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Authors: Yingwei Zhao, Haoran Zhu, Donald J. Wink, Siyoung Sung, Joseph M. Zadrozny, and Tom G Driver

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RESEARCH ARTICLE

Counterion Control of *t*-BuO-Mediated Single Electron Transfer to Nitrostilbenes Constructs *N*-Hydroxyindoles or Oxindoles

Yingwei Zhao,[†][a,b] Haoran Zhu,[†][a] Siyoung Sung,[c] Donald J. Wink,[a] Joseph M. Zadrozny*[c] and Tom G. Driver*[a]

Y. Zhao,[†] H. Zhu,[†] S. Sung, D. J. Wink, J. M. Zadrozny and T. G. Driver
[†] These authors contributed equally.

[a] Department of Chemistry
University of Illinois at Chicago
845 W Taylor St. MC 111, Chicago, IL 60607, USA
E-mail: tgd@uic.edu

[b] College of Chemical Engineering
Huaqiao University, Xiamen
668 Jimei Boulevard, Xiamen, Fujian, 361021 P.R. China

[c] Department of Chemistry
Colorado State University
Fort Collins, CO 80523

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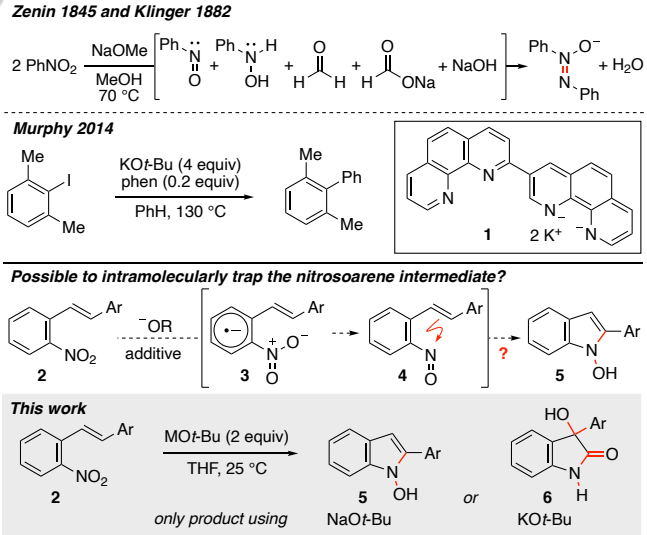
Abstract: *tert*-Butoxide unlocks new reactivity patterns embedded in nitroarenes. Exposure of nitrostilbenes to sodium *tert*-butoxide was found to produce *N*-hydroxyindoles at room temperature without an additive. Changing the counterion to potassium changed the reaction outcome to yield solely oxindoles through an unprecedented dioxygen-transfer reaction followed by a 1,2-phenyl migration. Mechanistic experiments established that these reactions proceed via radical intermediates and suggest that counterion coordination controls whether an oxindole or *N*-hydroxyindole product is formed.

Introduction

The ubiquitous nature of *N*-heterocycles in pharmaceuticals and organic materials has inspired the discovery of new reactivity patterns to facilitate their construction.[1],[2] The development of reductive methods to access these privileged scaffolds by constructing C–N bonds using nitroarenes has received significant attention because of the ready availability and robust nature of nitroarenes. While traditional C–N bond formation methods were developed using a superstoichiometric quantity of a reductant to deoxygenate the nitro-group,[3] recent efforts have focused on the development of catalytic processes that use the combination of a transition metal-[4] a base-metal-[5] or a phosphine[6] catalyst and a stoichiometric reductant. In contrast to these approaches, 175 years ago,[7] sodium methoxide was reported to reduce nitrobenzene to azoxybenzene in boiling methanol (Scheme 1). Subsequent mechanistic investigations in 1962 by Ogata and Mibae suggested that electron-transfer from alkoxide triggered deoxygenation to produce an ArNO intermediate which reacted with an *N*-hydroxybenzene to produce the azoxy product.[8] After these mechanistic studies, interest in exploiting electron-transfer from alkoxides waned, until a recent resurgence in the use of potassium *tert*-butoxide as a single-electron reductant.[9] In 2010, the Hayashi and Shi groups reported that *tert*-butoxide mediated the transition metal-free couplings of iodoarenes.[9a, 9b] Investigations by Murphy and co-workers established that electron-transfer to the iodoarene occurred from the in situ-generated phenanthroline dianion **1**.[9d] Inspired by these reports, we were curious if exposure of a nitrostilbene to an alkoxide would generate a nitrosoarene intermediate that might be intercepted intramolecularly to afford an *N*-heterocycle (Scheme 1). In contrast to our expectations, we found that nitrostilbene **2** could be converted to *N*-hydroxyindole **5** using simply NaO*t*-Bu at room temperature without an additive. Strikingly, changing the counterion to potassium triggered an unprecedented dioxygen transfer and [1,2] aryl migration tandem reaction to afford oxindole **6** *as the only* N-*heterocycle* from nitrostilbene **2**.



