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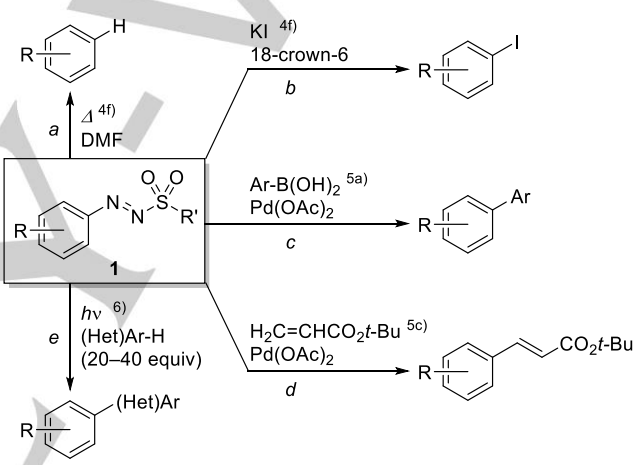
Rhodium(II)-Catalyzed Synthesis of *N*-Aryl-*N*'-Tosyldiazenes from Primary Aromatic Amines Using (Tosylimino)aryliodinane: A Potent Stable Surrogate for Diazonium Salts

Motoki Ito,* Arisa Tanaka, Kazuhiro Higuchi, and Shigeo Sugiyama*[a]

Abstract: The first example of the single-step synthesis of *N*-aryl-*N*'-tosyldiazenes from primary aromatic amines is described. A wide range of aromatic amines provided the corresponding products in high yields via an N−N bond formation with Rh(II)-nitrene intermediates, generated in situ from dirhodium(II) complex catalysts and (tosylimino)-2,4,6-trimethylphenyliodinane (TsN=IMes), followed by oxidation. The synthesized *N*-aryl-*N*'-tosyldiazene was successfully demonstrated to serve as a potent stable surrogate for diazonium salts in two-step deaminative transformations of primary aromatic amine.

Aryl diazonium salts represent unrivaled intermediates in a wide range of aromatic C−N bond transformations including the Sandmeyer, Gomberg-Bachmann, and Balz-Schiemann reactions since their discovery in the late 19th century.[1a,c,f] Despite their instability and explosibility, the synthetic importance of diazonium salts has further increased during the past four decades with the development of transition metal-catalyzed C−N bond transformations,[1b,d,e] pioneered by Kikukawa and Matsuda.[2] Consequently, it is not surprising that a great deal of effort has been devoted to use diazonium salts safely and remarkable progress has recently been achieved by exploiting one-pot diazotization/coupling protocols or flow reactor, as well as the development of storable salts (tetrafluoroborate, hexafluorophosphate, and tosylate).[1e] However, there still remains a need for the development of a surrogate for diazonium salts in terms of safety, handling, and accessibility from primary aromatic amines.[3]

N-Aryl-*N*'-sulfonyldiazenes **1**, known as stable azo compounds, have been paid little attention as substrates for C−N bond transformation until recently,[4−8] while it has been reported that **1** can act as precursors of aryl radicals or cations similar to diazonium salts.[4] For example, diazenes **1** are known to provide protodeazosulfonylation and iododeazosulfonylation products upon heating in DMF and treatment with potassium iodide in the presence of 18-crown-6, respectively (Scheme 1, *a* and *b*).[4f] Recently, the potent synthetic utility of diazenes **1** has been demonstrated by the work of Lu and Liu, in which the palladium(II)-catalyzed coupling of *N*-aryl-*N*'-sulfonylhydrazines with arylboronic acids or acrylates proceeded via the intermediacy of diazenes **1** generated by the oxidation of hydrazines (Scheme 1, *c* and *d*).[5,6] Furthermore, in 2016, Fagnoni and Protti reported the visible-light-induced arylation of **1** (R' = Me) without the use of a photosensitizer or photocatalyst in the presence of an excess amount of aromatic compounds (Scheme 1, *e*).[7]



Scheme 1. C−N Bond transformations of *N*-aryl-*N*'-sulfonyldiazenes **1**

On the other hand, the synthesis of diazenes **1** starting from primary aromatic amines generally requires multiple steps including a diazotization.[9] Hence, despite their growing synthetic importance, the lack of methods for the single-step synthesis of diazenes **1** has precluded their utilization as a surrogate for diazonium salts. In this context, we herein report the efficient synthesis of *N*-aryl-*N*'-tosyldiazenes **1** (R' = *p*-Tol) with a combinational use of dirhodium(II) complex catalysts and (tosylimino)aryliodinanes. This represents the first example of a single-step synthesis of **1** from primary aromatic amines **2**.

