Waste-Free and Facile Solid-State Protection of Diamines, Anthranilic Acid, Diols, and Polyols with Phenylboronic Acid

Gerd Kaupp,* M. Reza Naimi-Jamal, and Vladimir Stepanenko[a]

Abstract: Phenylboronic acid (**2**) reacts quantitatively by ball-milling in the solid state with *o*-phenylendiamine, 1,8-diaminonaphthalene, anthranilic acid, pyrocatechol, pyrogallol, pinacol, bicyclic *cis*-diols, mannitol, and inositol to form the five- or six-membered cyclic phenylboronic amides or esters. Catalysts or other auxiliaries are strictly excluded as they are not required and would have to be removed after the reactions. These varied model reactions provide pure protected products without the necessity of further purifying workup and the potential for protection chemistry is demonstrated. Some of the reactions can also be quantitatively performed if stoichiometric mixtures of the reactants are co-ground or co-milled and heated to appropriate temperatures either below the eutectics or above the melting points. The temperatures are much higher in the latter case. Similar reactions in solution suffer from less than 100% yield of the mostly sensitive compounds that are difficult to purify and thus create much waste. The hydrolysis (deprotection) conditions of the products are rather mild in most cases. Therefore, this particularly easy access to heteroboroles, heteroborolanes, heteroborinones, heteroborines, and heteroborinines is highly valuable for their more frequent use in protective syntheses.

Keywords: diamines · environmentally benign · phenylboronic acid · polyols · solid-state reactions

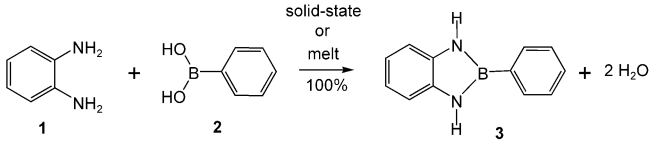
Introduction

Protection (deprotection) remains an important task in the field of bi- or polyfunctional alcohols, acids, amines, and thiols with mixed functionalities.[1] Both protection and deprotection should be easy and quantitative in order to save precious components and to minimize waste. We describe here particularly versatile applications of phenylboronic acid in protection chemistry. The protection reactions occur quantitatively in stoichiometric mixtures without solvents, catalysts, or other auxiliaries. Deprotection is easily achieved by rather mild techniques in most cases.

Results and Discussion

Free amino and hydroxy groups frequently require protection. If they are present in 1,2- or in favorable 1,3-positions, cyclic amides or esters may be formed for that purpose. The synthesis of some 1,3,2-dioxaborolanes/-dioxaborinines,[2] and 1,3,2-diazaborolanes/-diazaborinines[3] (five- and six-membered heterocyclic aryl boronic acid esters and amides) has been described. These cyclization reactions of 1,2-diamines and 1,2-diols were performed in solution or at functionalized polymer surfaces with yields ranging from 21 to 97%. We have now found that they proceed quantitatively in the solid-state or in stoichiometric melts, even though two equivalents of water are released per ring closure and must be removed during the reaction in some cases. For protection purposes, we chose unsubstituted phenylboronic acid (**2**) because it is most readily available and yields well crystallized protected products.

Aromatic 1,2- and peri-diamines: The most profitable solid-state technique provides compound **3** in quantitative yield without waste if equimolar mixtures of the reagents **1** (m.p. 103–105 °C) and **2** (m.p. 217–220 °C) are co-ground in a mortar at room temperature and heated to 40 °C in a vacuum for 1 h. Alternatively the mixture of reagents can be melted at 100–110 °C in a vacuum, while the water of reaction is removed by evaporation from the hot melt (Scheme 1). This reaction is superior to the corresponding solution reaction, which gave a 79%[3] or 92%[4] yield and required purifying



Scheme 1. Quantitative synthesis of **3** from a stoichiometric melt.

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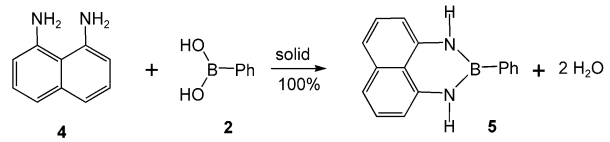
DOI: 10.1002/chem.200304793

workup. The deprotection of **3** has been described,[5] and it can also be quantitatively performed in boiling aqueous Na_2CO_3.

