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Catalyst free, base free microwave irradiated synthesis of aryl nitrites from potassium aryltrifluoroborates and bismuth nitrate

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Abstract

A mixture of bismuth nitrate pentahydrate and potassium aryltrifluoroborate in toluene under microwave heating at 120 °C for 20 min provides an interesting and mild reaction protocol for the synthesis of aryl nitrite. The conversion to aryl nitrites from aryltrifluoroborates without transition metal catalyst and base in high yields is remarkable.

Keywords

Bismuth nitrate as nitrite source; Catalyst free reaction; Potassium aryltrifluoroborates; Microwave

Nitration of aromatic compounds is an extensively studied field of organic synthesis.¹ Nitro group addition provides important physical and chemical properties to target compounds. The metabolism of aromatic amines and aromatic nitro compounds is effectively interconnected. So, it is important to see a new development in aryl nitrite synthesis. Compared to classical strong conditions for the nitration process, a new milder technique of nitration of aromatic compounds by cross-coupling of aryl halides with sodium nitrite and potassium nitrite has been developed recently.² Potassium organotrifluoroborates have already proven to be unique boron reagents for organic transformations. Molander has pioneered several new developments using organotrifluoroborate salts.³ We also use organotrifluoroborates in various organic transformations.⁴ Very recently, we reported the palladium catalyzed cross-coupling of potassium styryl- and aryltrifluoroborates with sodium nitrite to give the corresponding styryl-, and aryl nitrites.⁵ In this work, we found bismuth nitrate is a good nitrite source that formed aryl nitrites when microwaved with potassium aryltrifluoroborates without adding transition metal catalyst and base (Scheme 1).

Our report of PdCl₂(d⁴bpf)-catalyzed cross-coupling reaction of styryl- and aryltrifluoroborates with sodium nitrite in the presence of NaH₂PO₄·H₂O encouraged us to seek the effect of bismuth nitrate for a similar study. Under those conditions, however, reaction failed. Bismuth nitrate arrives from the vendor in hydrated form: Bi(NO₃)₃·5H₂O. To counterbalance the hydrated nature of the bismuth nitrate, we swapped the hydrated base

with an anhydrous variant: NaH_2PO_4 , and found an interesting change (Scheme 2). 1:6 ratio of styryltrifluoroborate and bismuth nitrate pentahydrate showed the predicted styryl nitrite without homocoupling product, but compared to the organonitrite reaction process run with sodium nitrite⁵, this process is sluggish and reproducibility is also low. Concurrently, when we applied bismuth nitrate pentahydrate with potassium *p*-tolyltrifluoroborate, clean transformation to *p*-tolyl nitrite was observed (Scheme 3). Many control experiments were run to optimize reaction conditions, and the best conditions for complete conversion to *p*-tolyl nitrite were found to be one equivalent of *p*-tolyltrifluoroborate and one equivalent of bismuth nitrate in toluene microwaved at 120 °C for 20 min (Table 1). *p*-Tolyl nitrite **3a** from *p*-tolyltrifluoroborate **1a** and bismuth nitrate pentahydrate **2** is a representative procedure (Table 1, entry 1). To an oven dried reaction tube with magnetic stirrer bar were added *p*-tolyltrifluoroborate (49.4 mg, 0.25 mmol), bismuth nitrate (121.3 mg 0.25 mmol), and anhydrous toluene (2.0 mL) under an inert atmosphere of Argon, followed by insertion of the reaction tube into the microwave and heating at 120 °C for 20 min. The resulting reaction product was filtered through a sintered funnel with a Celite bed using 50 mL ethyl acetate. The product solution was analyzed by GC-MS, evaporated, and purified by preparative TLC. Mass spectra, ¹H NMR, and ¹³C NMR confirmed the product. LRMS: Calculated for $\text{C}_7\text{H}_7\text{NO}_2$ M^+ 137. Found: 137. ¹H NMR (Acetone-*d*₆, 300 MHz) δ 8.14–7.47 (m, 4H), 2.47 (s, 3H); ¹³C NMR (Acetone-*d*₆, 75.5 MHz) δ 147.2, 131.1, 130.5, 129.8, 124.2, 21.5. Reactions were carried out via standard dry system under an inert atmosphere of Argon or in open air. Both systems were equally effective but the Argon atmosphere condition provided cleaner looking result. All potassium aryltrifluoroborates shown in Table 1 were prepared from the corresponding arylboronic acids by applying the known method.⁶