Electrophilic Rh(II)-nitrene species generated from dirhodium(II) complexes and (*N*-arylsulfonylimino)aryliodinanes are presumed to be intermediates in the inter- and intramolecular C−H amination of both aliphatic and aromatic compounds as well as the aziridination of alkenes.[10] In contrast, X−H (X = heteroatom) insertion reactions of metal-nitrene have remained unexplored.[11] However, based on the analogy between the reactivity of nitrenes and carbenes,[12] we envisioned that the reaction between primary aromatic amines **2** and a Rh(II)-nitrene should provide *N*-aryl-*N*'-sulfonyldiazenes **1** via the N−H insertion of nitrene followed by oxidation (Scheme 2).[13,14]

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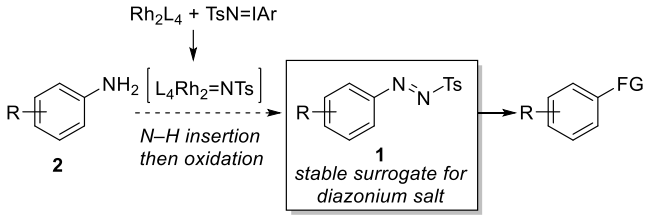
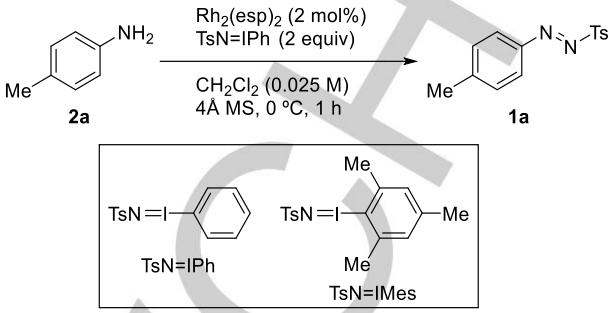


Scheme 2. Strategy for a single-step synthesis of *N*-aryl-*N*'-sulfonyldiazenes **1** via N−H insertion of Rh(II)-nitrene intermediates.

On the basis of the above anticipation, we initially examined the reaction of *p*-toluidine (**2a**) with 2 equiv of (tosylimino)phenyliodinane (TsN=IPh) in CH_2Cl_2 using 2 mol% of $Rh_2(esp)_2$ (esp = α,α,α,α-tetramethyl-1,3-benzenedipropanoate).[15] The reaction proceeded smoothly to completion at 0 °C in less than 1 h, affording *N*-(*p*-tolyl)-*N*'-tosyldiazene (**1a**) in 74% yield (Table 1, entry 1, determined by ^{1}H NMR). To our surprise, **1a** could be obtained even in the absence of catalyst albeit in low yield (entry 2).[16] The use of $Rh_2(OAc)_4$ in place of $Rh_2(esp)_2$ provided **1a** in only 45% yield (entry 3). An increase in the reaction temperature or the concentration of the substrate was accompanied by a decrease in the product yield (entries 4 and 5). The reaction in the absence of 4Å MS also resulted in a slight drop in the product yield (entry 6). Solvents such as Et_2O, MeCN, toluene, and benzotrifluoride were less effective than CH_2Cl_2 (entries 7−10). Finally, switching the nitrene precursor from TsN=IPh to (tosylimino)-2,4,6-trimethylphenyliodinane (TsN=IMes) dramatically improved the product yield,[17] providing **1a** in 86% yield (determined by ^{1}H NMR) and in 66% yield after column chromatography on silica gel (entry 11).[18,19]

