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Diborane-Mediated Deoxygenation of *o*-Nitrostyrenes To Form Indoles

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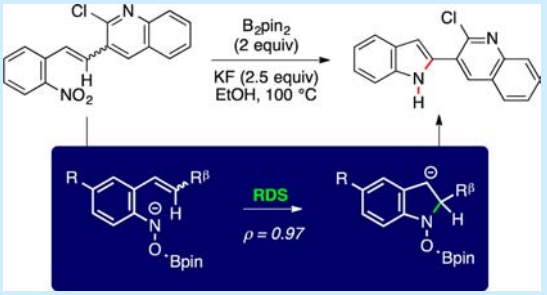
Supporting Information

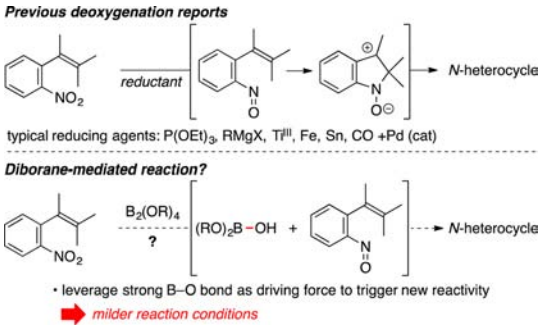
ABSTRACT: A mild, transition metal-free, diborane-mediated deoxygenation of nitro groups was discovered that in situ generates nitrosoarene reactive intermediates. This new reactivity mode of B_2pin_2 was leveraged to construct indoles from *o*-nitrostyrenes through a reductive-cyclization reaction that exhibits a Hammett ρ-value of +0.97 relative to σ_{para} values. Our new deoxygenation reaction is efficient, practical, and scaleable, enabling access to a broad range of indoles.



The construction of carbon−nitrogen bonds by unlocking the reactivity embedded in readily available, stable nitroarenes continues to inspire synthetic chemists because of the ubiquity of the C−NAr bond in bioactive small molecules, agrochemicals, and electronic materials.[1,2] Many of these methods have been aimed creating the indole structural motif and have eased the synthesis of this important and privileged scaffold. Because of their widespread availability, nitroarenes have received significant attention as the reactive nitrogen precursor in these transformations. The nitrosoarene can be accessed from the nitro group by exposing it to a range of different reductants.[3−8] Phosphite reagents were the first reducing agents discovered,[3] and Grignard,[4] iron,[5] zinc,[6] and titanium(III) reagents[7] or carbon monoxide in combination with a palladium catalyst have emerged as alternate methods.[8] While these methods have eased the synthesis of this important *N*-heterocyclic motif, the often harsh reaction conditions, e.g., high pressures of CO, high temperatures, or strongly basic anhydrous media, limit the functional group tolerance and underscore the necessity for the development of mild conditions to access the nitrosoarene reactive intermediate. In pursuit of this goal, we envisioned that deoxygenation of nitroarenes might be accomplished using a diborane reagent because formation of the B−O bond would provide a strong driving force for the reduction (Scheme 1). Despite diborane's widespread use in organic synthesis,[9,10] its use as a deoxygenation reagent remains underdeveloped and currently limited to removing oxygen from *N*-oxides and carbon dioxide.[11] Herein, we address this gap and report a novel and practical B_2pin_2-mediated transformation of *o*-nitrostyrenes into indoles.

Because of its ready availability, *o*-nitrocinnamic acid (**1a**) was chosen as the test substrate for the optimization study (Table S1, see the Supporting Information).[12]

Scheme 1. Development of Mild Deoxygenation Conditions To Access Nitrosoarenes from Nitroarenes



After careful screening using commercially available *o*-nitrocinnamic acid **1a** as the nitrostyrene, the optimized condition eventually emerged as 1 equiv of **1a** with 2 equiv of B_2pin_2 with 2.5 equiv of KF as base in EtOH at 100 °C. Changing the identity of the base or diborane had deleterious effect on the success of the reaction.[12] Using these conditions, the scope and limitations of this transformation were explored (Table 1). First, we demonstrated that our reaction could be performed on a gram-scale without significant reduction in yield by simply increasing the reaction time from 12 to 16 h (entry 1). Next, the effect of changing the substituents on the aromatic ring of the *o*-nitrocinnamic acid was investigated. With the exception of an R^1-dimethylamino group, all other electron-releasing and electron-withdrawing R^1 and R^2 groups were well tolerated in our transformation to produce indoles **2a−j** (entries 2−10). The