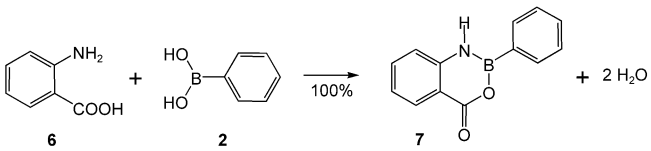
1,8-Diaminonaphthalene (**4**) reacts with **2** in the solid state at 0 °C and provides the six-membered diazaborinine **5** in quantitative yield (Scheme 2). Previously, **5** was obtained by reaction of **4** with phenylboronic dichloride in benzene (3 h reflux, 64 %)[6] or with phenylboronic anhydride (100–140 °C, 71 %).[7]



Scheme 2. Quantitative solid-state synthesis of **5** in a ball-mill.

Now, both products **3** and **5** can be obtained directly in the pure state without the need for further purification when starting with the pure reagents. There are no difficulties with intermolecular bridging, and linear boronic amides do not form with the new technique. Compound **5** is not easily deprotected but requires strong acid or strong base.[6] It is unusually stable, except for slow oxidation with oxygen, and may be useful for electrophilic aromatic substitutions.

Anthranilic acid: If equimolar mixtures of anthranilic acid (**6**) and phenylboronic acid (**2**) are ball-milled, compound **7** with its O,B,N six-membered ring is quantitatively formed, again without waste (Scheme 3). Both, a primary amino and a carboxylic acid group are protected here. The same product **7** was obtained in a solution reaction, however, in only 90 % yield.[3]

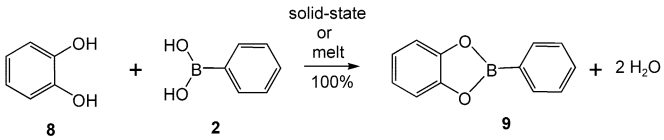


Scheme 3. Quantitative solid-state synthesis of **7** in a ball-mill.

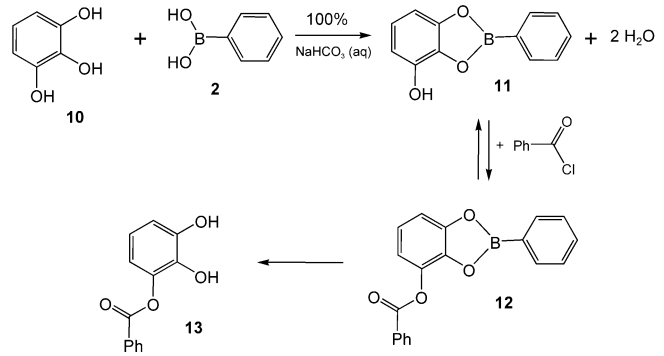
The deprotection of **7** with aqueous $NaHCO_3$ at 90 °C is complete after 1 h to give the sodium salt of **6** and PhB(OH)ONa.

Reactions of natural α-amino acids with phenylboronic acid have not been described in the literature. The α-amino acid L-proline reacts with **2** in the solid state (60 °C) and in a melt (100 °C), however, it was not yet possible to get a pure cyclic product due to facile hydrolytic deprotection. On the other hand, the reaction shows promise as a route for obtaining 3,1,2-oxazaborilidin-4-ones if the water of reaction is efficiently removed under the reaction conditions. N-acylated or N-tosylated amino acids seem to lack reactivity and require phenylboronic dichloride for their protection.[8]

Aromatic 1,2-diols: Pyrocatechol (**8**) and pyrogallol (**10**) react quantitatively with phenylboronic acid when stoichiometric mixtures are ball-milled at 80 °C (Scheme 4 and Scheme 5). In the case of **11**, the yield is increased from 98 % to 100 % by



Scheme 4. Quantitative solid-state synthesis of **9** in a ball-mill.

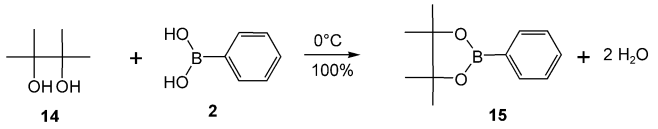


Scheme 5. Quantitative solid-state synthesis of **11** and its use as a protected reagent.

drying the product in a vacuum at 80 °C. The yields of **9** and **11** in solution were 51 %[9] and 90 %[2], respectively.