With optimized conditions in hand, we then investigated the applicability of the reaction to a range of aromatic amines **2** (Table 2). Aniline (**2b**) provided *N*-phenyl-*N*'-tosyldiazene (**1b**) in 68% yield (entry 1).[20] High product yields were consistently observed with amines bearing *tert*-butyl, chloro,[21] trifluoromethyl, alkoxycarbonyl, methoxy,[18] or trifluoromethoxy groups at the *para* position on the benzene ring (71–99% yield, entries 2−8). Again, the advantage of the use of TsN=IMes over TsN=IPh was demonstrated with 4-chloroaniline (**2d**), 4-trifluoromethylaniline (**2e**), or methyl 4-aminobenzoate (**2f**) (TsN=IMes; 78−99%, TsN=IPh; 30−49%, see entries 3−5), although the reason for these results is not clear at present. It is also notable that no trace of the aziridination product was observed with allyl ester **2g** (entry 6). Acid-sensitive functional groups like *tert*-butyldimethylsilyl and trityl ethers remained untouched during the reaction (entries 9 and 10). No detectable benzylic C−H amination or oxidative removal of the *p*-methoxybenzyl ether was observed under the reaction conditions (entry 11). Furthermore, the present protocol was found to be applicable to amino acid and steroid derivatives **2m** and **2n** providing diazenes **1m** and **1n** in 70% and 79%, respectively (entries 12 and 13).

Table 1. Synthesis of diazene **1a** from *p*-toluidine (**2a**) catalyzed by dirhodium(II)-complexes.[a]

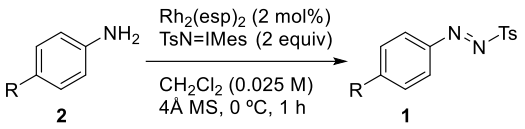


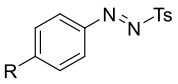
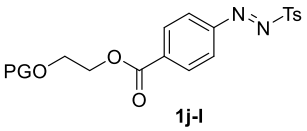
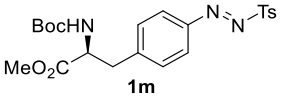
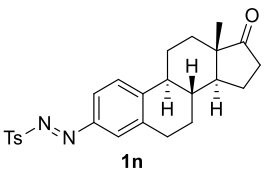
Entry	Conditions	Yield[b]
1	standard	74%
2	without $Rh_2(esp)_2$	23%
3	$Rh_2(OAc)_4$ instead of Rh_2 $(esp)_2$	45%
4	rt instead of 0 °C	62%
5	0.1 M instead of 0.025 M	58%
6	without 4Å MS	59%
7	Et_2O instead of CH_2Cl_2	10%
8	MeCN instead of CH_2Cl_2	42%
9	toluene instead of CH_2Cl_2	48%
10	$CF_3C_6H_5$ instead of CH_2Cl_2	56%
11	**TsN=IMes instead of TsN=IPh**	**86% (66%)**[c]

[a] Reactions were carried out as follows, unless otherwise noticed: iminoiodinane (0.2 mmol) was added to a mixture of **1a** (0.1 mmol), Rh(II) catalyst (0.002 mmol, 2 mol%) and 4Å MS (powder, 40 mg) in the indicated solvent (4 mL) at the indicated temperature under Ar atmosphere. [b] Yields were determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard (average of two trials). [c] Yield in parenthesis refers to isolated yield. Ts = tosyl.

We next examined *ortho*-substituted amines as substrates (Table 3). However, unfortunately, sterically hindered *ortho*-substituted amines **2o−s** were found to be less effective substrates under the catalysis by $Rh_2(esp)_2$ (<30% yield). To our delight, the yield of *N*-(2-bromophenyl)-*N*'-tosyldiazene (**1o**) was greatly improved by switching the catalyst to $Rh_2(HNCOCF_3)_4$[15b] with less bulky amidate ligands (entry 1).[22] High yields were maintained with electron-withdrawing methoxycarbonyl or sterically bulky phenyl groups at the *ortho* position on the benzene ring (entries 2 and 3). In contrast, the introduction of electron-donating methyl and methoxy groups markedly diminished the yields (entries 4 and 5). In addition, $Rh_2(HNCOCF_3)_4$ was found to be well suited for the transformation of a heteroaromatic amine, namely 3-aminopyridine (**2t**), providing diazene **1t** as the sole product in 70% yield (entry 6).[13]

Table 2. Synthesis of diazenes **1** catalyzed by $Rh_2(esp)_2$.[a]

