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Graphical Abstract

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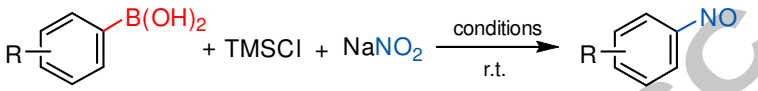

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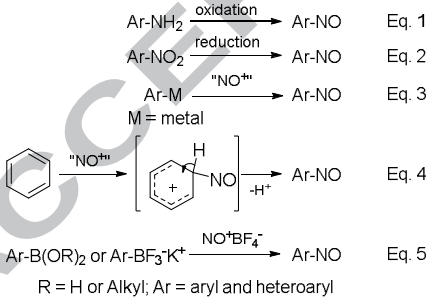
ABSTRACT

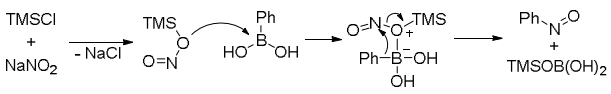
Nitroso compounds are versatile reagents in synthetic organic chemistry. Herein, we disclose a feasible protocol for the *ipso*-nitrosation of aryl boronic acids using chlorotrimethylsilane-sodium nitrite unison as nitrosation reagent system.

Bearing a lone pair of electrons on nitrogen and a highly polarized N-O double bond, nitroso compounds can act both as nucleophiles and electrophiles. Such dually reactive nature allows nitroso compounds to participate in many chemical transformations,[1] such as ene reactions,[2] nitroso aldol reactions,[3] coupling reactions with alkynes[4] and amines,[5] and Grignard reactions.[6] Moreover, nitroso compounds have been exploited in



Scheme 1. Synthetic routes towards nitrosoarenes

various cycloaddition reactions[7] and redox reactions.[8,9] Apart from these synthetic utilities, nitrosobenzenes have also been utilized as radical scavengers,[10] antioxidants in lubricating oil,[11] metal coordinating agents,[12] and antiviral compounds.[13] Although nitroso compounds have been widely utilized, facile synthetic approach towards these compounds are still limited. Up to date, several methods have been developed for aromatic nitrosoarene synthesis, including oxidation of aniline derivatives (Scheme 1, Eq. 1), reduction of nitroarenes (Scheme 1, Eq. 2), and electrophilic nitrosation of aryl metallic compounds (Scheme 1, Eq. 3).[14,15] Direct nitrosation of arenes can also be achieved using nitrosonium salts (NO^+X^-)[16] through a Wheland intermediate ($Ar(H)NO^+$) (Scheme 1, Eq. 4).[17] In addition to nitrosonium salts, other nitrosating agents, such as alkyl nitrites,[18] have also been utilized. Despite the fact that many nitrosoarenes have been obtained via the above mentioned methods, these methods remain disadvantaged in some aspects, such as substrate scope, regioselectivity, or the availability of relevant reagents. Recently, Molander and co-worker disclosed the facile *ipso*-nitrosation of aryl and heteroaryltrifluoroborates as well as arylboronic acid and esters using nitrosonium tetrafluoroborate ($NO^+BF_4^-$), which demonstrates remarkable selectivity and substrate scope (Scheme 1, Eq. 5).[19] To seek for an alternative synthetic protocol exploiting readily available nitrosating reagents, we describe the *ipso*-nitrosation reaction of arylboronic acids with sodium nitrite and chlorotrimethylsilane.



Scheme 2. Proposed mechanism of *ipso*-nitrosation of phenylboronic acid with $NaNO_2$ and TMSCl.

