

Boron Trichloride/Tetra-*n*-Butylammonium Iodide: A Mild, Selective Combination Reagent for the Cleavage of Primary Alkyl Aryl Ethers

Paige R. Brooks, Michael C. Wirtz, Michael G. Vetelino, Diane M. Rescek, Graeme F. Woodworth, Bradley P. Morgan, and Jotham W. Coe*

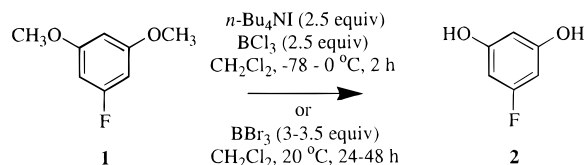
Central Research Division, Pfizer, Inc., Groton, Connecticut 06340

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A number of reagents are routinely used to cleave primary alkyl aryl ethers¹ such as BBr₃,² EtSn/DMF,³ TMSI,⁴ py-HCl,⁵ and HBr/AcOH.^{6,7} Boron-based reagents are particularly versatile for this transformation, as the Lewis acidity of the boron center and the nucleophilic nature of the ligands can be effectively manipulated (e.g., 2-bromo-1,3,2-benzodioxaborole,⁸ 9-Br-BBN,⁹ and Me₂-BBR¹⁰). We report herein that a mixture of BCl₃ and anhydrous *n*-Bu₄NI is a powerful reagent combination for the facile cleavage of primary alkyl aryl ethers at low to ambient temperatures.¹¹ Boron trichloride alone does not remove isolated aryl methyl groups at low temperatures,¹² although it is extremely effective when chelation is possible.¹³ With *n*-Bu₄NI present (1.1 equiv), however, BCl₃ reactivity toward primary alkyl aryl ethers is greatly enhanced. The resulting combination reagent system is mild, generally applicable, and operationally simple, and it can provide results superior to those of BBr₃ for the cleavage of numerous substrates. Further-

more, the combination reagent provides selective dealkylation in certain cases.

A comparative example highlights the reactivity of the BCl₃/*n*-Bu₄NI reagent system. In procedures described by Sun et al.,¹⁴ variously substituted dimethoxyfluorobenzenes (e.g., **1**) were cleaved with BBr₃ (3 equiv/CH₂Cl₂). The reaction typically requires 24–48 h at ambient temperatures, and additional BBr₃ is often required (0.5 equiv) to completely drive the conversion of **1** to **2**.



Using our modified BCl₃/*n*-Bu₄NI procedure, *n*-Bu₄NI (2.5 equiv) and 3,5-dimethoxyfluorobenzene (**1**) in CH₂Cl₂ (0.2 M) are treated with BCl₃ (2.5 equiv, 1 M CH₂Cl₂) at –78 °C and then warmed to 0 °C. Complete conversion to 5-fluororesorcinol (**2**) occurs in 2 h (77% isolated yield).

To determine the generality of the method, we have studied the dealkylation of a variety of substrates. In a typical experiment, a 0.2–0.5 M solution of substrate and *n*-Bu₄NI¹⁵ (1.1 equiv) in anhydrous CH₂Cl₂ is treated with BCl₃ at –78 °C (1 M in CH₂Cl₂). The reaction solution is monitored and then treated as indicated (see Table 1 and the Experimental Section for equivalents, temperature, and time). Aqueous workup and chromatography provide the target phenols.

Methyl-, ethyl-, and benzyl naphthyl ethers are readily cleaved (**3**, **4**, **6**, **7**); however, isopropyl naphthyl ether is stable under these conditions (**5**).^{13f} Severe steric constraints also retard the reaction (**8** vs **9**). Selective cleavage of benzyl ethers in the presence of methyl ethers is achieved (**10**), and methylenedioxy groups are readily cleaved at –78 °C (**11**).^{13d}

Other functionalities are well tolerated¹⁶ but may alter the required BCl₃/substrate stoichiometry. For instance,

