the industry. Our target is "to eliminate organic solvents from organic chemistry" by substitution with water and/or development of solvent-free synthetic approaches.²⁴ This motivated us to reinvestigate and optimize Fischer's approach for the synthesis of aryl azides in water media. Utilization of this approach promises simplicity, high efficiency, atom economy, ecological safety, while giving opportunities to avoid particular disadvantages of conventional methods.

Results and discussion

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Initially we prepared 4-nitrophenyl azide from 4-nitrophenyl diazonium chloride, obtained *in situ*, and hydroxylammonium chloride at room temperature (Fischer's conditions).²² The obtained yield was 65% (Scheme 2).



Scheme 2. Fischer's synthesis of 4-nitrophenyl azide: a: NaNO₂, HCl, H₂O, 0 - 5 °C; b: NH₂OH·HCl, r. t.

To optimize the reaction conditions we tried to obtain 4nitrophenyl azide by addition of hydroxylammonium chloride to 4-nitroaniline, before diazotation reaction. In the result, 4nitrophenyl azide was obtained in 30% yield. Presumably, the decrease in the yield might be due to the side reaction of hydroxylamine with nitrous acid leading to the formation of hyponitrous acid.

In the next step of optimization, we performed the reaction of hydroxylammonium chloride with commercially available, stable 4-nitrophenyl diazonium tetrafluoroborate (Scheme 3). Luckily, we obtained 95% yield of the resulting product.

Further, we studied the influence of the nature of the counterion on the yield of the reaction. We performed one-pot

diazotation of 4-nitroaniline with further <u>addition_onlof</u> hydroxylammonium chloride in presence of 10 ne 32 (five a entry of HBF4. The resulting yield of the product decreased to 32%. The same reaction, but with the addition of hydroxylammonium chloride at the first step, have led to even lower yield of 21%. Finally, we tested the influence of the increased acidity of the media on the yield of the reaction of diazonium tetrafluoroborate with hydroxylammonium chloride. In presence of two equivalents of HBF4 the yield decreased to 26%. Thus, the optimum conditions of the synthesis of aryl azide is interaction of diazonium tetrafluoroborate with hydroxylammonium chloride in water at room temperature.

To determine the scope of the Fischer's modified method we performed the synthesis of azides from substrates of different chemical nature, bearing electron donor, and electron withdrawing substituents in *ortho-*, *meta-*, and *para-*positions (Scheme 3). The obtained yields vary from moderate (**2i**) up to virtually quantitative (**2g**, **2l**, **2o**). The yields of the reactions correlate with the stability of the corresponding diazonium salts. The more stable the diazonium salt is, the better yield was obtained. Thus, yields over 76% were obtained for nitro-, cyano-, and carbomethoxy-substituted substrates.

₂ O, r.t., 24 h	IJ
2 a-0)
2i R = 2-Br, 52% 2j R = 3-Cl, 66% 2k R = 3-CF ₃ , 60% 2l R = 2-CN, 99% 2m R = 2-Me, 65% 2n R = 4-CO ₂ Me, 3 2o R = 2-CO ₂ Me, 5	76% 99%
	20, r.t., 24 h 2 a-c 2i R = 2-Br, 52% 2j R = 3-Cl, 66% 2k R = 3-CF ₃ , 60% 2l R = 2-CN, 99% 2m R = 2-Me, 65% 2n R = 4-CO ₂ Me, 5 20 R = 2-CO ₂ Me, 5

Scheme 3. Scope of the synthesis of aryl azides. ^{*a*} See ESI for synthetic procedures. ^{*b*} Isolated yields.

It is worth noting that the synthetic procedure is extremely While, simple, robust and easily reproducible. diazotization/azide formation sequence demands particular care (especially in the first step) and high synthetic skills. In our case, easily accessible, stable, in many cases, commercially available, tetrafluoroborate diazonium salt are used. Thus, the developed synthetic procedure might be considered as a "click" reaction.²⁵ To obtain a good, or even high yield of aryl azide one should simply mix aryl diazonium salt, hydroxylamine chloride and water in any sequence at room temperature. Moreover, in some cases, products (usually bearing electron withdrawing substituents) are solids not soluble in water; they form crystals in the reaction media, which can be filtered off easily.

