Pergamon

Tetrahedron Letters 43 (2002) 1387–1389

TETRAHEDRON
LETTERS

Facile access to aryltellurium compounds from arylboronic acids

Aaron R. Clark,[a] Rashmi Nair,[a] Frank R. Fronczek[b] and Thomas Junk[a,]*

[a]*Department of Chemistry, University of Louisiana at Monroe, Monroe, LA 71203, USA*
[b]*Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, USA*

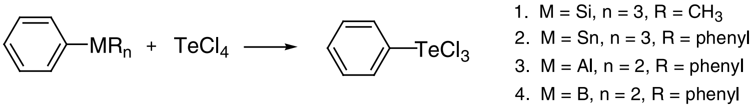
Received 13 November 2001; accepted 14 December 2001

Abstract—Arylboronic acids were treated with tellurium tetrachloride to generate substituted aryltellurium trichlorides, which were reduced to the corresponding diaryl ditellurides in good to excellent overall yields. Representative products include diphenyl ditelluride, bis(2-nitrophenyl) ditelluride, bis(3-nitrophenyl) ditelluride, bis(4-methylphenyl) ditelluride and bis(2-chlorphenyl) ditelluride. 3,5-Dimethylphenyl 2′-nitrophenyl telluride and 3,5-dimethylphenyl 3′-nitrophenyl telluride were prepared in analogous fashion, in modest yields, from 3,5-dimethylphenyltellurium tribromide and the corresponding nitrophenylboronic acids. © 2002 Published by Elsevier Science Ltd.

The preparation of aryltellurium compounds by treatment of arylmagnesium[1–3] or aryllithium[4,5] precursors with elemental tellurium is well established, but lacks universal scope.[1,2] Thus, diaryl tellurides and -ditellurides which contain nitro groups are inaccessible following these procedures, while others, e.g. bis(2-chlorophenyl) ditelluride, have not been isolated in pure form due to poor yields and extensive byproduct formation.[3] Methods of access to aryltellurium compounds via organomercury precursors[6–8] are of general utility, but are impeded by limited access to and high toxicity of the corresponding mercury compounds. Notably, the synthesis of precursors suitable for the preparation of N, Te heterocycles (tellurazoles, tellurazines) represents a synthetic challenge.[9,10,26]

Several examples can be found in the literature illustrating the preparation of aryltellurium trichlorides by reaction of arylsilicon, -tin, -aluminum and -boron compounds with tellurium tetrachloride (Scheme 1).[10–13] Unfortunately, these reactions are of limited utility, but they encouraged us to attempt the preparation of aryl tellurium halides from arylboronic acids. Boronic acids have been utilized previously for the preparation of diarylamines and diaryl ethers[14–16] and are readily prepared from arylmagnesium or -lithium precursors.[17–19] Arylboronic acids are also accessible from aromatic triflates[20] and can be functionalized by nitration, halogenation, side chain oxidation, or Sandmeyer displacement, reactions that are difficult to carry out with diaryl ditellurides.[18,21,22]

We now report the facile synthesis of diaryl ditellurides starting with arylboronic acids and tellurium tetrachloride, as outlined in Scheme 2. This method is characterized by good to excellent yields and convenient experimental conditions. Aryltellurium trichlorides formed in this procedure were reduced to diaryl ditellurides without prior isolation. The formation of diaryltellurium dichlorides was suppressed by employing a 10% excess of tellurium tetrachloride. All arylboronic acids were prepared according to the literature[18] and dried in vacuo at 70°C for 48 h to avoid hydrolytic losses of tellurium tetrachloride. It is probable that the acids were converted, in part or entirely, to the corresponding anhydrides upon drying.[17] Identities of previously reported products were confirmed by comparison with authentic samples, prepared according to alternate procedures.

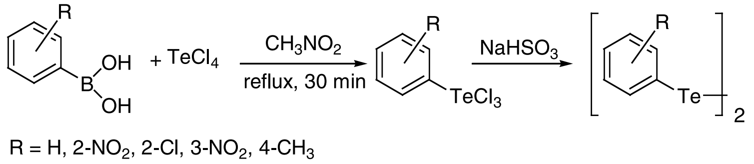


Scheme 1. Aryltellurium trichlorides from arylsilicon, -tin, -aluminum and -boron compounds.

Keywords: ditellurides; tellurides; boronic acids.