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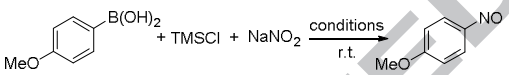
We previously reported the *ipso*-nitration of arylboronic acids using TMSCl and nitrate salts,[20] which allowed the in situ generation of the nitrating species $TMSONO_2$. Parallel to this work, Yamamoto et al. recently showed that in situ generated R_3SiONO could serve as an effective nitrosating reagent to react with silyl enol ethers.[21] On the basis of these reports, we envisioned that *ipso*-nitrosation of arylboronic acids could be achieved using $NaNO_2$-TMSCl system. We began our investigation with 4-methoxyphenylboronic acid (4-$MeOPhB(OH)_2$), which was expected to possess enhanced reactivity due to the electron-donating MeO- group. The reaction was performed by adding 4-$MeOPhB(OH)_2$ (1.0 equiv, 93% boroxine content, determined by ^1H NMR)[22] to a stirred mixture of $NaNO_2$ (2.2 equiv) and TMSCl (2.2 equiv) in anhydrous dichloromethane under argon at room temperature. GC-MS analysis of the reaction mixture did not show any detectable progress even after stirring for 72 h (Table 1, Entry 1). This unsuccessful result was probably due to the low ionic dissociation constant of sodium nitrite in dichloromethane. Further investigation was thus carried out under similar reaction conditions with the addition of 0.5 eq. of water (Table 1, Entry 2). GC-MS and TLC analysis of the reaction mixture indicated the formation of 4-methoxynitrosobenzene and the complete consumption of 4-$MeOPhB(OH)_2$ after 3 h, confirming the crucial role of water. Additional optimization revealed that the reaction could also be promoted with moisture in air, thereby considerably streamlining the operation (Table 1, Entry 3). With these reaction conditions in hand, further exploration was focused on solvent effects. Similar to the nitration reactions using TMSCl and $NaNO_3$,[20] chlorinated solvents were generally suitable for the present reaction (Table 1, Entries 4 and 5), whereas highly polar/coordinating solvents generally led to inferior results (Table 1, Entries 6-8).

Table 1. Optimization of reaction conditions[a]

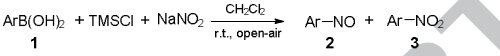


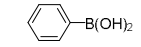
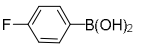
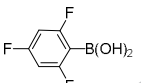
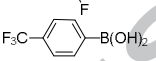
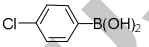
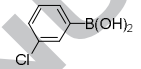
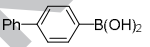
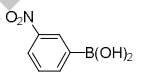
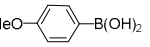
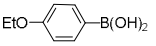
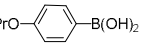
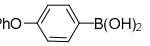
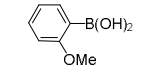
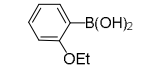
entry	solvent/conditions	time (h)	yield (%)
1	CH_2Cl_2 (dry, argon)	72	0[b]
2	CH_2Cl_2 (0.5 eq. H_2O, argon)	3	65[a]
3	CH_2Cl_2	3	72[a]
4	$CHCl_3$	6	66[a]
5	ClC_2H_4Cl	4	44[a]
6	CH_3CN	72	<5[b]
7	THF	72	0[b]
8	DMF	72	0[b]

[a]Isolated yield; [b]determined by GC-MS analysis without calibration.

With the optimized reaction conditions in hand, we examined the scope of the protocol. As shown in Table 2, although 2,4,6-trifluorophenylboronic acid and 4-phenylphenylboronic acid were inert under the reaction conditions, most arylboronic acids could participate in the reaction. It was found that 4-alkoxy- and 4-phenoxyboronic acids underwent the reaction smoothly to afford the corresponding nitrosoarenes in both high yields and good chemoselectivities (Table 2, Entries 9-12). Noticeably, although arylboronic acids bearing electron-withdrawing substituents also participated in the reaction, nitroarenes were obtained as the major products (Table 2, Entries 1, 4-6, 8, 14). In general, the amount of nitro products was found to decrease with the increase of the electron donating ability of the substituents (through resonance effects). Despite the fact that 2-alkoxy substituted phenylboronic acids are also considered to be "electron-rich", relatively lower yields and poor chemoselectivities were obtained with these substrates (Table 2, Entries 13 and 14), implying that the inductive effect of oxygen may also play a pivotal role in reaction yield. Experimental procedure and the spectral data of the isolated nitroso products are given in the reference section.[25]

Table 2. *ipso*-Nitrosation of arylboronic acids[a]