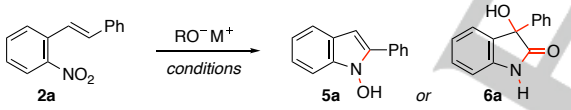
Scheme 1. *tert*-Butoxide-mediated *N*-heterocycle formation from nitroarenes.

Results and Discussion

Investigation of the scope and limitations of *N*-heterocycle formation. To test our hypothesis that nitrosoarene intermediates could be accessed using an alkoxide and trapped to afford an *N*-heterocycle, the reactivity of nitrostilbene **2a** was examined (Table 1). While no reaction was observed upon exposure of **2a** to sodium methoxide in boiling methanol, changing the solvent to tetrahydrofuran resulted in the formation of *N*-hydroxyindole **5a** at room temperature (entries 1 and 2). The yield of **5a** was improved by changing the identity of the alkoxide with the best outcome obtained when *tert*-butoxide was used (entries 2 – 4). Increasing the temperature or the reaction time, however, did not further increase the yield (entries 5 and 6). The reaction was not light-dependent:[10] performing the reaction in a foil-covered vessel provided *N*-hydroxyindole **5a** in 55% yield (entry 7). A solvent screen revealed that *N*-hydroxyindole formation occurred smoothly in ethereal solvents, but was attenuated in *tert*-butanol (entries 7 – 10).[11] To our surprise, the identity of the counterion was critical to the reaction outcome: while no reaction was observed when lithium- or magnesium *tert*-butoxide was employed, 3-phenyl-3-hydroxy-2-oxindole **6a** was obtained as the only product using potassium *tert*-butoxide irrespective of exposure to light (entries 11 – 13). The formation of **6a**, whose structure confirmed by X-ray crystallography,[12] involves not only oxygen transfer to the *ortho*-alkenyl substituent but also a [1,2]-phenyl shift. While oxygen transfer from nitroarenes to pendant acetylenes has been reported to afford *N*-heterocycles,[13] this oxidation-migration tandem reaction of *ortho*-alkenyl substituents is unprecedented.

The scope and limitations of the NaO*t*-Bu-mediated reductive cyclization was explored by developing conditions to alkylate the *N*-hydroxyl group as well examining the effect of changing the electronic- and steric environment of the nitrostilbenes (Table 2). The substrates for this study were either commercially available or readily prepared in one-step from 2-bromonitroarenes and styrene using a Heck reaction.[14] Because *N*-alkoxy- or *N*-acetoxyheterocycles are more stable,[15] we explored telescoping the reaction by adding an electrophile to determine if the sensitive *N*-hydroxy functionality could be alkylated or acetylated. We found that a methyl-, benzyl-, or benzoate group could be easily added to the initially formed *N*-hydroxyindole to improve the reproducibility of the reaction sequence and ease purification. Our investigation of a series of nitrostilbenes that varied their electronic- and steric nature revealed that higher yields were obtained in the presence of electron-donating groups positioned

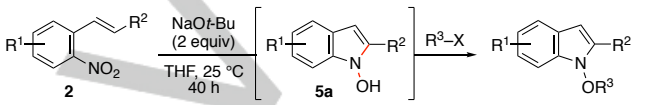
Table 1. Development of reductive and divergent *N*-heterocycle formation.