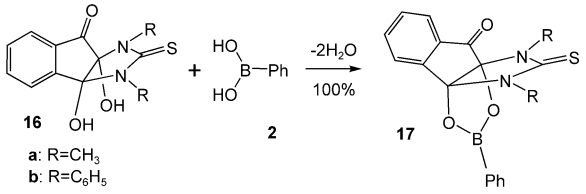
The free hydroxy group in **11** can be quantitatively benzoylated to give **12** (Scheme 5). Conversely, the yield of **12** in the pyridine solution reaction was only 65 %.[2] Compound **12** is a precursor to 1-benzoyloxy-2,3-dihydroxy benzene (**13**) by deprotection with mannitol.[2] The deprotection of **9** and **11** can also be achieved by heating with aqueous $NaHCO_3$ to 40 °C for 2 h.

Aliphatic 1,2-diols: The cyclization reaction of aliphatic 1,2-diols is equally versatile and waste-free with pinacol (**14**). Ball-milling of a stoichiometric mixture of **14** and **2** at 0 °C gives quantitatively **15** (Scheme 6). Previous reactions in solution afforded **15** with yields of 59 %[10] or 80 %.[11]



Scheme 6. Quantitative solid-state synthesis of **15** in a ball-mill.

Interestingly, also the [3.3.3]heteropropellanes **17** can be quantitatively obtained by the solid–solid technique when stoichiometric mixtures of **16a** or **16b**[12] and **2** are ball-milled at 50 or 95 °C, respectively (Scheme 7). The polyfunctional



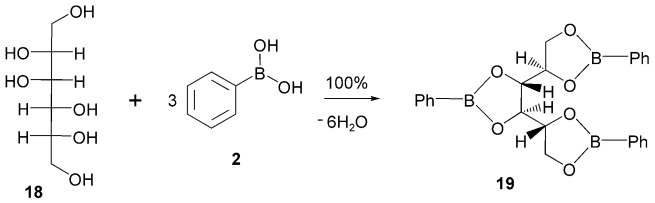
Scheme 7. Quantitative solid-state synthesis of heteropropellanes **17**.

propellanes **17** are remarkably stable crystalline compounds.

The deprotection of **15** and **17a, b** in 0.01N HCl, followed by neutralization is achieved under rather moderate conditions.

Polyhydroxy compounds: mannitol and inositol: Sugar alcohols and cyclic polyalcohols form both five- and six-membered ring heterocycles with phenylboronic acid.[13] Interestingly, some of these reactions occur also in the solid state. This observation is of great importance as such protection with easy deprotection gains increased importance in carbohydrate chemistry.

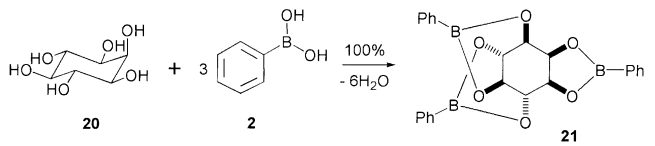
D-Mannitol (**18**) reacts quantitatively with three molecules **2** in the ball-mill to give the 1:2,3:4,5:6-product **19** (Scheme 8) as a nonsticky powder which has the same structure as the product obtained in solution in only 68% yield.[10, 13] The



Scheme 8. Quantitative solid-state reaction of mannitol with phenylboronic acid.

(*R*,*R*, *R*, *R*)-configuration has been confirmed by X-ray crystal structure analysis.[14] Interestingly, the solution-state chemistry of **18** and **2** seems to favor a cyclic diester of mannitol in which both primary OH groups are free for chemical reaction.[15] However, the crystals that separate from solution are the triester **19**. A very easy partial deprotection in aqueous solution is clearly indicated and can be used for selective reactions of **19**.

The cyclic hexol *myo*-inositol (**20**) reacts with phenylboronic acid (**2**) in a 1:3 ratio in the ball-mill at 95 °C to give the racemic tris-borolic ester **21** with one five-membered and two six-memebered rings according to the relative positions of the OH groups in the initial chair conformation of **20** in 100% yield (Scheme 9). Compound **21** corresponds in all respects to



Scheme 9. Quantitative solid-state reaction of *myo*-inositol with phenylboronic acid.

the quantitatively obtained product from the melt at 230 °C and to the previously reported product from the corresponding solution reaction (75%).[16] The molecular structure of **21** was confirmed by X-ray crystal structure analysis.[16] The deprotection is quantitative if **21** is dissolved in 0.01N HCl and left for 1 h at room temperature.