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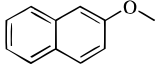
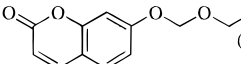
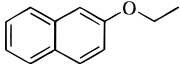
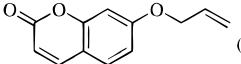
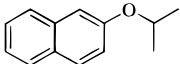
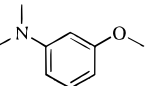
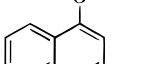
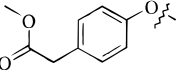
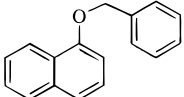
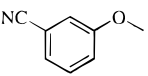
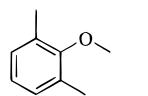
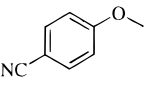
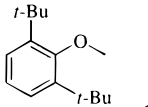
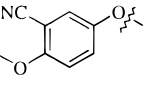
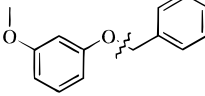
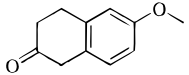
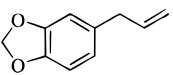
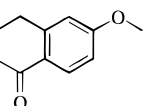
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(16) Unsatisfactory performance of this reagent combination is observed with 1-NH-indoles, nitro aromatics (partial nitro reduction), and some conjugated derivatives, such as 6-methoxytetralone (**20**, methyl stable to conditions, see text). Peculiar results have been observed with 2-bromo-1,3,5-trimethoxybenzene; debromination occurs, instead of ether cleavage and, after workup, provides the parent 1,3,5-trimethoxybenzene.

Table 1. $\text{BCl}_3/n\text{-Bu}_4\text{NI}$ Mediated Primary Alkyl Aryl Ether Cleavage

Compd	Alkyl Aryl Ether	BCl_3 (equiv)	Yield Temp Time	Compd	Alkyl Aryl Ether	BCl_3 (equiv)	Yield Temp Time
3		(1.5 eq.)	96% -78 - 0 °C 1 h	12		(1.5 eq.)	90% -78 °C 1 h
4		(1.5 eq.)	92% -78 - 0 °C 1 h	13		(2.5 eq.)	96% -78 - 20 °C 2 h
5		(1.5 eq.)	N.R. ^a -78 - 20 °C 20 h	14		(2.5 eq.)	95% -78 - 0 °C 1 h
6		(1.5 eq.)	98% -78 - 0 °C 1 h	15		(2.5 eq.) ^b	84% -78 - 20 °C 1 h
7		(1.5 eq.)	90% -78 - 0 °C 1 h	16		(2.5 eq.)	74% -78 - 10 °C 1 h
8		(1.5 eq.)	70% -78 - 20 °C 2 h	17		(2.5 eq.)	70% -78 - 20 °C 2 hr
9		(1.5 eq.)	N.R. ^a -78 - 20 °C 20 h	18		(3.5 eq.)	87% -78 - 20 °C 1 h
10		(1.5 eq.)	64% -78 - 0 °C 1 h	19		(2.5 eq.)	70% -78 - 0 °C 1 h
11		(2.5 eq.)	88% -78 °C 1 h	20		(2.5 eq.)	N.R. ^a -78 - 20 °C 6 hr

^a N.R. (no reaction). ^b With 1.3 equiv of *n*-Bu₄NI (see the Experimental Section).

although 7-ethoxymethoxychromen-2-one (**12**) cleaves readily at -78 °C, the corresponding 7-allyloxychromen-2-one (**13**) requires additional BCl_3 and warming to complete the conversion (2.5 equiv total, 20 °C, 2 h).^{7c} For substrates possessing multiple Lewis base sites, additional BCl_3 will be required to chelate the more basic spectator groups (**13**–**19**). Additionally, the rate of ether cleavage is demonstrably reduced with resonance delocalization by electron-withdrawing groups. Thus, *meta*-positioned target ethers are more rapidly cleaved than *ortho*- or *para*-resonance delocalized ethers. This is successfully exploited in the selective cleavage of the 5-methyl ether of 2,5-dimethoxybenzonitrile (**18**).

As a general rule, 1.5 equiv of BCl_3 is sufficient to effect dealkylation, provided that 1.0 equiv of additional BCl_3 is introduced for each additional basic group.