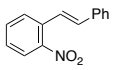
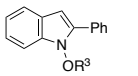
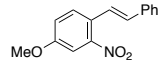
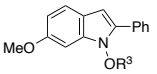
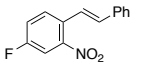
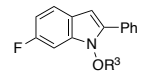
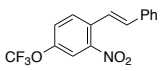
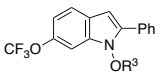
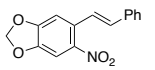
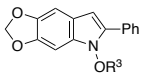
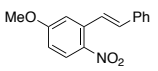
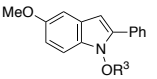
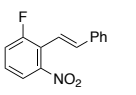
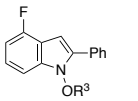
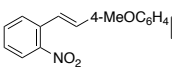
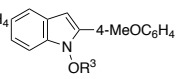
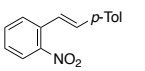
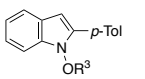
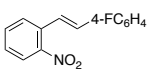
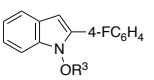
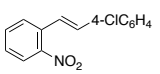
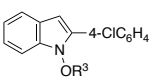
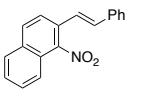
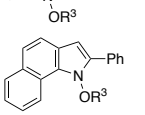


entry	MOR (2 equiv)	solvent	h	T (°C)	yield, %[a]	**5a**:**6a**
1	NaOMe	MeOH	16	70	n.r.	…
2	NaOMe	THF	16	25	14	>20:1
3	NaOEt	THF	16	25	26	>20:1
4	NaO*t*-Bu	THF	16	25	55	>20:1
5	NaO*t*-Bu	THF	16	60	57	>20:1
6	NaO*t*-Bu	THF	40	25	60	>20:1
7[b]	NaO*t*-Bu	THF	40	25	55	>20:1
8	NaO*t*-Bu	dioxane	40	25	53	>20:1
9	NaO*t*-Bu	2-MeTHF	40	25	55	>20:1
10	NaO*t*-Bu	*t*-BuOH	40	25	38	>20:1
11	LiO*t*-Bu	THF	16	25	0	…
12	Mg(O*t*-Bu)$_2$	THF	16	25	0	…
13[c,d]	KO*t*-Bu	THF	16	25	62	<1:20

[a] Isolated after silica gel chromatography. [b] Reaction performed in a foil-covered vessel. [c] The outcome of the reaction did not change if light was excluded. [d] The X-Ray structure of **6a** was deposited in the Cambridge Crystallographic Database (CCDC 198003). THF = tetrahydrofuran.

Table 2. Scope of NaO*t*-Bu-mediated *N*-hydroxindole formation.



entry	#	nitroarene **2**	*N*-heterocycle **5**	R^3	yield, %[a]
1	**a**			H Me Bn Bz	60 67 (63)[b] 60 59
2	**b**			H Me	58 62
3	**c**			H Me	53 42
4	**e**			H Me	24 (38)[c] 22 (44)[c]
5	**g**			Me	63
6	**h**			Me	44
7	**i**			H Me	25 (60)[c] 17 (63)[c]
8	**l**			H Me	46 60
9	**m**			H Me	68 75
10	**n**			H Me	67 59
11	**o**			H Me	25 (53)[c] 28 (55)[c]
12	**q**			Me	52

[a] Isolated after silica gel chromatography. [b] Reaction performed on 2 mmol scale. [c] The *tert*-BuO-mediated reduction was performed at 100 °C for 16 h.

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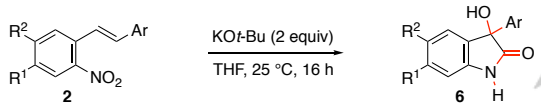
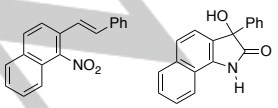
para to the styryl group (entries 2 and 5). In contrast, the presence of electron-withdrawing groups severely attenuated the reaction yield. Gratifyingly, the yield of *N*-hydroxyindole could be rescued if the reaction was heated to 100 °C (entries 4 and 7). Changing the electronic nature of the β-aryl group had less of an overt effect on the reaction outcome: while higher yields were observed for electron-rich aryl groups, the presence of a fluorine did not diminish the yield as substitution on the nitroarene moiety (entries 8 – 11). While adding a stronger electron-withdrawing Cl did reduce the yield, increasing the temperature of the reaction increased the yield of **5o**. The reactivity of naphthalene-derived **2q** illustrated that *N*-hydroxyindole formation was relatively insensitive to steric constraints (entry 12).