* Corresponding author. Tel.: (318) 342-1830; fax: (318) 342-1859; e-mail: chjunk@ulm.edu

0040-4039/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0040-4039(02)00025-4



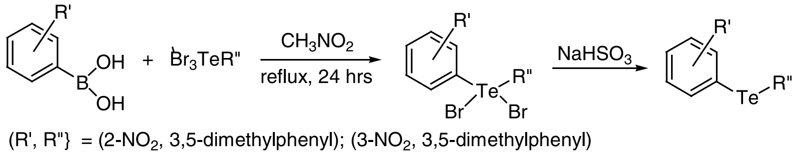
Scheme 2. Preparation of diaryl ditellurides from arylboronic acids.

Similarly, two non-symmetrical diaryl tellurides were prepared by condensation of 2- and 3-nitrophenylboronic acids with 3,5-dimethylphenyltellurium tribromide, followed by reduction (Scheme 3). Yields for these reactions were improved by the addition of copper(I) bromide, but were lower than those of ditellurides. All syntheses are summarized in Table 1, yields refer to isolated products and were calculated based on boronic acids as limiting reactants.

Example 1: Preparation of bis(2-nitrophenyl) ditelluride. A 50 mL round bottom flask equipped with magnetic stirring and a reflux condenser was charged with 0.50 g (3.0 mmol) 2-nitrophenylboronic acid, 0.89 g (3.3 mmol) tellurium tetrachloride and 10 mL dry nitromethane. The mixture was heated to reflux for 30 min, then allowed to cool and poured into 50 mL ice water. The mixture was buffered by addition of 2 g sodium acetate, followed by addition of 2 g sodium bisulfite and 50 mL dichloromethane. Stirring for 12 h completed the reduction of 2-nitrophenyltellurium chloride. The organic phase was collected and the aqueous phase extracted with 5×25 mL dichloromethane. Solvents were removed from the combined organic phases, followed by flash chromatography (neutral alumina/dichloromethane). The product was crystallized from toluene.

Example 2: Preparation of 3,5-dimethylphenyl 2′-nitrophenyl telluride. A 50 mL round bottom flask equipped with magnetic stirring and a reflux condenser was charged with 0.50 g (3.0 mmol) 2-nitrophenylboronic acid, 1.28 g (3.0 mmol) 3,5-dimethylphenyltellurium tribromide, 50 mg copper(I) bromide and 15 mL dry nitromethane. The mixture was heated to reflux for 24 h, then allowed to cool and poured into 50 mL ice water. Reduction was achieved by the addition of 2 g sodium bisulfite and stirring for 12 h. The product was extracted with 2×50 mL dichloromethane, purified by flash chromatography (neutral alumina/dichloromethane) and crystallized from petroleum ether, followed by recrystallization from ethanol.

2-Phenethylboronic acid did not react with tellurium tetrachloride to generate any isolable organotellurium compounds, suggesting that only aryltellurium compounds can be prepared from boronic acids.



Scheme 3. Preparation of diaryl ditellurides from arylboronic acids.

Table 1. Diaryl ditellurides and diaryl tellurides prepared from arylboronic acids

Reactants	Isolated product	Yield (%)	References
Phenylboronic acid; tellurium tetrachloride	Diphenyl ditelluride	95	3
2-Nitrophenylboronic acid; tellurium tetrachloride	Bis(2-nitrophenyl) ditelluride	85	23,24
3-Nitrophenylboronic acid; tellurium tetrachloride	Bis(3-nitrophenyl) ditelluride	81	25
4-Methylphenylboronic acid; tellurium tetrachloride	Bis(4-methylphenyl) ditelluride	60	3
2-Chlorophenylboronic acid; tellurium tetrachloride	Bis(2-chlorophenyl) ditelluride	80	3[a],24
2-Nitrophenylboronic acid; 3,5-dimethylphenyltellurium tribromide	3,5-Dimethylphenyl 2′-nitrophenyl telluride	46	(None)[b]
3-Nitrophenylboronic acid; 3,5-dimethylphenyltellurium tribromide	3,5-Dimethylphenyl 3′-nitrophenyl telluride	54	(None)[c]

[a] Previously characterized as red oil. Orange crystals, mp 41–2°C.