6-Methoxy-1-tetralone (**20**) is an exception and is not cleaved under these reaction conditions.¹⁷ In this case, resonance interactions sufficiently reduce the basicity of the target ether, rendering complexation with boron impossible.¹⁸

In our view, the $\text{BCl}_3/n\text{-Bu}_4\text{NI}$ reagent combination reactivity is between that of BBr_3 and BI_3 .¹⁹ These vigorous reagents presumably dissociate more readily to provide oxonium ion activation ($\text{ArOR}'\text{BX}_2^+$) and free nucleophilic halide ion (X^-). With the $\text{BCl}_3/n\text{-Bu}_4\text{NI}$ reagent combination, iodide may act as both a stabilizing ligand on boron, favoring formation of a reactive oxonium ion species ($\text{ArOR}'\text{BIX}^+$), and a source of potent nucleophilic iodide.^{20–22} We have found that the reaction does not proceed in the absence of iodide: 3-methoxybenzoni-

(18) An orange complex forms with **20** and *n*-Bu₄NI upon addition of BCl_3 that is stable at 20 °C for >6 h. ¹¹B NMR experiments reveal that a 1/1 mixture of BCl_3 and **20** exhibits one predominant signal at -50.5 ppm (CD_2Cl_2). A 2/1 mixture of BCl_3 and 6-methoxy-1-tetralone **20** exhibits two signals at -50.5 and -12.6 ppm: one is substrate complexed BCl_3 and one is free, uncomplexed BCl_3 . In contrast, isomeric tetralone **19** exhibits multiple complexed ¹¹B NMR signals with both 1 and 2 equiv of BCl_3 ; however, no signal for free BCl_3 is observed at -12.6 ppm. These results suggest that direct boron-oxygen complex formation is a requirement for ether cleavage.

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trile is stable to 2.5 equiv of BCl_3 /1.1 equiv of BnEt_3NCl at 20 °C for 24 h and at 40 °C for 5 h in CH_2Cl_2 . With the $\text{BCl}_3/n\text{-Bu}_4\text{NI}$ reagent combination, this conversion is complete between 0 and 10 °C (<2 h).^{23,24}

The $\text{BCl}_3/n\text{-Bu}_4\text{NI}$ reagent combination adds a powerful option to the methods available for the cleavage of primary alkyl aryl ethers by providing mild, selective ether cleavage at low temperature in short reaction times.²⁵

Experimental Section

Unless otherwise noted, all materials were purchased from commercial sources. Anhydrous CH_2Cl_2 (99.8%), 1 M BCl_3 in CH_2Cl_2 (in Sure/Seal bottles), and $n\text{-Bu}_4\text{NI}$ were handled under a dry nitrogen atmosphere. Thin-layer chromatography was performed with EM separation technology silica gel F_{254} . Silica gel chromatography was carried out with J. T. Baker 40 μm silica gel according to Still's procedure.²⁶ All glassware was flame dried under a dry nitrogen purge, prior to use. ^1H NMR spectra were collected at 400 MHz with residual CHCl_3 as standard (7.26 ppm). ^{13}C NMR spectra (160 MHz) were obtained on a Bruker DMX500 Avance spectrometer using direct detection with a 10 mm broad-band probe. The spectra were acquired at ambient temperatures using 90° pulses, 1.0 s relaxation delay, a sweep width of 500 ppm with 32K points, and 32 scans. The data were collected using either a 1 H decoupling pulse sequence or spin-echo with 20 ms echo time to reduce the broad signal from the NMR tube. A 1 Hz line broadening was used to process the spectra. Chemical shifts were measured in ppm using BCl_3 in CD_2Cl_2 , set to -12 ppm as the external reference. Melting points are uncorrected. All spectroscopic data for known compounds were in complete accord with literature values.

Registry numbers. Substrates: **1**, 52189-63-6; **3**, 93-04-9; **4**, 93-18-5; **5**, 15052-09-2; **6**, 5328-01-8; **7**, 607-58-9; **8**, 1004-66-6; **9**, 1516-95-6; **10**, 21144-16-1; **11**, 94-59-7; **13**, 31005-03-5; **14**, 15799-79-8; **15**, 23786-14-3; **16**, 1527-89-5; **17**, 874-90-8; **18**, 5312-97-0; **19**, 1078-19-9; **20**, 2472-22-2. Products: **2**, 75996-29-1; **3** and **4**, 135-19-3; **6** and **7**, 90-15-3; **8**, 576-26-1; **10**, 150-19-6; **11**, 1126-61-0; **12** and **13** 93-35-6; **14**, 99-07-0; **15**, 14199-15-6; **16**, 873-62-1; **17**, 767-00-0; **18**, 180526-90-3; **19**, 52727-28-3.