After our initial investigation into the scope of using NaO*t*-Bu as the reductant, we turned our attention to exploring the reactivity of nitrostilbenes towards KO*t*-Bu (Table 3). Analysis of the reactivity patterns revealed several differences in comparison to *N*-hydroxyindole formation. First, the success of the oxygen-transfer-migration reaction was less dependent on the electronic nature of the nitrostilbene with chloro-, bromo- and even trifluoromethyl groups tolerated (entries 2 – 10). Further, the opposite electronic trend was observed for β-aryl groups: more electron-deficient groups led to higher oxindole yields (entries 11 – 15). Naphthalene **2q** demonstrated that oxindole formation

Table 3. Scope of KO*t*-Bu-mediated oxindole formation.

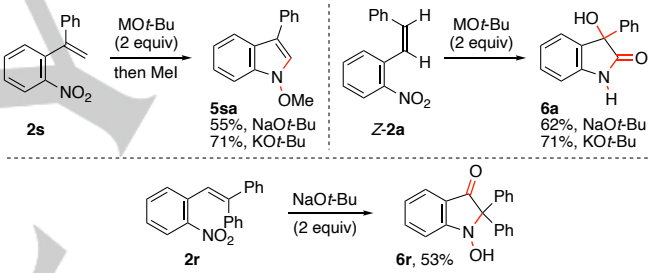


entry	#	R^1	R^2	Ar	yield, %[a]
1	**a**	H	H	Ph	62 (55)[b]
2	**b**	MeO	H	Ph	43
3	**c**	F	H	Ph	43
4	**d**	Cl	H	Ph	48
5	**e**	F_3CO	H	Ph	57
6	**f**	F_3C	H	Ph	38
7	**g**	O–CH_2–O		Ph	41
8	**h**	H	MeO	Ph	49
9	**j**	H	F	Ph	74
10	**k**	H	Br	Ph	49
11	**l**	H	H	4-$MeOC_6H_4$	41
12	**m**	H	H	*p*-Tol	38
13	**n**	H	H	4-FC_6H_4	56
14	**o**	H	H	4-ClC_6H_4	50
15	**p**	H	H	4-$CF_3C_6H_4$	66
16	**q**				41

[a] Isolated after silica gel chromatography. [b] Reaction performed on 2 mmol scale.

tolerated an increased steric environment around the nitro-group to afford **6q** albeit in diminished yield relative to **6a** (entry 16). In contrast to *N*-hydroxyindole formation, the yield was not improved when the reaction temperature was increased.

To assess the impact of the *ortho*-styryl substituent on the reaction outcome, substrates **2s,** *Z*-**2a** and **2r** were investigated (Scheme 2). The position of the phenyl substituent was found to control which *N*-heterocycle was formed: exposure of α-phenylnitrostyrene **2s** to *tert*-butoxide afforded only *N*-methoxyindole **5sa** using either KO*t*-Bu or NaO*t*-Bu after telescoping the reaction with MeI, although an increased reaction temperature was required using NaO*t*-Bu. The stereochemistry of the 2-nitrostilbene was also critical to the reaction outcome. While *E*-nitrostilbene formed either *N*-hydroxyindole **5a** or oxindole **6a** depending on identity of the *tert*-butoxide counterion, the reaction of *Z*-**2a** afforded only oxindole **6a** irrespective of whether sodium- or potassium *tert*-butoxide was used. Similar reactivity was observed when nitrostilbene **2r** was exposed to NaO*t*-Bu, which produced only oxindole **6r** where one of the oxygen atoms was transferred to the *ortho*-alkenyl substituent.[16] These results suggest that steric interactions between the β-phenyl substituent and a reactive intermediate or stabilization of a radical- or charged intermediate by the α-phenyl substituent can override the counterion effect.



Scheme 2. Effect of phenyl substituent position on the reaction outcome.

Mechanistic EPR investigations. To investigate if the *tert*-butoxide-mediated *N*-heterocycle formation involved the formation of radical intermediates, the reaction was analyzed using X-band, solution-phase EPR spectroscopy (Figures 1 and 2). At room temperature, reaction mixtures from addition of KO*t*Bu and NaO*t*Bu exhibit EPR spectra near g = 2.00. The additional most-common feature of the spectra is the existence of a three-line pattern, typical for a radical interacting with a ^{14}N (I = 1) nucleus. We attribute these peaks to radical intermediates of an electron transfer from *tert*-butoxide (E_{ox} = +0.10 V vs SCE)[17] to nitrostilbene (E_{red} = –1.13 V vs SCE).[4g, 18] The high potential gap of ΔE = 1.03 V between the oxidation peak potential of *t*-BuO^- and the reduction peak potential of nitrostilbene suggests that coordination of the counterion occurs to facilitate the transfer.[19] This hypothesis is supported by the simulation of the X-band EPR spectrum from the NaO*t*-Bu-mediated reaction, which afforded the best match with experiment when a nitro radical anion was assumed coordinated to the sodium counterion (Figure 1a).[20]