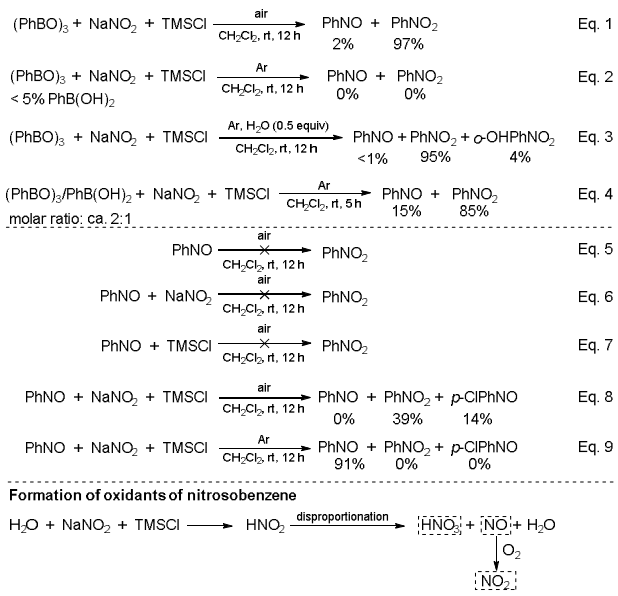


Entry	Substrate	Conversion (%)[b]	Time (h)	Yield (%)[b] Ar–NO	Yield (%)[b] Ar–NO_2
1		>99	12	2	97
2		>99	12	59	41
3		0	12	-	-
4		>99	12	10	85
5		>99	12	14	65
6		>99	12	28	64
7		0	12	0	0
8		>99	12	0	95
9		>99	2	96(72)[c]	1
10		>99	2	87(48)[c]	12
11		>99	2	94(58)[c]	1
12		>99	4	60(52)[c]	36
13		>99	12	12	7
14		>99	12	12	38

[a]Reaction conditions: arylboronic acid (0.5 mmol), TMSCl (1.1 mmol) and sodium nitrite (1.1 mmol) in CH_2Cl_2, stirred under air at room temperature; the conversion was determined by GC-MS; [b]conversions and yields were determined by GC and were not calibrated; [c]the numbers in parentheses are isolated yields.

To elucidate the mechanistic aspects of the reaction, a series of control experiments were carried out. As it is known that arylboronic acids can trimerize to form the corresponding boroxines, we determined the composition of two samples of phenylboronic acid (A and B). According to ^1H NMR spectroscopy,[22] Samples A and B contained respectively 95 mol% and 68 mol% triphenylboroxine $(PhBO)_3$. While the *ipso*-substitution reaction with $(PhBO)_3$ (Sample A) proceeded smoothly under open air conditions, the reaction was found to be retarded under argon-protected anhydrous conditions (Scheme 3, eq. 2). By adding 0.5 equiv. of water to the reaction with Sample A (containing 95 mol% $(PhBO)_3$), nitrobenzene was obtained as the major product, thereby suggesting the essential role of water (Scheme 3, Eq. 3). In contrast, using Sample B as the starting material, nitrosobenzene and nitrobenzene were afforded in a ratio of 15:85% in the absence of water and oxygen (Scheme 3,

Eq. 4). The delineated observation could be ascribed to the in situ trimerization of $PhB(OH)_2$, which could release a small amount of water to facilitate the reaction. It is worth mentioning that the necessity of water was also noticed by Molander and co-worker in the reaction between aryltrifluoroborates and sodium nitrite.[19] However, water in Molander's reaction was proposed to allow the formation of tricoordinate boron species from aryltrifluoroborates, which in turn facilitates the nitrosation.



Scheme 3. Mechanistic elucidation of the formation of nitroarenes.

Since nitrobenzene was obtained as a major product even under argon atmosphere, dioxygen (O_2) could be excluded as a potential oxidant responsible for the formation of nitrobenzene (Scheme 3, Eq. 2-4). This hypothesis was made further evident by the fact that nitrosobenzene was not oxidized in the presence of TMSCl or $NaNO_2$ under open-air conditions (Scheme 3, Eq. 5-7). On the other hand, although nitrosobenzene was found to convert to nitrobenzene with a mixture of TMSCl and $NaNO_2$ in the presence of air, such a conversion was not observed under inert atmosphere (Scheme 3, Eq. 8 and 9). This result showed that the oxidation of nitrosobenzene originated from a combination of TMSCl, $NaNO_2$ and water which could presumably lead to the formation of HNO_2. As HNO_2 can readily undergo disproportionation to render HNO_3 and NO,[23] the in situ oxidation of nitrosobenzene can be ascribed to the presence of these two species.[24] Noticeably, the in situ oxidation of nitrosoarenes was also observed in the reaction between aryltrifluoroborates and $NO^+BF_4^-$, indicating the intrinsic lability of nitrosoarenes under direct nitrosation reaction conditions.