3,5-Dihydroxyfluorobenzene (2). 3,5-Dimethoxyfluorobenzene (**1**, 585 mg, 3.75 mmol) and $n\text{-Bu}_4\text{NI}$ (3.46 g, 9.39 mmol) were stirred in dry CH_2Cl_2 (18 mL) at -78 °C under N_2 . A solution of BCl_3 (9.38 mL, 1 M in CH_2Cl_2 , 9.38 mmol) was added over 2 min. After 5 min, the solution was warmed to 0 °C and was stirred for 2 h. The reaction solution was quenched with ice and H_2O , stirred for 30 min, and partially concentrated to remove CH_2Cl_2 . After H_2O was added, the mixture was extracted with Et_2O . The combined organic layer was washed with saturated aqueous NaCl solution, dried over Na_2SO_4 , concen-

trated, and purified by chromatography on silica gel to provide a white crystalline solid (370 mg, 77%): mp 134–136 °C; R_f 0.31 (1:3 EtOAc:hexanes); ^1H NMR (CD_3OD , δ) 6.05 (m, 1 H), 5.99 (dd, $J = 10.6, 2.1$ Hz, 1 H); GC-MS m/z 128 (M^+).

1-Naphthol (Cleavage of 6). 1-Ethoxynaphthalene (**6**, 861 mg, 5.0 mmol) and $n\text{-Bu}_4\text{NI}$ (2.03 g, 5.50 mmol) were stirred in dry CH_2Cl_2 (25 mL) at -78 °C under N_2 . A solution of BCl_3 (7.5 mL, 1 M in CH_2Cl_2 , 7.50 mmol) was added over 2 min. After 5 min, the solution was allowed to warm to 0 °C and was stirred for 1 h. The reaction solution was quenched with ice and H_2O , stirred for 30 min, diluted with saturated aqueous NaHCO_3 solution, and extracted with CH_2Cl_2 . The combined organic layer was dried by filtration through a cotton plug, concentrated, and purified by chromatography on silica gel to provide 1-naphthol (709 mg, 98%): mp 89–90 °C; R_f 0.73 (1:3 EtOAc:hexanes); ^1H NMR (CDCl_3 , δ) 8.21 (m, 1 H), 7.83 (m, 1 H), 7.49–7.28 (4 H), 6.80 (d, $J = 7.5$ Hz, 1 H), 5.29 (br s, OH); GC-MS m/z 144 (M^+).

2-(4-Hydroxyphenyl)acetate (Cleavage of 13). Methyl 2-(4-hydroxyphenyl)acetate (**13**, 538 mg, 3.00 mmol) and $n\text{-Bu}_4\text{NI}$ (1.43 g, 3.88 mmol) were stirred in dry CH_2Cl_2 (15 mL) at -78 °C under N_2 . A solution of BCl_3 (7.5 mL, 1 M in CH_2Cl_2 , 7.50 mmol) was added over 2 min. After 5 min, the reaction solution was allowed to warm to 20 °C and was stirred for 1 h. The reaction solution was quenched with ice and H_2O , stirred 30 min, diluted with saturated aqueous NaHCO_3 solution, and extracted with CH_2Cl_2 . The combined organic layer was dried by filtration through a cotton plug, concentrated, and purified by chromatography on silica gel (1/9 EtOAc/hexanes) to provide methyl 2-(4-hydroxyphenyl)acetate (382 mg, 84%): mp 53–54 °C; R_f 0.37 (1:3 EtOAc:hexanes); ^1H NMR (CDCl_3 , δ) 7.09 (d, $J = 8.2$ Hz, 1 H), 6.73 (d, $J = 8.2$ Hz, 1 H), 5.78 (br s, OH), 3.69 (s, 3 H), 3.55 (s, 2 H); GC-MS m/z 166 (M^+).