The Prokash group used a mixture of silver nitrate salt and chloromethylsilane as nitrating agent and produced nitroarenes when treated with arylboronic acid at room temperature for 30–72 h in poor to moderate yields (20–98%).⁷ In this Letter the nitration process is mild and yields are high. Bismuth nitrate pentahydrate is a successful Lewis acid and provides a nitro group when reacted with potassium aryltrifluoroborate as its Lewis base. The high electron affinity of bismuth toward fluorine enhances the nitration process.⁸ In case of 4-methoxyaryltrifluoroborate, yield was low (Table 1, entry 2). No nitration product was observed when 4-pyridinyltrifluoroborate was employed as arylating agent (Table 1, entry 9). Most likely, the basic nature of the pyridine moiety is competing with the trifluoroborate moiety of aryltrifluoroborate. A proposed mechanism that accounts for this nitration is portrayed in Scheme 4.

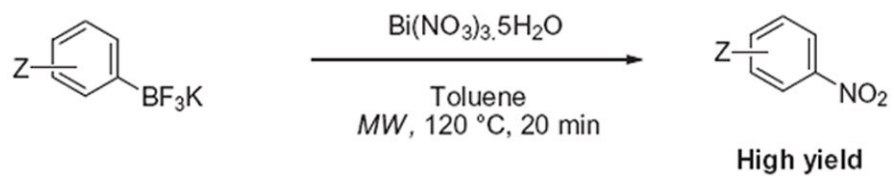
The microwave heated minute reaction between potassium aryltrifluoroborates and bismuth nitrate is a new process and a clear improvement on existing nitration techniques. In summary, we find a new application of potassium aryltrifluoroborates with bismuth nitrate and present an efficient process for the synthesis of aryl nitrites without catalyst and base. Application of this nitration process in natural product synthesis and in highly substituted aryltrifluoroborates is currently under investigation.

Acknowledgments

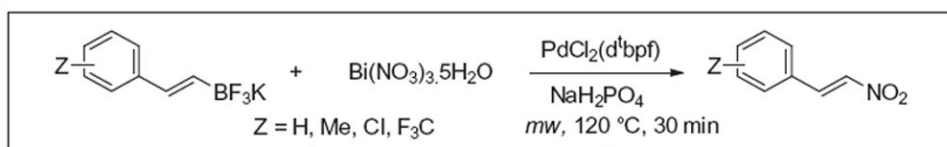
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- Electron affinity of Bi, Si, Sn, and F are 91.2 KJ/mol, 133.6 KJ/mol, 107.3 KJ/mole, and 329 KJ/mol, respectively; electronegativity Bi, Si, Sn, and F are 2.02, 1.9, 1.96, and 3.98 respectively; valence of Bi, Si, Sn, and F are 5, 4, 4, and 1, respectively. Norman NC. *Chemistry of Arsenic, Antimony and Bismuth*. Springer publisher 1998



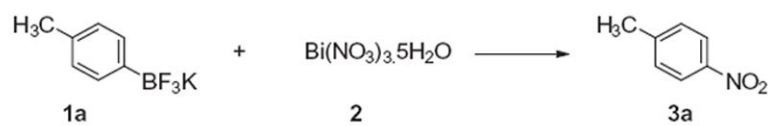
Scheme 1.

		
Styryltrifluoroborate	Bi(NO ₃) ₃ ·5H ₂ O	Styryl Nitrite
1	1	None
1	4	None ^a
1	6	Nitrite product observed in GC-MS

Scheme 2.

Styrylnitrites from cross-coupling of styryltrifluoroborates and Bi(NO₃)₃·5H₂O in toluene.

^aReported condition with base NaH₂PO₄ (*Tetrahedron Lett.* **2013**, *54*, 1141.)