The foregoing outcome suggests that counterion identity is critical to directing the radical formation pathway. For example, the EPR spectrum obtained from the NaO*t*-Bu-mediated reaction displays only three well-resolved peaks and no further couplings to ^1H in Figure 1a. The absence of additional peaks from the latter

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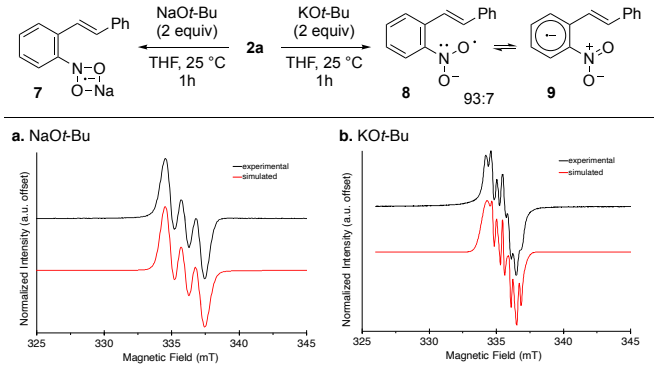
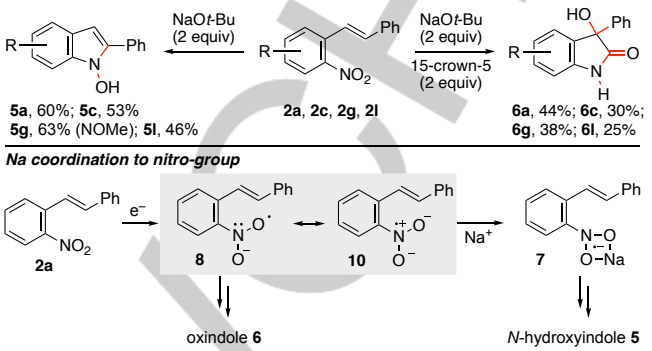


Figure 1. Experimental (black) and simulated (red) X-band EPR spectra of *tert*-butoxide-mediated reduction of nitrostilbene **2a** (THF, 298 K, 1 h) (**a**, result of NaO*t*-Bu reaction, **b**, result of KO*t*-Bu reaction) Data collection parameters: Frequency = 9.4306 GHz, Power = 0.2 mW, Modulation = 0.1 G; a. Fitting parameters for **7** are g_{iso} = 2.005, A_{iso} = 29 MHz, and an line width for isotropic broadening, lw =[0.81 0.53] in mT (the first Gaussian and the latter Lorentzian broadening); b. Fitting parameters for **8** are g_{iso} = 2.009, A = [22.1 18.2] MHz, lw = 1.09 mT, τ_{corr} = 5 ns, and weight = 0.85; and fitting parameters for **9** are g_{iso} = [2.007], A = [21.2 14.7 11.9 8.7], and lw = 0.2 mT, relative contributions to spectral intensity are 93% **8** and 7% **9**.

couplings strongly suggests that the spin density is localized only in the nitro group, not delocalized onto the aromatic ring. We propose that the small size as well as strong Lewis acidity of Na^+ allows for effective binding to the nitro group and prevention of spin density delocalizing on the aryl ring. In contrast, a spectrum displaying significantly more complicated hyperfine interactions was observed when KO*t*-Bu was employed (Figure 1b).[21],[22] Simulation of the spectra with a variety of possible radicals revealed a best match when assuming a mixture of 93% of **8** and 7% of **9**. We interpret these data to suggest that the nitro radical is less effective in coordinating the larger potassium counterion. As a result of the weaker coordination, the formation of two spin isomers is allowed, one featuring an NO_2 radical and one with spin density delocalized onto the aryl ring. We note that this preliminary interpretation requires that the radical is not delocalized across both moieties. This outcome could occur if interactions with K^+ drive the nitro-groups away from planarity with the stilbene.[23] Extension of this interpretation could explain the less complex EPR spectrum for the Na^+ system: stronger binding of the nitro radical anion to Na^+ produces only one, NO_2-localized isomer. We tentatively interpret the difference in coordination in these simulated spectra to account for the difference in reaction outcome: the lack of coordination to the counterion could enable oxygen-atom transfer from **8** to the *ortho*-styryl substituent to afford oxindole **6a**, which would not be possible when it is bound to the sodium ion.[24]