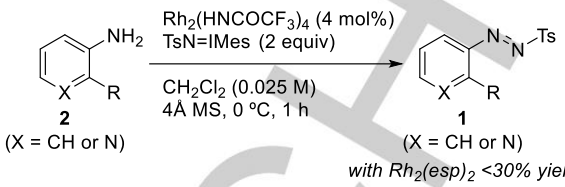


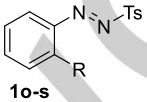
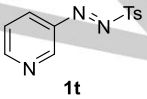
Entry	Diazene **1**		Yield[b]
1	 **1b-i**	R = H (**1b**)	68%
2		*t*-Bu (**1c**)	83%
3		Cl (**1d**)	99% (49%)[c]
4		CF_3 (**1e**)	88% (30%)[c]
5		CO_2Me (**1f**)	86%[d] (31%)[c]
6		CO_2Allyl (**1g**)	85%
7		OMe (**1h**)	73%
8		OCF_3 (**1i**)	71%
	 **1j-l**		
9	PG = TBS (**1j**)		81%
10	Tr (**1k**)		78%
11	PMB (**1l**)		85%
12[e]	 **1m**		70%
13	 **1n**		79%

[a] All reactions were performed on a 0.1 mmol scale. [b] Isolated yield. [c] Yields in parentheses refer to yields obtained when TsN=IPh was used instead of TsN=IMes. [d] 1.0 mmol scale. [e] 4 mol% of $Rh_2(esp)_2$ was used. TBS = *tert*-butyldimethylsilyl, Tr = trityl, PMB = *p*-methoxybenzyl, Boc = *tert*-butoxycarbonyl.

A plausible reaction mechanism for this transformation is illustrated in Scheme 3. The nucleophilic addition of aromatic amine **2** to Rh(II)-nitrene would generate zwitterionic intermediate **I**. The formation of diazene **1** from **I** can be rationalized with two pathways. Path A involves the formation of a formal N−H insertion product, namely *N*-aryl-*N*'-tosylhydrazine **3**, via a proton transfer from **I**, followed by oxidation with the iminoiodinane to afford diazene **1**. Alternatively, trapping of **I** by the iminoiodinane can generate intermediate **II** possessing an N−I(III) bond, which, upon elimination of iodoarene and *p*-toluenesulfonamide, provides diazene **1** without the intermediacy of hydrazine **3** (path B).[23] To gain an insight into the reaction mechanism, the reaction of **2a** with 1 equiv of TsN=IMes was performed [Eq. (1)].

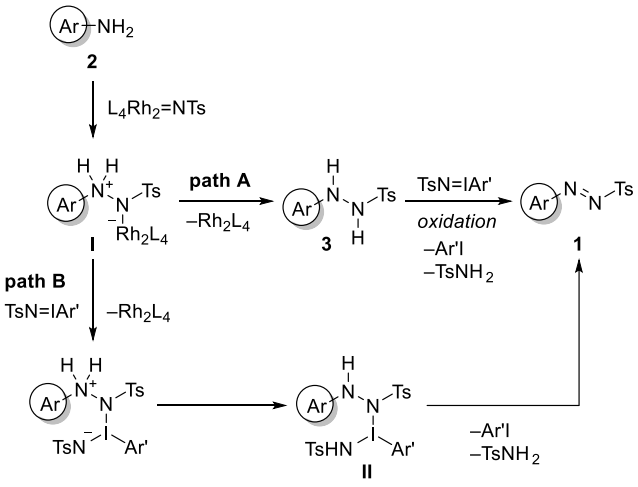
Table 3. Synthesis of *ortho*-substituted- and heteroaromatic diazenes **1** catalyzed by $Rh_2(HNCOCF_3)_4$.[a]



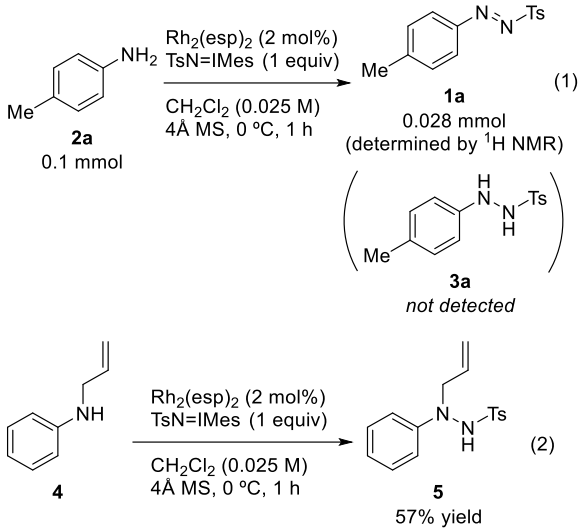
Entry	Diazene **1**		Yield[b]
1	 **1o-s**	R = Br (**1o**)	79%
2		CO_2Me (**1p**)	79%
3		Ph (**1q**)	67%
4		Me (**1r**)	ND
5		OMe (**1s**)	20%
6	 **1t**		70%

[a] All reactions were performed on a 0.1 mmol scale. [b] Isolated yield. ND = not detected.