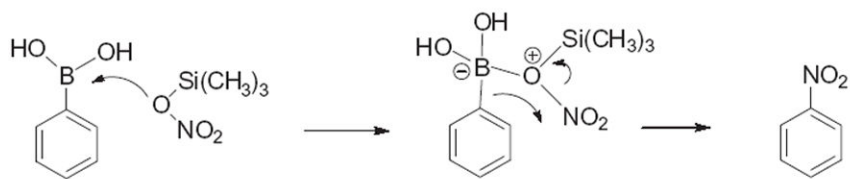


Run	Ratio 1a : 2	Catalyst	Base	Toluene ^a
1	1 : 4	PdCl ₂ (d ^t bpf)	NaH ₂ PO ₄	4 mL
2	1 : 6	PdCl ₂ (d ^t bpf)	NaH ₂ PO ₄	4 mL
3	1 : 1	PdCl ₂ (d ^t bpf)	NaH ₂ PO ₄	4 mL
4	1 : 1	PdCl ₂ (d ^t bpf)	NaH ₂ PO ₄	2 mL
5	1 : 1	None	NaH ₂ PO ₄	2 mL
6	1 : 1	None	None	2 mL
7	1 : 1	None	None	8 mL ^b

Scheme 3.

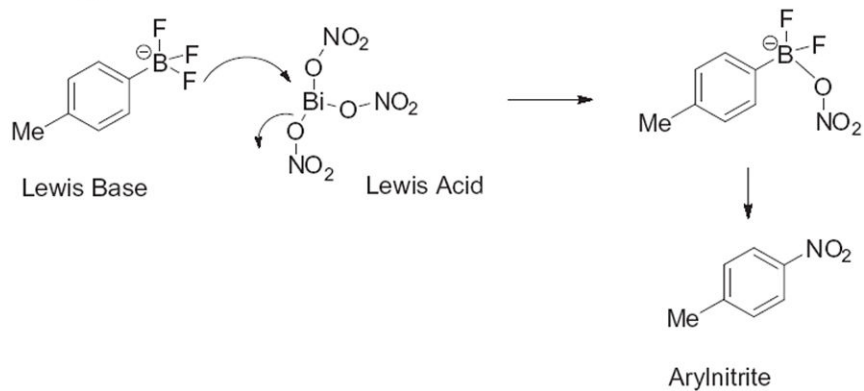
^a0.25 mmol scale. ^b1.0 mmol scale. Best condition was found in **Run 6**.

Olah-Prakash



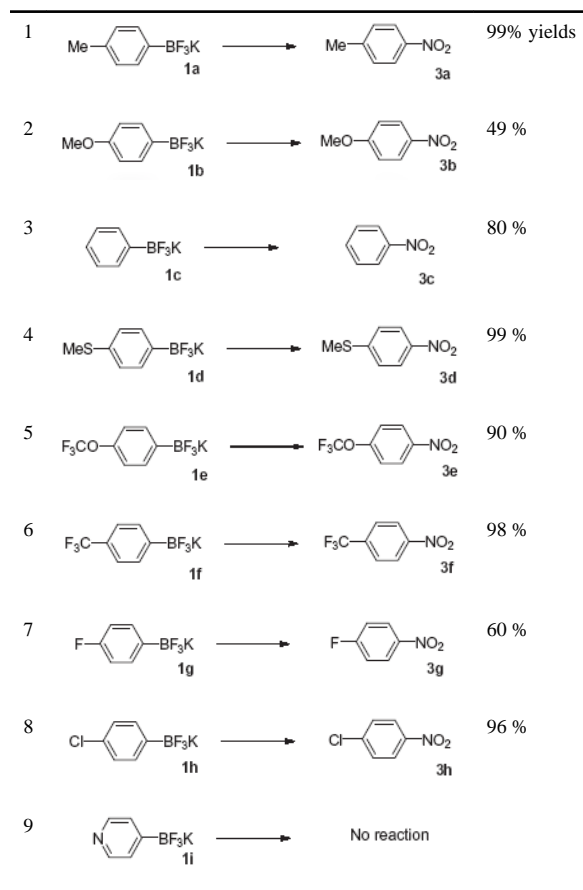
Lewis Acid

Our Approach



Scheme 4.

Table 1

Reaction of aryltrifluoroborates **1** and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ **2** for aryl nitrites **3**^a

^a0.25 mmol of aryltrifluoroborate, 0.25 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, and 2.0 mL of toluene microwaved at 120 °C for 20 min. Preparative TLC technique was used for purification.