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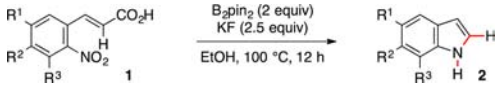
Table 1. Examination of the Scope and Limitations of Indole Formation



entry	#	R^1	R^2	R^3	2 yield, %[a]
1	a	H	H	H	**2a**, 95 (86)[b]
2	b	Me_2N	H	H	**2b**, 40
3	c	MeO	H	H	**2c**, 70
4	d	Me	H	H	**2d**, 84
5	e	F	H	H	**2e**, 85
6	f	Cl	H	H	**2f**, 78
7	g	H	F	H	**2g**, 72
8	h	H	Cl	H	**2h**, 86
9	i	H	Br	H	**2i**, 65
10	j	H	MeO_2S	H	**2j**, 62
11	k	H	H	Me	**2k**, 25
12	l	H	H	Cl	**2l**, trace

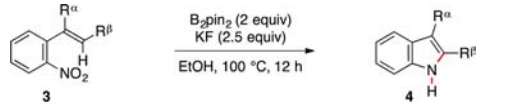
[a]Isolated after silica gel chromatography. [b]10 mmol of **1a** used; 16 h reaction time.

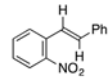
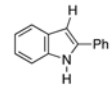
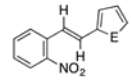
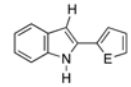
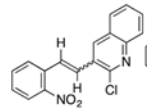
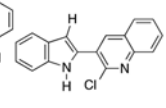
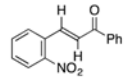
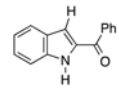
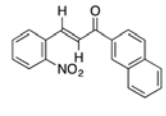
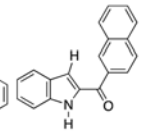
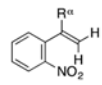
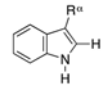
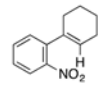
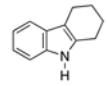
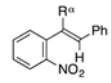
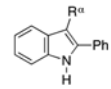
mildness of our transformation was demonstrated using nitroarenes bearing halo and sulfonyl groups, which were transformed into indoles without competing reduction of these sensitive functionalities. In contrast to traditional Fischer indole processes, which can afford a mixture of 4- and 6-substituted indole isomers,[13] our reductive-cyclization reaction produces only 6-substituted indoles from nitroarenes **1g−j** as single regioisomers (entries 7−10). 7-Substituted indoles, however, were formed in lower conversions, suggesting that the B_2pin_2-mediated deoxygenation is sensitive to the steric environment of the nitro group (entries 11 and 12).

Next, changing the identity of the 2-alkenyl unit was investigated to establish the generality of our B_2pin_2-mediated deoxygenation of nitroarenes (Table 2). To our delight, we found that a broad range of nitrostyrenes could be converted into indoles. The β-carboxylic acid substituent could be swapped with a β-aryl or β-heteroaryl substituent to access 2-substituted indoles **4a−d** (entries 1−4). Even the presence of a Lewis basic β-quinoline did not adversely affect the yield of the transformation (entry 4). *o*-Nitrochalcones could also be transformed into indoles using our method without competing quinoline formation, although aprotic reduction conditions were required to obtain the highest yields (entries 5 and 6). α-Substituted nitrostyrenes were subsequently examined (entries 7−9). In addition to α-phenyl, substrates bearing α-benzyl or α-ester groups were readily converted into 3-substituted indoles. Finally, we examined α,β-disubstituted nitrostyrenes as potential substrates (entries 10−14). In addition to α-phenyl and α-alkyl substituents, α-cyano- and α-ester-substituted nitrostyrenes were smoothly converted into 2,3-disubstituted indoles. Together with the substrates in Table 2, we believe these results illustrate that the mildness of the B_2pin_2-mediated deoxygenation reaction leads to a practical and general process for indole formation.