[b] Previously unreported. Orange crystals, mp 131–2°C, ^{1}H NMR (CD_3COCD_3, 400 MHz): δ 8.43 (dd, 1H), 7.61 (s, 2H), 7.48 (m, 1H), 7.42 (m, 1H), 7.29 (dd, 1H), 7.19 (s, 1H), 2.35 (s, 6H). ^{13}H NMR ($CDCl_3$, 300 MHz): δ 21.3, 117.9, 123.4, 126.4, 126.8, 131.6, 133.6, 134.7, 139.1, 139.8, 147.7. ^{125}Te NMR ($CDCl_3$, 300 MHz): δ 797.8. EIMS, *m*/*z* 356.9991 (M^+).

[c] Previously unreported. Yellow crystals, mp 52–4°C, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.40 (m, 1H), 8.06 (m, 1H), 8.46 (s, 2H), 7.31 (t, 1H), 7.99 (s, 1H), 2.28 (s, 6H). ^{13}H NMR ($CDCl_3$, 300 MHz): δ 21.2, 112.8, 117.3, 122.4, 129.9, 130.8, 131.1, 137.4, 139.7, 142.2, 148.5. ^{125}Te NMR ($CDCl_3$, 300 MHz): δ 728.0. EIMS, *m*/*z* 356.9997 (M^+).

References

1. Irgolic, K. J. *Houben-Weyl Methoden der organischen Chemie*, 4th ed.; Müller, E., Ed.; Georg ThiemeVerlag: Stuttgart, 1990; Vol. E12b.
2. Petragnani, N. *Tellurium in Organic Synthesis*; Academic Press: New York, 1994.
3. Haller, W. S.; Irgolic, K. J. *J. Organomet. Chem.* **1972**, *38*, 97–103.
4. Seebach, D.; Beck, A. K. *Chem. Ber.* **1975**, *108*, 314–321.
5. Akiba, M.; Cava, M. P. *Synth. Commun.* **1984**, *14*, 1119–1128.
6. Nath, A.; Sauer, C.; Halpern, A. *J. Chem. Phys.* **1983**, *78*, 5125–5128.
7. Hellwinkel, D.; Stahl, H. *Z. Naturforsch. B* **1993**, *48*, 521–538.
8. Junk, T.; Irgolic, K. J. *Phosphorus Sulfur* **1988**, *38*, 121–135.
9. Junk, T.; Fronczek, F. R. *Tetrahedron Lett.* **1996**, *37*, 4361–4362.
10. Sadekov, I. D.; Maksimenko, A. A. *J. Gen. Chem. USSR* **1977**, *47*, 1755–1756.
11. Schumann, H.; Magerstaedt, M. *J. Organomet. Chem.* **1982**, *232*, 147150.
12. Rainville, D. P.; Zingaro, R. A. *J. Organomet. Chem.* **1980**, *190*, 277–288.
13. Schumann, H.; Magerstaedt, M. *J. Organomet. Chem.* **1982**, *232*, 147–150.
14. Chan, D. M. T.; Monaco, K. L.; Wang, R.-P.; Winters, M. P. *Tetrahedron Lett.* **1998**, *39*, 2933–2936.
15. Cundy, D. J.; Forsyth, S. A. *Tetrahedron Lett.* **1998**, *39*, 7979–7982.
16. Theil, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 2345–2347.
17. Seaman, W.; Johnson, J. R. *J. Am. Chem. Soc.* **1931**, *53*, 711–723.
18. Bean, F. R.; Johnson, J. R. *J. Am. Chem. Soc.* **1932**, *54*, 4415–4425.
19. Letsinger, R. L.; Dandegaonker, S. H. *J. Am. Chem. Soc.* **1959**, *81*, 498–501.
20. Ishiyama, T.; Itoh, Y.; Kitano, T.; Miyaura, N. *Tetrahedron Lett.* **1997**, *8*, 3447–3450.
21. Fry, A. J.; Britton, W. E. *J. Org. Chem.* **1973**, *38*, 4016–4021.
22. Serafin, B.; Makosza, M. *Tetrahedron* **1963**, *19*, 821–826.
23. Wiriyachitra, P.; Falcone, S. J.; Cava, M. P. *J. Org. Chem.* **1979**, *44*, 3957–3959.
24. Bis(2-nitrophenyl) ditelluride and bis(2-chlorophenyl) ditelluride were characterized by X-ray crystallography. Coordinates and geometries have been deposited with the Cambridge Crystallographic Data Centre.
25. Irgolic, K. J.; Grassi, A.; Pappalardo, G. C. *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *67*, 1–6.
26. Evers, M. J.; Christiaens, L. E.; Renson, M. J. *J. Org. Chem.* **1986**, *51*, 5196–5198.