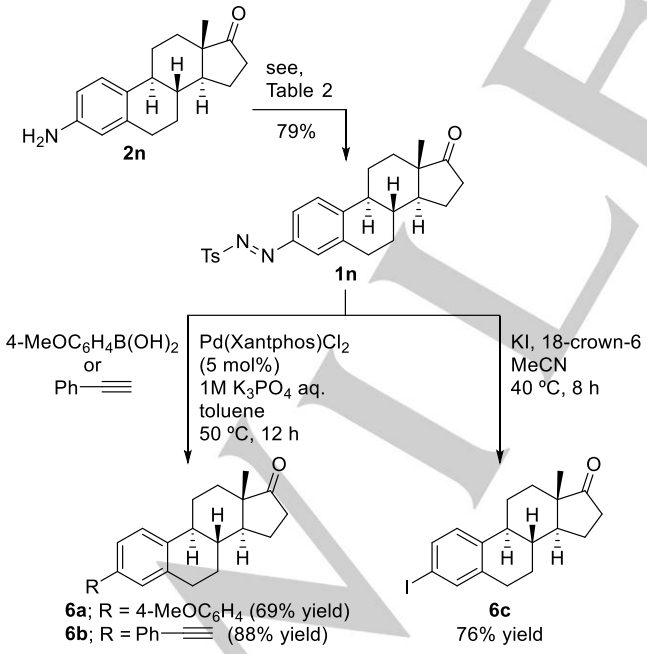
As a result, no signs of the formation of hydrazine **3a** were detected by NMR spectroscopy of the crude reaction mixture, while **1a** was obtained in 28% yield. This result should not be inconsistent with a mechanism involving a formal N−H insertion, but neither it supports such a pathway.[24] Hence, at this point, both reaction pathways are equally possible. On the other hand, the reaction of *N*-allylaniline (**4**) provided the N−H insertion product **5** in 57% yield under the same conditions [Eq. (2)]. This result indirectly suggests the formation of hydrazine **3** from primary amine **2**.



Scheme 3. Plausible reaction mechanism.



Finally, transformations of the obtained diazene **1** were examined under both catalytic and transition metal-free conditions (Scheme 4). The palladium(II)-catalyzed coupling of diazene **1n**, derived from 3-aminoestrone (**2n**), with 4-methoxyphenylboronic acid[5a] or phenylacetylene[5b] provided biaryl **6a** and diarylethyne **6b** in 69% and 88% yields, respectively. 3-Iodo-3-deoxy-estrone (**6c**) was obtained by treatment of **1n** with KI in the presence of 18-crown-6.[4f] These reactions constitute a novel two-step deaminative transformation of primary aromatic amines **2** using diazenes **1** as key intermediates. Thus, the exceptional utility of **1** as a surrogate for diazonium salts has been successfully demonstrated.



Scheme 4. Transformations of diazene **1n**.

In summary, we have developed a new and efficient method for the synthesis of *N*-aryl-*N*'-tosyldiazenes with a combinational use of dirhodium(II) complex catalysts and iminoiodinane. This represents the first example of the synthesis of *N*-aryl-*N*'-tosyldiazenes in a single step starting from primary aromatic amines through an N−N bond formation with Rh(II)-nitrene followed by oxidation. The obtained *N*-aryl-*N*'-tosyldiazene was successfully demonstrated to serve as a potent stable surrogate for diazonium salts in a two-step deaminative transformation of aromatic amines. Further studies aimed to expand the utility of diazenes are currently in progress as well as the applications of this method to the synthesis of bioactive compounds.

Acknowledgements

We thank T. Koseki of the Analytical Center of Meiji Pharmaceutical University for mass spectral measurements.

Keywords: amines • azo compounds • rhodium • nitrene • aromatic substitution

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[14] Lacour and co-workers reported that the reaction of Rh(II)-nitrene with the Tröger base, a chiral bicyclic aminal, provides formal C−N insertion products via an N−N bond formation followed by the 1,2-rearrangement of the aminal carbon. S. A. Pujari, L. Guénée, J. Lacour, *Org. Lett*. **2013**, *15*, 3930−3933.