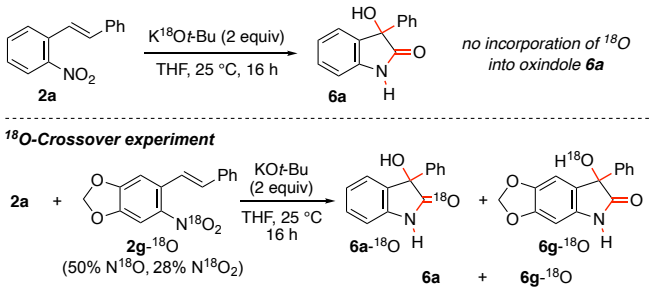
These EPR experiments spurred us to examine the effect of a crown ether on the reaction outcome (Scheme 3). When 15-crown-5 was added in combination with NaO*t*-Bu, we found that *N*-hydroxyindole **5a** was no longer formed, and oxindole **6a** was produced as the only *N*-heterocyclic product. This phenomenon proved to be general: exposure of 2-nitrostilbenes **2c, 2g,** or **2l** produced only oxindoles **6c**, **6g**, or **6l** albeit in lower yield than using KO*t*-Bu.[25] In contrast, the addition of 18-crown-6 to the KO*t*-Bu-mediated reaction resulted in no change to the outcome—oxindole **6a** was the only *N*-heterocycle formed.

Analysis of the reaction using EPR spectroscopy reveals a substantial change in spectral shape when the crown ether is present, potentially suggesting changes in spin identity via crown-ether binding to the counterion.[26] Together, these experiments suggest that coordination of the counterion controls whether *N*-hydroxyindole **5** or oxindole **6** is produced.



Scheme 3. Effect of 15-crown-5 on the reaction outcome.

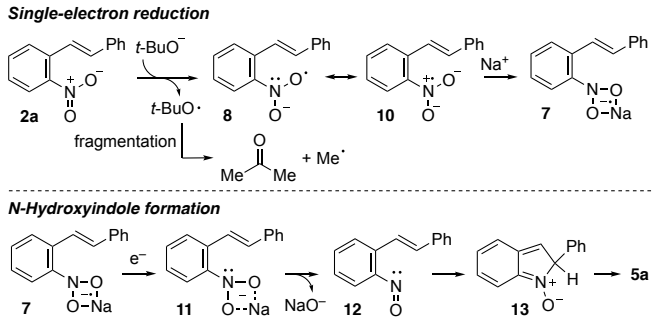
Reactivity of ^{18}O-labeled reagents. To determine if the C2- and C3 oxygens in oxindole **6** originated from an intra- or intermolecular reaction, the reactivity of ^{18}O-labeled potassium *tert*-butoxide and ^{18}O-labeled nitrostilbene **2g** was investigated (Scheme 4). When K^{18}O*t*-Bu was used, no ^{18}O-incorporation into **6a** was observed to suggest that both oxygens were transferred from the nitro-group. To test if oxygen transfer occurred intermolecularly, a mixture of **2a** and **2g**-^{18}O were submitted to reaction conditions and double crossover of the labeled- and unlabeled oxygens to the oxindole product was observed to afford 16% of **6a** and **6a**-^{18}O and 64% of **6g**-$^{18}O_2$ and **6g**-^{18}O. Analysis of the mass spectrum showed an increase of the $[M + 2]^+$ signal for **6a** and $[M - 2]^+$ signal for **6g**-^{18}O to suggest that only one of the oxygen atoms is transferred, and the parent ion $[(M) - OH]^+$ revealed that intermolecular O-transfer occurred only to the C2-position of the oxindole.



Scheme 4. Investigation of an intra- or intermolecular mechanism for oxygen transfer.