In conclusion, we have demonstrated that the combination of chlorotrimethylsilane-nitrite salt could be used as a viable system for the *ipso*-nitrosation of electron-rich arylboronic acids. Arylboronic acids bearing electron-withdrawing groups, although undergo *ipso*-functionalization, generally lead to nitration products instead of desired nitroso compounds. This observation is similar to many other direct nitrosation reactions, in which nitrosoarenes are in situ oxidized. Attempts to tackle this problem are currently under investigation in our laboratory.

Acknowledgment

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25. *Experimental:* Unless otherwise mentioned, all the chemicals were purchased from commercial sources and used without further purification. Silica gel chromatography was performed to isolate the products using Biotage SNAP Cartridges KP-Sil 10 g or 25 g with hexane-dichloromethane, dichloromethane or dichloromethane-ethyl acetate solvent systems as eluent. ^{1}H and ^{13}C spectra were recorded on 400 MHz Varian NMR spectrometer. ^{1}H NMR chemical shifts were determined relative to residual solvent peak of $CDCl_3$ (at 7.26 ppm). ^{13}C NMR shifts were determined relative to the solvent peak of $CDCl_3$ (at 77.16 ppm). Mass spectra were recorded on spectrometer in the ESI mode. The yields determined by GC-MS analysis were not calibrated with internal standard.

General procedure for the ipso-nitrosation of arylboronic acids with $NaNO_2$ and TMSCl: To CH_2Cl_2 (5 mL) in a 15 mL pressure tube were added $NaNO_2$ (76 mg, 1.1 mmol) and TMSCl (120 mg, 1.1 mmol) with stirring. Arylboronic acid (0.5 mmol) was added after 5 min. The tube was purged with argon after the color change (15-60 min) and continued to stir. The reaction was monitored by TLC (CH_2Cl_2/ethyl acetate = 6:4) and GC. After TLC showed the complete consumption of the arylboronic acid, the mixture was filtered. The filtrate was dried over Na_2SO_4 and the volatile materials were evaporated under reduced pressure. The crude product was purified by column chromatography using CH_2Cl_2 as eluent.

1-Methoxy-4-nitrosobenzene: Green-blue oil, 72% yield. The product was contaminated with 5 mol% 1-methoxy-4-nitrobenzene as indicated by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.92 (d, br, ^3J = 7.9 Hz, 2H), 7.03 (d, ^3J = 9.1 Hz, 2H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 165.0, 164.0, 124.5 (br), 113.9, 56.0.

1-Ethoxy-4-nitrosobenzene: Green-blue oil, 48% yield. The product was contaminated with 3 mol% 1-ethoxy-4-nitrobenzene as indicated by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.89 (d, br, ^3J = 6.8 Hz, 2H), 6.99 (d, ^3J = 9.2 Hz, 2H), 4.17 (q, ^3J = 7.0 Hz, 2H), 1.46 (t, ^3J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 165.1, 164.0, 124.5 (br), 114.2, 64.5, 14.6.

1-Isopropoxy-4-nitrosobenzene: Green-blue oil, 58% yield. The product was contaminated with 9 mol% 1-isopropoxy-4-nitrobenzene as indicated by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.89 (br, 2H), 6.98 (d, ^3J = 7.9 Hz, 2H), 4.73 (hept, ^3J = 6.4 Hz, 6H), 1.41 (d, ^3J = 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 164.4, 163.9, 124.5 (br), 115.0, 71.0, 21.9.

1-Phenoxy-4-nitrosobenzene: Green-blue oil, 52% yield. The product was found to be contaminated with 15 mol% 1-phenoxy-4-nitrobenzene as indicated by ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.90 (d, br, ^3J = 7.9 Hz, 2H), 7.45 (d, ^3J = 7.6 Hz, 2H), 7.27 (d, ^3J = 7.4 Hz, 1H), 7.12 (d, ^3J = 8.7 Hz, 2H), 7.08 (d, ^3J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 164.3, 163.8, 154.5, 130.3, 125.5, 125.0 (br), 120.8, 116.7.