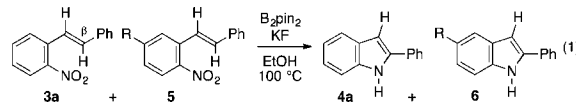
To provide insight into the mechanism of indole formation, a series of intermolecular competition experiments were performed and correlated to the Hammett equation (eq 1, Figure 1). While modifying the electronic nature of the β-aryl group did not affect the relative rate of the reaction,[14] the electronic nature of the R substituent in nitroarene **5** impacted the rate of indole formation.

Table 2. Investigation of the *o*-Alkenyl Effect on Indole Formation



entry	#	nitrostyrene	indole	yield, %[a]
1	a			**4a**, 71
2	b			**4b**, 80, E = O
3	c			**4c**, 72, E = S
4	d			**4d**, 61
5[b]	e			**4e**, 72
6[b]	f			**4f**, 71
7	g			**4g**, 72, R^α =Ph
8	h			**4h**, 72, R^α = Bn
9	i			**4i**, 95, R^α = CO_2Et
10	j			**4j**, 54
11	k			**4k**, 65, R^α= Me
12	l			**4l**, 72, R^α = Ph
13	m			**4m**, 83, R^α = CO_2Et
14	n			**4n**, 76, R^α = CN

[a]Isolated after silica gel chromatography. [b]B_2pin_2 (2 equiv), Na_2CO_3 (2.5 equiv), MeOH, 100 °C, 12 h.



We found that electron-deficient substrates reacted faster than more electron-rich substrates. Our data contrasts with other common reductive-cyclization reactions of nitroarenes in which electron-rich substrates react faster to imply that differently charged reactive intermediates are being formed in the mechanism.[3b,7,15] The difference in the rate of **5** was examined using the Hammett equation, and the best linear correlation was obtained using σ_{para} values.[16,17] The positive ρ-value of 0.97 suggests negative charge buildup during or before the rate-limiting step of *N*-heterocycle formation.[18]

Together with inability of the β-aryl group to affect the rate of the reaction, this data suggests that the reaction occurs first at the nitro group of nitroarene and not the *o*-alkenyl substituent.

Several other competition experiments were performed to examine the role of the *o*-alkenyl substituent in the mechanism

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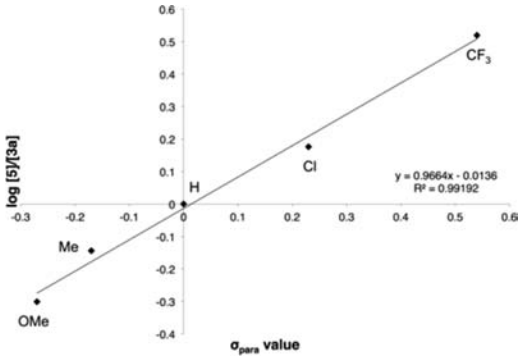
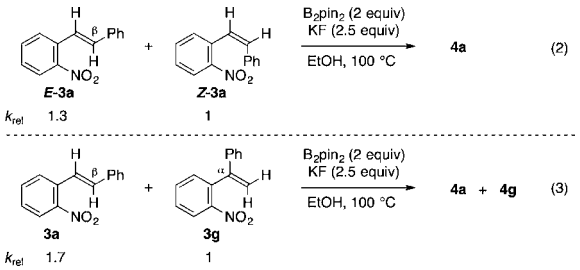


Figure 1. Intermolecular Hammett analysis of B_2pin_2-mediated indole formation.

