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Iodination of organotrifluoroborates: synthesis of vinyl and alkynyl iodides

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Abstract—Vinyl- and alkynyltrifluoroborates are rapidly converted to vinyl and alkynyl iodides under mild conditions using sodium iodide in the presence of chloramine-T. The reaction is stereospecific and proceeds in excellent yield.

Vinyl- and alkynyl iodides are versatile reagents in organic synthesis.[1] Applications include palladium catalyzed coupling reactions[2] and free-radical chemistry.[3] They are also important in medicinal and pharmaceutical research.[4] Organometallic reagents are convenient precursors for the preparation of vinyl- and alkynyl iodides but their use is somewhat restricted due to the high reactivity and toxic properties of many of the starting materials.[1,5] Vinylboronic acids and esters can be iodinated using iodine monochloride or sodium iodide in the presence of an oxidizing agent but the reactions generally require the addition of sodium hydroxide.[6,7,8]

Potassium organotrifluoroborates are more nucleophilic than the corresponding boronic acids. They are also air and moisture stable and can be synthesized readily from the corresponding boronic acids by addition of KHF_2.[9] Studies indicate that trifluoroborate salts have many advantages when compared to boronic acids.[10] We recently reported that potassium aryltrifluoroborates are rapidly converted to aryl iodides under mild conditions using sodium iodide in the presence of chloroamine-T. We wish to report that vinyl- and alkynyltrifluoroborates can be iodinated under similar conditions in excellent yields.[11] (Fig. 1)

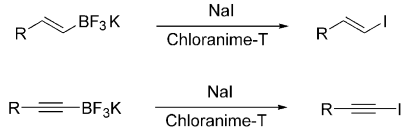

Figure 1.

The iodination reactions are carried out using potassium vinyl- and alkynyltrifluoroborate in 50% aqueous tetrahydrofuran in the presence of chloramine-T.[12] The method tolerates a wide variety of functional groups and affords the products in excellent yields. Tables 1 and 2 contain the results of the study. The stereochemistry of the alkene is retained, which provides ready access to a variety of *E* and *Z* vinyl iodides.

The reaction is also suitable for preparing 1-iodoalkynes (Table 2). To our knowledge, this is the first report of alkynylboron derivatives being used as precursors to iodoalkynes.

In conclusion, we report a convenient procedure for preparing vinyl- and alkynyl iodides from potassium vinyl- and alkynyltrifluoroborates.

Acknowledgements

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Keywords: Iodination; Organotrifluoroborates; Vinyl iodides; Alkynyl iodides.

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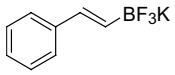
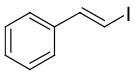
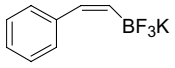
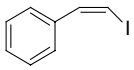
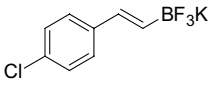
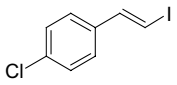
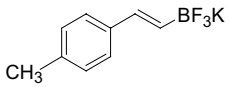
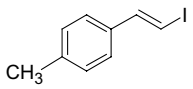
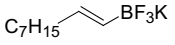
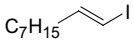
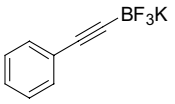
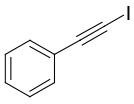
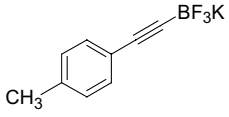
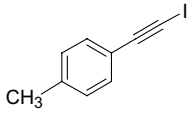
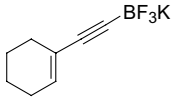
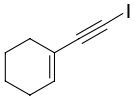
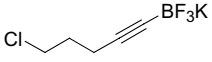
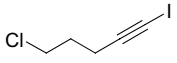
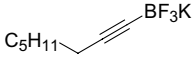
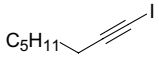
Table 1. The synthesis of vinyl iodides from potassium vinyltrifluoroborates[a,b]

Entry	Substrate	Product	Time (min)	Yield (%)[c]
1			10	95
2			10	92
3			10	90
4			10	92
5			10	91

[a] Reaction conditions: trifluoroborate (1.00 mmol), sodium iodide (1.05 mmol), and chloramine-T (1.00 mmol) in aqueous THF (50%) of room temperature.
[b] All products were characterized ^{1}H, ^{13}C NMR spectroscopy and comparison to authentic samples.
[c] Isolated yield.

Table 2. The synthesis of 1-iodoalkynes from potassium alkynyltrifluoroborates[a,b]

Entry	Substrate	Product	Time (min)	Yield (%)[c]
1			20	96
2			20	93
3			20	94
4			20	94
5			20	95

[a] Reaction conditions: trifluoroborate (1.00 mmol), sodium iodide (1.05 mmol), and chloramine-T (1.00 mmol) in aqueous THF (50%) of room temperature.
[b] All products were characterized ^{1}H, ^{13}C NMR spectroscopy and comparison to authentic samples.
[c] Isolated yield.