5-Hydroxy-2-methoxybenzointrile (Cleavage of 18). 2,5-Dimethoxybenzointrile (**18**, 816 mg, 5.00 mmol) and $n\text{-Bu}_4\text{NI}$ (2.03 g, 5.50 mmol) were stirred in dry CH_2Cl_2 (25 mL) at -78 °C under N_2 . A solution of BCl_3 (17.5 mL, 1 M in CH_2Cl_2 , 17.50 mmol) was added over 2 min. After 5 min, the solution was allowed to warm to 20 °C and was stirred for 40 min (translucent brown solution). The reaction mixture was quenched with ice, stirred for 30 min, diluted with saturated aqueous NaHCO_3 solution, and extracted with CH_2Cl_2 . The combined organic layer was dried through a cotton plug, concentrated, and purified by chromatography on silica gel to provide a crystalline solid (650 mg, 87%): mp 114–116 °C; R_f 0.28 (2:3 EtOAc:hexanes); ^1H NMR (CDCl_3 , δ) 7.04 (m, 2 H), 6.84 (d, $J = 10.0$ Hz, 1 H), 5.47 (OH), 3.86 (s, 3 H); NOE difference data, irradiation of δ 3.86 (methyl) causes enhancement of δ 6.84 doublet; GC-MS m/z 149 (M^+). Anal. Calcd for $\text{C}_8\text{H}_7\text{NO}_2$: C, 64.4; H, 4.7; N, 9.4. Found: C, 64.5; H, 4.7; N, 9.4.

7-Ethoxymethoxychromen-2-one (12). 7-Hydroxychromen-2-one (2.0 g, 12.34 mmol), $n\text{-Bu}_4\text{NI}$ (50 mg), and DMF (50 mg) were stirred in THF (50 mL) under N_2 and treated with $t\text{-BuOK}$ (1.57 g, 14.00 mmol). After being stirred for 5 min, the yellow dispersion was treated with chloromethylethyl ether (1.28 g, 13.57 mmol). After 18 h at room temperature, the reaction mixture was treated with Et_2O (50 mL) and 1 N NaOH (50 mL). The organic layer was separated, washed with water and brine, and dried over Na_2SO_4 . Evaporation afforded a crude oil which was purified by chromatography on silica gel to provide a white crystalline solid (1.65 g, 61%): mp 79–81 °C; R_f 0.51 (1:3 EtOAc:hexanes); ^1H NMR (CDCl_3 , δ) 7.62 (d, $J = 9.5$ Hz, 1 H), 7.36 (d, $J = 8.5$ Hz, 1 H), 7.00 (d, $J = 2.5$ Hz, 1 H), 6.94 (dd, $J = 8.5, 2.5$ Hz, 1 H), 6.25 (d, $J = 9.5$ Hz, 1 H), 5.26 (s, 2 H), 3.71 (q, $J = 7.0$ Hz, 2 H), 1.20 (t, $J = 7.0$ Hz, 3 H); AP-CI MS m/z 221.1 ($(\text{M} + 1)^+$). Anal. Calcd for $\text{C}_8\text{H}_7\text{NO}_2$: C, 65.5; H, 5.5. Found: C, 65.5; H, 5.7.

(22) ^{13}C NMR studies of equimolar quantities of BCl_3 and $n\text{-Bu}_4\text{NI}$ in CD_2Cl_2 at 20 °C (~2 h) indicate a ratio of peak heights of 23/1/9/3 at -51.6, -71.8, -101.7, and -140.3 ppm, respectively. For ^{13}C NMR results with coordinated BX_3 complexes, see: Anton, K.; Nöth, H.; Pommerening, H. *Chem. Ber.* **1984**, *117*, 2479.

(23) The order of addition that we have found to be the most experimentally convenient is to add BCl_3 to a combination of $n\text{-Bu}_4\text{NI}$ and substrate. We have observed no qualitative or quantitative differences in ether cleavage performance by adding BCl_3 to substrate followed by $n\text{-Bu}_4\text{NI}$ in CH_2Cl_2 .

(24) Benzyl iodide and 3-methoxyphenol were isolated from the cleavage of **10**. No benzyl chloride was detected (GC-MS).

(25) Attempts to use catalytic $n\text{-Bu}_4\text{NI}$ with stoichiometric alkali metal halides have not met with success. Also see ref 11.

(26) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.