[15] a) C. G. Espino, K. W. Fiori, M. Kim, J. Du Bois, *J. Am. Chem. Soc*. **2004**, *126*, 15378−15379; b) K. W. Fiori, J. Du Bois, *J. Am. Chem. Soc*. **2007**, *129*, 562−568.

[16] It is reported that the reactions of primary aromatic amines with iodine(III) reagents afford aromatic azo compounds via oxidative dimerization. K. Monir, M. Ghosh, S. Mishra, A. Majee, A. Hajra, *Eur. J. Org. Chem*. **2014**, 1096−1102.

[17] TsN=IMes can be readily prepared by condensation of $TsNH_2$ with commercially available 2-(diacetoxyiodo)mesitylene, [$MesI(OAc)_2$]. See Supporting Information for details of the preparation. The consideration about the beneficial effect of the mesityl group on the product yield is also described in Supporting Information.

[18] It was found that electron-rich diazenes, such as **1a** and **1h**, underwent partial decomposition during column chromatography on silica gel (neutral).

[19] Unfortunately, in situ generation of iminoiodinane from corresponding (diacetoxyiodo)arene and *p*-toluenesulfonamide led to the undesired oxidation of starting amines. See also Ref [16]

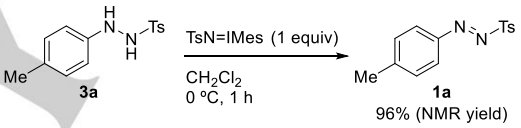
[20] No traces of the C(sp^2)−H amination product was observed. As the reviewer pointed out, nitrenes rarely undergo C(sp^2)−H insertion. a) J. Jiao, K. Murakami, K. Itami; *ACS Catal*. **2016**, *6*, 610−633; b) R. Singh, K. Nagesh, M. Parameshwar, *ACS Catal*. **2016**, *6*, 6520−6524.

[21] With 4-chloroaniline (**2d**), it was observed that lowering the catalyst loading from 2 mol% to 1 mol% led to a decrease in the product yield (2 mol%: 99%, 1 mol%: 69%).

[22] In the reactions of *para*-substituted amines, $Rh_2(HNCOCF_3)_4$ (2 mol%) provided similar levels of product yields as those obtained with $Rh_2(esp)_2$ (73% yield for **1c**, 95% yield for **1f**, see Table 1, entries 2 and 5).

[23] It is reported that the zwitterionic intermediate generated from primary aromatic amines and Rh(II)-carbene intermediates can be trapped by a variety of electrophiles. Y. Zhu, C. Zhai, L. Yang, W. Hu, *Eur. J. Org. Chem*. **2011**, 1113−1124 and references therein.

[24] It was confirmed that reaction of hydrazine **3a** with 1 equiv of TsN=IMes afforded diazene **1a** in virtually quantitative yield in the absence of the dirhodium(II) complex catalyst.



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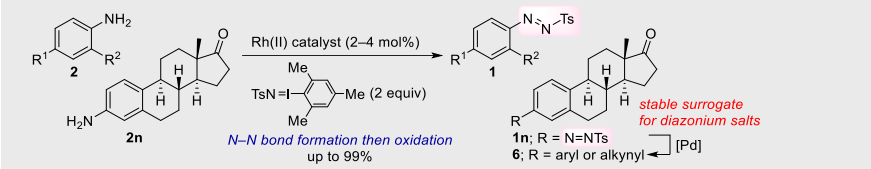

N-Aryl-*N*'-tosyldiazenes **1** have been obtained in a single step from aromatic amines **2** via an N−N bond formation with Rh(II)-nitrene, generated in situ from an iminoiodinane and a dirhodium(II) complex catalyst, followed by oxidation. The synthesized diazene **1** was successfully demonstrated to serve as a potent stable surrogate for diazonium salts in two-step deaminative transformations of primary aromatic amine.

Dr. Motoki Ito, Arisa Tanaka, Dr. Kazuhiro Higuchi, Prof. Dr. Shigeo Sugiyama**

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Rhodium(II)-Catalyzed Synthesis of *N*-Aryl-*N*'-Tosyldiazenes from Primary Aromatic Amines Using (Tosylimino) aryliodinane: A Potent Stable Surrogate for Diazonium Salts