Conclusion

Our solid-state or solvent-free techniques for obtaining cyclic phenylboronic esters and amides are largely superior to their syntheses in solvents, as we get the products in pure form directly in quantitative yield when starting with stoichiometric mixtures of pure reactants excluding auxiliaries. The necessary reaction temperatures vary, but solid-state conditions can be found at considerably lower temperatures than the melt reactions in most cases. Finely co-ground or co-milled powders can be heated to appropriate temperatures for quantitative reaction in the solid state in favorable cases of melting points. This option is of importance if the required reaction temperature exceeds the more comfortable heating capabilities of the milling equipment. Melt reactions suffer from the higher temperatures that must be applied, but the yield may also remain quantitative in favorable cases, although the risk of side reactions increases in melt reactions. Large amounts of water are released in the polyol reactions, but it is not necessary to use the phenylboronic anhydride for improvement as the water of reaction can be removed by moderate heating in a vacuum. The high crystallinity of the phenylboronic esters or amides is very favorable. Certainly, extensions to tailor-made protections with substituted arylboronic acids instead of **2** are possible, if required.

Remarkably, the same products occurred exclusively in the solid-state polyol reactions, these products crystallized in much lower yield from the solution reactions. Apparently, the most stable conformations are reactive and lead to the more stable boronic esters both in the solid state and in the liquid state. However, it remains to be clarified if further products remain in the mother liquors of the solution reactions. The protection of diols, diamines, amino acids, and polyols is of widespread importance in organic syntheses and the versatility of the solid-state technique or, if necessary, the solvent-free stoichiometric melt technique is particularly promising in that respect. The deprotections of the various boronic esters or amides are generally successful under mild conditions but vary markedly. Thus, the cyclizations that are facilitated by acid require weak base for the reversion, but acid-catalyzed hydrolysis followed by neutralization is successful if the cyclization requires elevated temperatures.

Ten varied examples in this work cover a broad range and should be helpful for further progress in this field of research as the protections occur waste-free and provide the highly sensitive products without the requirement for purifying workup.

Experimental Section

Melting points were determined with a Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded with a Perkin-Elmer 1720-X FT-IR spectrometer using potassium bromide pellets. All NMR spectra were recorded on a Bruker WP 300 at 300 MHz (^{1}H) or 75 MHz (^{13}C). $CDCl_3$/[D_6]DMSO mixtures contained up to 20% [D_6]DMSO. All δ values refer to the internal standard TMS. The ^{13}C resonances of the carbon atoms that were directly bound to the boron atom were not always found due to the quadrupole nuclei ^{10}B and ^{11}B. No particular effort was undertaken to make these signals visible as these did

not have a high diagnostic value. Mass spectra were obtained on a Finnigan MAT 212 System. Uniform heating of the stoichiometric melts without partial distillation or sublimation was carried out in closed flasks in a preheated oven. The ball-mill for the 2 mmol runs was a Retsch MM 2000 swing-mill with a 10 mL stainless steel double-walled beaker with fittings for circulating coolants. Two stainless steel balls with 12 mm diameter were used. Ball-milling was performed at a 20–25 Hz frequency usually at room temperature (without circulating liquid the temperature did not rise above 30 °C). Water of the appropriate temperature was circulated for heating or cooling. Completion of the solid-state reactions was checked by IR spectroscopy in KBr and weight, and product purity by m.p. and ^{1}H NMR spectroscopy.

2-Phenyl-2,3-dihydro-1*H*-1,3,2-benzodiazaborole (3)

a) Solid-state reaction: A mixture of *o*-phenylendiamine (**1**, 108 mg, 1.00 mmol) and phenylboronic acid (**2**, 122 mg, 1.00 mmol) was co-ground at room temperature and then heated to 40 °C in a vacuum for 1 h to give pure **3** (195 mg; 100 %) after drying at 80 °C in a vacuum.

b) Melt reaction: A mixture of *o*-phenylendiamine (**1**, 216 mg, 2.00 mmol) and phenylboronic acid (**2**, 244 mg, 2.00 mmol) was heated in an evacuated 100 mL flask in a drying oven for 30 min, briefly evacuated, heated for another 30 min, and evacuated at 80 °C for 1 h. A quantitative yield (388 mg, 100 %) of **3** (m.p. 207 – 208 °C; ref. [4]: 213–214 °C) was obtained.

The deprotection of **3** was achieved according to reference [5] or by refluxing **3** (200 mg) in 5 % aqueous Na_2CO_3 solution (10 mL) for 8 h, followed by extraction with dichloromethane to obtain **1** in almost quantitative yield.