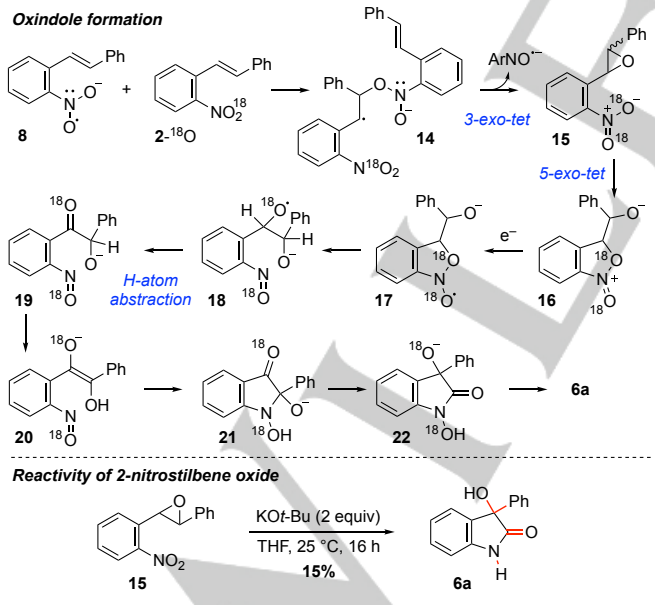
Potential mechanisms for *N*-heterocycle formation. Our data suggests a possible mechanism that accounts for the dependence of the reaction outcome on the identity of the counterion (Scheme 5). Electron transfer from *tert*-butoxide to nitrostilbene produces radical anion **8** and *tert*-butoxy radical,[27] which fragments to produce acetone and methyl radical.

Mesomer **10** traps sodium ion to produce **7**, which accepts a second electron to form **11**. Fragmentation of **11** produces nitrosostilbene **12**, which undergoes a 6π-electron-five atom electrocyclization to form **13** that isomerizes to produce *N*-hydroxyindole **5a**.[28]



Scheme 5. Potential mechanism for *N*-hydroxyindole formation.

Our data suggests that oxindole **6** is formed through an intermolecular mechanism when the counterion is not coordinated to the nitrostilbene radical anion (Scheme 6).[29] The intermolecular oxygen-atom transfer could occur by attack of radical anion **8** onto the nitrostilbene **2** at the β-position to afford nitrite **14**,[30] which undergoes a 3-*exo*-*tet* radical cyclization to produce epoxide **15**.[31],[32],[33] Ring-opening by the proximal nitro group could produce **16**.[34],[35],[36] *tert*-Butoxide-mediated single electron reduction followed by fragmentation produces **18**. Hydrogen-atom abstraction by *tert*-butoxy radical or methyl radical produces ketone **19**.[37],[38] Isomerization forms enol **20**,[39]



Scheme 6. Potential intermolecular mechanism for oxindole formation.

which attacks the nitroso group to produce *N*-heterocycle **21**. A subsequent 1,2 phenyl shift affords *N*-hydroxyoxindole **22**,[40] which is reduced to oxindole **6a**. To test if oxygen-transfer occurred via an epoxide intermediate, 2-nitrostilbene oxide was examined as a substrate. In line with our mechanistic hypothesis, treatment of **15** with KO*t*-Bu resulted in the formation of oxindole **6a**. Conversion of 2-nitrostilbene oxide to oxindole supports that the intermolecular reaction occurs between a nitroarene radical anion and a neutral nitroarene.

Conclusion

In conclusion, we have discovered a novel *tert*-butoxide-mediated reaction of 2-nitrostilbenes that produces either a *N*-hydroxyindole or an oxindole depending on the identity of the counterion. The reactivity patterns exhibited by the 2-nitrostilbenes suggest that the *N*-heterocyclic products are formed by either an intra- or intermolecular reaction, where the degree of coordination of the counterion to the radical anion dictate which mechanism occurs. Our findings illustrate that nitrosoarene reactive intermediates can not only be generated at room temperature from nitroarenes but that unprecedented reactivity patterns can be triggered divergently to produce functionalized *N*-heterocycles. In addition to leveraging this novel reactivity to construct different sized *N*-heterocycles, future studies are also aimed at obtaining a deeper understanding of the spin dynamics and spin Hamiltonian parameters of the observed radical intermediates to conclusively assign their identity.