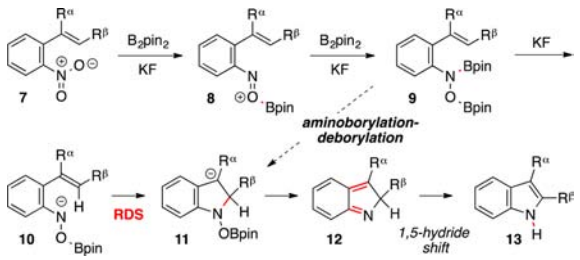
(eqs 2 and 3). While the electronic nature of the β-aryl substituent did not affect the rate of the reaction, changing the steric



environment at the β-position attenuated the rate: *E*-nitrostilbene **3a** was found to react 1.3 times faster than *Z*-nitrostilbene.[19] The position of the phenyl group on the *o*-alkenyl substituent also affected the relative rate of the reductive cyclization. We found that α-phenylnitrostyrene **3g** was converted to product nearly half as fast as *E*-nitrostilbene. Together with the Hammett correlation study, these competition experiments suggest that the *o*-alkenyl substituent is involved in the rate-determining step and that a negative or partial negative charge is generated that can delocalize into the π-system of the nitroarene portion of the substrate.

To accommodate these data, our mechanistic hypothesis is that indole formation proceeds through negatively charged reactive intermediates (Scheme 2).[20] Diborane-mediated deoxygenation

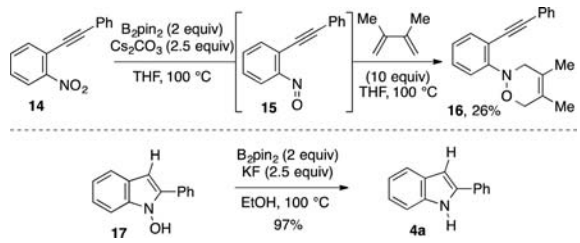
Scheme 2. Possible Mechanism for B_2pin-Mediated Indole Formation



of *o*-nitrostyrene **7** generates nitrosoarene borane **8** and a borate anion.[11c,21,22] Reaction with a second equivalent of B_2pin_2 produces **9**; KF-mediated deboronation produces nitrosyl anion **10**.[22c,23] Cyclization with the *o*-alkenyl substituent could occur through a 6π-electron-5-atom electrocyclization or an unfavorable 5-*endo*-*trig*-type cyclization. Computational studies by Houk and Davies into indole formation from nitrosoarenes concluded that cyclization occurred through a 6-electron-5-atom electrocyclization.[24] The resulting C3 benzyl anion **11** then eliminates OBpin to produce 2*H*-indole **12**. A 1,5-hydride shift then produces the indole product.[25] Alternatively, aminoboration of the *o*-alkenyl group could furnish **11** after deborylation of the C3-Bpin. Aminoboration, however, has only been reported for polarized carbon−heteroatom π-bonds or carbon−carbon triple bonds.[26] Our competition experiments suggest that the rate-determining step of *N*-heterocycle formation is the cyclization step because the substrates that reacted faster were either less sterically congested at the β-position or contained electron-withdrawing substituents on the nitroarene.

Additional experiments were performed to provide more insight into the identity of the reactive intermediates (Scheme 3).

Scheme 3. Attempted Interception of Potential Reactive Intermediates.



First, trapping of the putative nitrosoarene intermediate by 2,3-butadiene was attempted. While no oxazirine was formed upon addition of the diene to *o*-nitrostyrenes, the nitrosoarene could be intercepted from nitroarene **14** to produce **16** in 26% if aprotic reduction conditions were used. Second, *N*-hydroxyindole **17** could be deoxygenated to produce 2-phenylindole **4a** upon exposure to B_2pin_2 and KF. In the absence of the diborane, only partial deoxygenation occurred.

In conclusion, we have shown that the combination of B_2pin_2 and KF mildly converts *o*-nitrostyrenes into indoles. Our data suggest that this transformation is mechanistically distinct from existing reductive-cyclization reactions because it occurs through negatively charged reactive intermediates. Our future experiments are aimed at further investigating the mechanism of this transformation as well as extending this new reactivity to the synthesis of complex *N*-heterocycles from nitroarenes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01934.

Experimental procedures; spectroscopic and analytical data for the products (PDF)

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Notes

The authors declare no competing financial interest.

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