2-Phenyl-2,3-dihydro-1*H*-2-boraperimidine or 2-phenyl-2,3-dihydro-1*H*-naphtho[1,8-de][1,3,2]diazaborinine (5): Crystalline 1,8-diaminonaphthalene (**4**, 158 mg, 1.00 mmol) and **2** (122 mg, 1.00 mmol) were ball-milled at 0 °C for 1 h. Compound **5** was dried in a vacuum at 50 °C and obtained in spectroscopically pure form (244 mg, 100 %). It was stored under argon or N_2. **5**: m.p. 90.5–91.5 °C; ref. [6]: 92.5–93.5 °C (corrected, under N_2; after three recrystallizations and four sublimations). IR (KBr): $\tilde{\nu}$ = 2433, 1628, 1603, 1515, 1485, 1414 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 7.70–7.60 (m, 2H), 7.50–7.35 (m, 3H), 7.15–7.08 (m, 2H), 7.05–7.00 (m, 2H), 6.42 (ψd, 2H), 6.15 ppm (br p, 2NH); ^{1}H NMR ($CDCl_3$/[D6]DMSO, 1:1 v/v): δ = 7.92–7.73 (m, 2H), 7.50–7.19 (m, 3H + 2NH), 7.13–7.00 (m, 2H), 6.98–6.85 (m, 2H), 6.50 ppm (ψd, 2H); ^{13}C NMR ($CDCl_3$): δ = 141.1 (2C), 136.3, 134.0, 131.4 (2C), 130.1, 128.1 (2C), 127.5 (2C), 119.8, 117.6 (2C), 105.9 ppm (2C); ^{13}C NMR ($CDCl_3$/[D6]DMSO, 1:1 v/v): δ = 141.2 (2C), 135.7, 133.6, 131.4 (2C), 129.5, 127.4 (2C), 127.0 (2C), 119.0, 116.5 (2C), 105.4 ppm (2C); HRMS (70 eV): calcd for $C_{16}H_{13}BN_2$: 244.1172; found 244.1170.

2-Phenyl-1,2-dihydro-benzo[a][1,3,2]-oxazaborinin-4-one: Crystals of anthranilic acid (**6**, 274 mg, 2.00 mmol) and **2** (244 mg, 2.00 mmol) were ball-milled for 1 h at room temperature. After drying at 80 °C in a vacuum, spectroscopically pure crystals of **7** (445 mg, 100 %) were obtained; m.p. 224–226 °C; ref. [3]: 228 °C. Complete deprotection was achieved by boiling **7** (200 mg) in 5 % $NaHCO_3$ solution (20 mL) for 1 h.

2-Phenyl-1,3,2-benzodioxaborole (9): Pyrocatechol (**8**, 110 mg, 1.00 mmol) and **2** (122 mg, 1.00 mmol) were ball-milled at 80 °C for 1 h or co-ground in a mortar and heated to 115 °C for 1 h. Compound **9** was obtained in spectroscopically pure form (196 mg, 100 % in both cases) after drying at 80 °C in a vacuum; m.p. 108 °C; ref. [9]: 110 °C. The deprotection of **9** (200 mg) in 5 % $NaHCO_3$ (10 mL) was complete after 2 h at 40 °C. Compound **8** was extracted with dichloromethane.

2-Phenyl-1,3,2-benzodioxaborole-4-ol (11): Pyrogallol (**10**, 252 mg, 2.00 mmol) and **2** (244 mg, 2.00 mmol) were co-ground in a mortar and heated in an evacuated flask to 40 °C for 2 h in a drying oven. After drying at 80 °C in a vacuum, spectroscopically pure **11** (425 mg, 100 %) was obtained; m.p. 163–165 °C; ref. [2]: 166 °C.

4-Benzoyloxy-2-phenyl-1,3,2-benzodioxaborole (12): The phenol **11** (212 mg, 1.00 mmol) and benzoyl chloride (141 mg, 1.00 mmol) were heated to 90 °C for 3 h in an evacuated 100 mL flask in a drying oven. The HCl gas was condensed to a cold flask (77 K) through a vacuum line. The crystalline ester **12** was obtained in spectroscopically pure form (316 mg, 100 %); m.p. 176 °C; ref. [2]: 169–170 °C.

1-Benzoyl-pyrogallol 13: The deprotection of **12** with mannitol and $NaHCO_3$ and isolation of **13** followed the procedures of ref. [2].