Acknowledgments

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Keywords: *tert*-butoxide • single electron transfer • nitroarene

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[33] In order to obtain a yield greater than 50% of oxindole **6**, the nitrosoradical arene must be intercepted by a nitroarene or nitroarene radical anion, or that there is a competing intra- or intermolecular mechanism. Investigations are ongoing to disentangle these potential competive mechanisms

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[35] For related ring-opening of epoxides by nitrates, see: a) P. Golding, R. W Millar, N. C Paul, D. H Richards, *Tetrahedron Lett.* **1988**, *29*, 2731-2734; b) P. Golding, R. W. Millar, N. C. Paul, D. H. Richards, *Tetrahedron* **1993**, *49*, 7051-7062; c) N. Iranpoor, P. Salehi, *Tetrahedron* **1995**, *51*, 909-912; d) Y. A. Volkova, O. A. Ivanova, E. M. Budynina, E. B. Averina, T. S. Kuznetsova, N. S. Zefirov, *Tetrahedron Lett.* **2008**, *49*, 3935-3938.

[36] For related intramolecular ring-opening of *ortho*-nitrophenylcyclopropane to form 1-oxo-1,2-benzoxazolium- or 1-oxo-1,2-benzoxazinium ions, see: a) A. N. Fedotov, E. V. Trofimova, S. S. Mochalov, Y. S. Shabarov, *Zh. Org. Khim.* **1988**, *24*, 2403-2408; b) E. V. Trofimova, A. N. Fedotov, S. S. Mochalov, Y. S. Shabarov, *Zh. Org. Khim.* **1991**, *27*, 1193-1198; c) A. N. Fedotov, E. V. Trofimova, T. E. Gulov, S. G. Bandaev, S. S. Mochalov, N. S. Zefirov, *Russ. J. Org. Chem.* **2013**, *49*, 1534-1541.

[37] α-H-atom abstraction of a cage alkoxy radical was proposed by Barton and co-workers to account for ketone formation from a nitrite ester, see: a) D. H. R. Barton, R. H. Hesse, M. M. Pechet, L. C. Smith, *J. Chem. Soc., Perkin Trans. 1* **1979**, 1159-1165; b) G. Y. Ishmuratov, R. Y. Kharisov, A. K. Shayakhmetova, L. P. Botsman, O. V. Shitikova, G. A. Tolstikov, *Chem. Nat. Compd.* **2005**, *41*, 643-649.

[38] Alternatively, ketone **19** could be formed from **17** through an H-atom-abstraction fragmentation sequence, which would avoid the formation of alkoxy radical **18**.

[39] While formation of a ketyl radical could start a chain process, this appears unlikely because an excess of the *tert*-butoxide reductant is required for a positive reaction outcome.

[40] For reports of base-mediated [1,2] migrations to form 3-hydroxy-2-indolinones from 2-hyhydroxy-3-indolinones, see: a) R. M. Acheson, S. R. G. Booth, *J. Chem. Soc. C* **1968**, 30-32; b) S. Kafka, A. Klásek, J. Košmrlj, *J. Org. Chem.* **2001**, *66*, 6394-6399; c) I. Coldham, H. Adams, N. J. Ashweek, T. A. Barker, A. T. Reeder, M. C. Skilbeck, *Tetrahedron Lett.* **2010**, *51*, 2457-2460; d) M. Liu, C. Zhang, M. Ding, B. Tang, F. Zhang, *Green Chem.* **2017**, *19*, 4509-4514

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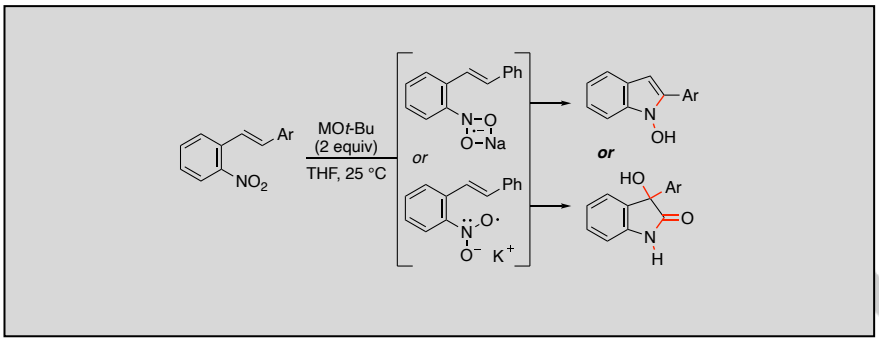

tert-Butoxide unlocks divergent reactivity embedded in nitrostilbenes to construct *N*-hydroxyindoles or oxindoles depending on whether sodium or potassium is the counterion.

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