References and notes

1. (a) Zweifel, G.; Arzoumanian, H. *J. Am. Chem. Soc.* **1967**, *89*, 5086; (b) Takai, K.; Kuroda, T.; Nakatsukasa, S.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1985**, *26*, 3769; (c) Michael, A.; Rassat, A. *Tetrahedron Lett.* **1999**, *40*, 8579.
2. (a) Damle, S. V.; Seomoon, D.; Lee, P. H. *J. Org. Chem.* **2003**, *68*, 7085; (b) Roush, W. R.; Riva, R. *J. Org. Chem.* **1988**, *53*, 710; (c) Nicolaou, K. C.; Liu, A.; Zeng, Z.; McComb, S. *J. Am. Chem. Soc.* **1992**, *114*, 9279; (d) Nerenberg, J. B.; Hung, D. T.; Somers, P. K.; Schreiber, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 12621.

3. Motherwell, W. B.; Crich, D. *Free Radical Chain Reactions in Organic Synthesis*; Academic: London, 1992; pp 8–9.
4. (a) Jeffrey, T. *J. Chem. Soc., Chem. Commun.* **1988**, 909; (b) Mazaitis, J. K.; Gibson, R. E.; Komai, T.; Eckelman, W. C.; Francis, B.; Reba, R. C. *J. Nucl. Med.* **1980**, *21*, 142; (c) Kabalka, G. W.; Shoup, T. M.; Goodman, M. M. *Nucl. Med. Biol.* **2000**, *27*, 279.
5. (a) Zou, M.; Deng, M. *J. Org. Chem.* **1996**, *61*, 1857; (b) Ochiai, M.; Tsuchimoto, Y.; Hayashi, T. *Tetrahedron Lett.* **2003**, *44*, 5381; (c) Hoshi, M.; Shirakawa, K. *Chem. Commun.* **2002**, 2146.
6. Kabalka, G. W.; Sastry, K. A. R.; Muralidhar, K. *J. Lab. Comp. Radiopharm.* **1982**, 795.
7. (a) Brown, H. C.; Hamaoka, T.; Ravindran, N. *J. Am. Chem. Soc.* **1973**, *95*, 5786; (b) Brown, H. C.; Campbell, J. B. *J. Org. Chem.* **1980**, *45*, 389; (c) Suseela, Y.; Prasad, A. S. B.; Periasamy, M. *J. Chem. Soc., Chem. Comm.* **1990**, 446.
8. (a) Morrill, C.; Grubbs, R. H. *J. Org. Chem.* **2003**, *68*, 6031; (b) Whiting, A.; Stewart, S. K. *Tetrahedron Lett.* **1995**, *36*, 3929.
9. (a) Vedejs, E.; Chapman, R. W.; Fields, S. C.; Lin, S.; Schrimpf, M. R. *J. Org. Chem.* **1995**, *60*, 3020; (b) Petasis, N. A.; Yudin, A. K.; Zavialov, I. A.; Prakash, G. K. S.; Olah, G. A. *Synlett* **1997**, 606; (c) Darses, S.; Genet, J.-P.; Brayer, J.-L.; Demoute, J.-P. *Tetrahedron Lett.* **1997**, *38*, 4393.
10. (a) Darses, S.; Michaud, G.; Genet, J.-P. *Tetrahedron Lett.* **1998**, *39*, 5045; (b) Batey, R. A.; Quach, T. D. *Tetrahedron Lett.* **2001**, *42*, 9099; (c) Molander, G. A.; Ito, T. *Org. Lett.* **2001**, *3*, 393; (d) Molander, G. A.; Biolattp, B. *Org. Lett.* **2002**, *4*, 1867; (e) Pucheault, M.; Darses, S.; Genet, J.-P. *Eur. J. Org. Chem.* **2002**, 3552; (f) Molander, G. A.; Rivero, M. R. *Org. Lett.* **2002**, *4*, 107; (g) Kabalka, G. W.; Venkataiah, B.; Dong, G. *Org. Lett.* **2003**, *5*, 3803.
11. Kabalka, G. W.; Mereddy, A. R. *Tetrahedron Lett.* **2004**, *45*, 243.
12. General procedure: To a solution of potassium vinyl- or alkynyltrifluoroborate (1.00 mmol) in 50% aqueous tetrahydrofuran (5 mL) contained in a round bottomed flask (which was shielded from light), chloramine-T (1.00 mmol) was added followed by sodium iodide (1.05 mmol). The resulting mixture was stirred at room temperature for the required length of time (Tables 1 and 2). After the reaction was complete, 10% aqueous sodium thiosulfate (2 mL) was added to decompose excess iodine. The mixture was extracted with ethyl acetate (3×25 mL), the combined organic extracts washed with water (20 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The product was purified by column chromatography using silica gel (100–200 mesh) and petroleum ether/ethyl acetate as eluent (98:2). The products were identified by comparison of the physical and spectral properties with literature values.