2-Phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15): Pinacol (**14**, 236 mg, 2.00 mmol) and **2** (244 mg, 2.00 mmol) were ball-milled at 0 °C for 1 h. After drying in a good vacuum at room temperature, spectroscopically pure **15** (325 mg, 100 %) was obtained; m.p. 35–37 °C; ref.[10]: 29–30 °C; ref. [11]: 28–30 °C. The hydrolysis of **15** was most easily achieved in 0.1N HCl at room temperature for 1 h and **14** was almost quantitatively extracted with dichloromethane after neutralization.

6,8-Dimethyl-10,11-benzo- (17a) and 6,8-diphenyl-10,11-benzo-tricyclo[3.3.3.0]-3-bora-2,4-dioxa-6,8-diaza-9-oxo-7-thioxo-undecene-10 (17b): Compound **16a**[12] (265 mg, 1.00 mmol) or **16b**[12] (388 mg, 1.00 mmol) and **2** (122 mg, 1.00 mmol) were ball-milled at 50 °C or 95 °C, respectively, for 1 h. After drying at 80 °C in a vacuum **17a** (350 mg, 100 %) or **17b** (475 mg, 100 %) was obtained in pure form.

Alternatively, co-ground 1:1 mixtures of **16a, b** and **2** were heated to 140 °C for 1 h to form **17a, b** in 100 % yield.

17a: m.p. 222–224 °C (decomp); IR (KBr): $\tilde{\nu}$ = 1733, 1603, 1333, 1076, 1033, 750, 698, 661, 619, 510 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 8.00–7.78 (m, 5H), 7.79 (m, 1H), 7.50 (m, 1H), 7.38 (m, 2H), 3.52 (s, 3H), 3.49 ppm (s, 3H); ^{13}C NMR ($CDCl_3$): δ = 198.0, 189.9, 144.6, 137.3, 135.3 (2C), 134.8, 132.8, 131.8, 128.0 (2C), 126.2, 124.9, 100.6, 97.8, 30.1, 29.8 ppm; HRMS (70 eV): calcd for $C_{18}H_{15}BN_2O_3S$: 350.0896; found 350.0896.

17b: m.p. 257–259 °C; IR (KBr): $\tilde{\nu}$ = 3427, 1736, 1604, 1440, 1378, 1329, 1101, 747, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 8.00–7.80 (m, 3H), 7.60–7.30 ppm (m, 16H); ^{13}C NMR ($CDCl_3$): δ = 189.1, 182.8, 144.6, 137.0, 136.0, 135.8, 135.5 (2C), 134.6, 133.0, 131.9, 129.8 (2C), 129.5 (2C), 129.3 (2C), 129.2 (3C), 129.1, 128.2 (2C), 126.0, 125.4, 101.7, 98.8 ppm; HRMS (70 eV): calcd for $C_{28}H_{19}BN_2O_3S$: 474.1209; found 474.1209.

Deprotection (removal of the borole ring) of **17a, b** to obtain **16a, b** with quantitative yield was achieved by hydrolysis in 0.01N HCl, neutralization, filtration, and washing with water.

(2*R*,3*R*,4*R*,5*R*)-**1:2,3:4,5:6-O^1:O^2,O^3:O^4,O^5:O^6-tris(phenylboranato)-D-mannitol (19)**: D-Mannitol (**18**, 364 mg, 2.00 mmol) and **2** (732 mg, 6 mmol) were ball-milled at room temperature for 1 h and the solid nonsticky product (IR) dried at 80 °C in a vacuum. Compound **19** (880 mg, 100 %) was obtained in pure form; m.p. 132–133 °C, ref. [10]: 134–135 °C. It was identical to the product obtained from solution in 66 % yield[10] and structurally confirmed by X-ray diffraction.[14]

***rac*-1:2,3:5,4:6-O^1:O^2,O^3:O^5,O^4:O^6-tris(phenylboronato)-*myo*-inositol (21)**: A mixture of *myo*-inositol (**20**) (360 mg, 2.00 mmol) and **2** (732 mg, 6 mmol) was ball-milled at 95 °C for 1 h or melted in a high vacuum at 230 °C for 1 h in a 250 mL flask. Pure nonsticky **21** (875 mg, 100 %) was obtained in both cases; m.p. 228–230 °C; ref. [16]: 204–208 °C. The ^{1}H and ^{13}C NMR spectra were identical with those of the product from the analogous solution reaction,[16] the structure of which was confirmed by X-ray diffraction.[16]

The deprotection of **21** to recover **20** was achieved in 0.01N HCl solution at room temperature for 1 h.

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft. We thank Mrs. Ludmila Hermann for her reliable help in the experimental work.

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Received: January 31, 2003
Revised: April 7, 2003 [F4793]