In analogy with the synthesis of aryl azides, interaction of aryl diazonium tetrafluoroborates with N-aryl hydroxylamines might lead to the formation of 3-hydroxy-1,3-diaryltriazenes. Hydroxytriazenes are utilized as chelating ligands for determination of ions of main group and transition metals.²⁶ This class of compounds exhibit various biologic activity: antifungal,²⁷ antibacterial,^{27a-c, 27e, 28} insecticide,²⁹ analgesic,³⁰ Published on 30 September 2016. Downloaded by Cornell University Library on 30/09/2016 22:41:21

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and anti-inflammatory.³¹ Moreover, 3-hydroxytriazenes are useful substrates for photoinduced synthesis of azo dyes.³²

The very first attempt to conduct the reaction of Nphenylhydroxylamine and 4-cyanophenyl diazonium tetrafluoroborate under modified Fischer's conditions in water at room temperature was successful. Corresponding 3hydroxytriazene was obtained in 91% yield. Inspired by such an easy success, we performed studies of the scope of this reaction (Scheme 4). 3-Hydroxy-1-aryl-3-phenyltriazenes were obtained in good to excellent yields ranging from 58% up to 95%. Contrary to the synthesis of azides, no particular trends in reactivity of diazonium salts towards phenylhydroxylamine can be traced. Synthesis of a number of triazinoles (3a, 3e, 3f, 3h, 3i, 3j, 3l, 3o) is reported for the first time.



Scheme 4. Scope of the synthesis of 3-hydroxy-1-aryl-3-phenyltriazenes. ^{*a*} See ESI for synthetic procedures. ^{*b*} Isolated yields.

We tested the possibility to conduct the synthesis of the azides using the new method under "green" conditions, using no solvent at any stage, and the recycled water as the reaction media. Thus, we performed the synthesis of 4-cyanophenyl azide. Pure product was isolated using filtration. The reaction media was reused. The second and the following steps were performed just by addition of new portions of diazonium salt and hydroxylamine chloride. Results for the "green" experiments are presented in Table 1. In the first three stages, virtually quantitative yields were obtained. In the fourth stage, after third reuse of reaction media, the yield of the product decreased to 47%. Evidently, this is due to the increase of the acidity of the reaction media, that leads to the decrease in the yield (see above). Next three runs were performed using the addition of one equivalent of NaHCO₃ to neutralize excess of acid. The yields slightly decreased to 87%. Total yield for the first three steps is virtually quantitative, 98%. Total yield for 7 runs (including low yielding stage 4, when no base was added) is 86%.

The measure of "greenness" of the process is the Sheldon's *E*-factor.³³ Calculated values of *E*-factor for the developed methodology are extremely low if comparing to previously published approaches. To compare, the *E*-factor, calculated for three runs is as low as ~ 1.0. While for conventional synthesis of phenyl azide by the reaction of sodium azide with diazonium salt the calculated *E*-factor is as high as 53.7.³⁴ Utilization of the alternative methods might lead to even higher values: 90, ^{8c} 130,⁷

400. ^{10a}	Thus,	the	new	meth	lodol	logy	1S	the	"gı	reei	neşt	ew/	kno	FACH	a _{li} te
date.								D	OI:	10.1	039/	/C6	GC)237	79G

Table	1.	"Green"	synthesis	of	4-cyanophenyl	azide	using
recycle	ed v	vater reac	tion media	. <i>a</i>			

Stage	Solvent reuse	Yield $[\%]^b$	E-factor		
1	0	94	1.1		
2	1	100	1.0		
3	2	100	1.0		
4	3	47	3.2		
5	4	87 ^[b]	2.0		
6	5	87 ^[b]	2.0		
7	6	87 ^[b]	2.0		
Total 3 runs	2	98	1.0		
Total 7 runs	6	86	1.6		

^a See the Supporting Information for synthetic procedures. [b] Isolated yields.
^b 1 equivalent of NaHCO₃ was added.

Conclusions

To conclude, we report on the development of the general approach for the synthesis of aryl azides and triazinoles from stable (in many cases available commercially) aryldiazonium tetrafluoroborates. The new method gives good to quantitative yields. Reaction procedure is very simple, robust, and easily reproducible. All reagents are easily accessible and cheap.

It is worth mentioning that our approach towards the synthesis of aryl azides enables isotope labeling of azide group at any position (see Scheme 1, nitrogen atoms depicted with different colours). Indeed, consequent addition of nitrogen atoms to the aryl moiety takes place. The source for the first nitrogen atom is labelled aniline, the second nitrogen atom –sodium nitrite, and the third nitrogen atom – hydroxylammonium chloride. Such labelling might be helpful for mechanistic studies of reactions of aryl azides and their derivatives.³⁵

The new method is unprecedentedly "green" – water is used as the reaction media. Moreover, this media can be further reused several times with no significant loss in yields. Utilization of transition metals is also avoided. Since aryl azides are widely used in medicinal chemistry, trace amounts of metals are unwanted contaminants in bioactive substances. Notably, we avoided the utilization of toxic and explosive sodium azide. Our approach is safer, and might be very helpful for scaling of the synthesis of aryl azides. We believe that our approach will make aryl azides more available and widely utilized both in laboratory and in industry.

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