

A Stereospecific Convergent Coupling of Nucleophilic and Electrophilic Chiral Carbons

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Abstract: (*S,S*)-DIPED (α -*R*)- α -chloro boronic esters (**1**) (98–99% de) were converted via α -tributylstannyl boronic esters (**2**) to (α -*R*)- α -tributylstannyl alcohols (**3**). Known chemistry led to α -stannyl ethers (**4**) and (α -*R*)- α -lithio ethers (**5**) (98–99% ee). Stereospecific coupling of **1a** ($R^1 = n$ -butyl) with **5a** at $-78^\circ\text{C} \rightarrow 25^\circ\text{C}$ yielded **6a**, which for proof of structure was converted with hydrogen peroxide to **7a** and hydrolyzed to known **8a** (96% de). With sterically hindered **1b** and **5b** ($R^1 =$ isopropyl), initial reaction had to be at -100°C in order to avoid reversal of **5b** + Bu_4Sn to **4b** + BuLi and preferential reactions of the BuLi with **1b**. The de of **6b** was 98% as shown by comparison of the ^1H NMR spectrum with that of diastereomer **11b**, which was synthesized from **1b** and lithio ether **10b** (enantiomer of **5b**) derived from (*R,R*)-2,3-butanediol (α -*S*)- α -chloro boronic ester **9**. The structure of **6b** was further confirmed by conversion to diol **8b**. Convergent connection of four contiguous chiral centers was illustrated by the coupling of **1c** [$R^1 = (R)$ -2-pentyl] with **5c** to form **6c**.

We report the conversion of α -chloro boronic ethers (**1**) of high chiral purity (98–99% de) to α -lithio esters (**5**) (98–99% ee) and the stereospecific coupling of **5** with **1**.¹ Several chiral syntheses extend a carbon chain linearly, including boronic ester chemistry,^{2–4} aldol condensations,^{5,6} and epoxide chemistry.⁷ However, convergent stereospecific coupling of two independently created chiral centers is unprecedented. The coupling of two pairs of chiral centers (**1c** + **5c**) to assemble four contiguous chiral centers (**6c**) suggests the synthetic potential. The absolute configuration of each chiral center can be selected independently. We have chosen to explore the new method by synthesizing symmetrical diols in order to simplify the proof of stereoselectivity, but the potential scope of the reaction based on known chemistry^{2–4} is clearly far wider than this.

DIPED^{8,9} α -chloro boronic esters (**1**) are efficiently converted via α -tributylstannyl boronic esters (**2**)¹⁰ to α -tributylstannyl alcohols (**3**), which by the method of Still and Sreekumar lead to α -lithio ethers (**5**) with retention of configuration (Scheme I).¹¹ Pure **4** (98–99% ee), valuable synthetic intermediates,^{11,12} are made available in multigram quantities by our route. Alternative routes to **4** have also been discovered recently.¹³ Stereospecific coupling

of the nucleophile **5** with the electrophile **1** yields **6**. Observed de's were 96–98%.¹⁴

Coupling **1a** ($R^1 = n$ -butyl) with **5a** to form the intermediate borate⁴ proceeded readily at -78°C in THF and after ~ 15 h at 25°C efficiently yielded **6a**. Hydrogen peroxide deboronated **6a** to **7a**, which was hydrolyzed to (*S,S*)-decanediol (**8a**),² 96% de.¹⁵ This de and all others measured in this work are consistent with the estimated purities of the α -chloro boronic esters **1** used as starting materials, as if all subsequent steps are stereospecific and the conditions used convert both diastereomers in approximately equal yields.

Since our ultimate objective was to be able to couple two chains of several chiral centers constructed via our boron chemistry, a more highly branched model system was required. However, repeated attempts to couple **1b** ($R^1 =$ isopropyl) with **5b** under the conditions used for the coupling of **1a** with **5a** yielded at best 20% **6b**, with recovery of much **4b**. All of the chloro boronic ester **1b** was consumed (disappearance of the *CHCl* doublet from the NMR, δ 3.35) with apparent replacement of the chlorine of **1b** by *n*-butyl (formation of an oily saturated boronic ester never freed entirely from tetrabutyltin; DIPED ester (*CHOB*), δ 3.8). We concluded that formation of **5b** from **4b** and butyllithium is rapidly reversible at -78°C and that **1b** captures butyllithium in preference to **5b**. The impasse was overcome by adding the **1b** to **5b** at -100°C (95% ethanol/liquid nitrogen bath) to yield 68–72% **6b**.

Coupling of **1c** [$R^1 = (R)$ -2-pentyl] with **5c** similarly yielded 68% **6c**. The preparation of **1c** followed the same route previously established for synthesis of its pinanediol ester analogue,² except that DIPED propylboronate was the starting material. The preparation of **5c** from **1c** entirely paralleled that of **4b** from **1b** with respect to conditions and yields.

The de of **6b** was $\sim 98\%$ by ^1H NMR (*OCH₂OCH₃* group) (Figure 1). For structure proof, **6b** was converted to (*S,S*)-DIPED (**8b**). For comparison of diastereomers, as well as for proof that the method can be used to synthesize either diastereomer, the immediately available (*R,R*)-2,3-butanediol ester **9**¹⁶ was

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(14) If the isomer ratio is 100:1 in both **1a** and **5a**, random coupling yields the isomer ratio 10000:200:1 for (*S,S*):(*R,S*):(*R,R*)-**8a**, 96% de (diastereomeric excess) as measured, 99.98% ee (enantiomeric excess) calculated.

(15) On the basis of ^{13}C NMR (CDCl_3): δ 74.51 (*S,S*) and 74.67 (meso), crude sample. In exploratory studies, we had similarly coupled (*S*)-pinanediol (1*S*)-(1-chloropentyl)boronate² (the pinanediol ester analogue of the enantiomer of **1a**), $\sim 97\%$ de, with the enantiomer of **5a** prepared from butanediol (1*S*)-(1-chloropentyl)boronate,¹⁶ $\sim 86\%$ de, and obtained (*R,R*)-decanediol, $\sim 84\%$ de. A pinanediol ester analogue of tin intermediate **2** failed to undergo peroxidic deboronation, and hence the less hindered DIPED or butanediol esters have been used.

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equivalent and a chiral carbanion equivalent followed by their stereospecific connection.

Several known methods of connection directed toward similar products utilize the chirality of one fragment to induce chirality in the other. One example is the diastereoselective coupling of α -lithio ethers with aldehydes to produce predominantly *syn*-diol precursors.¹⁸ The anti diastereomers were produced by coupling the same α -lithio ethers with *N,N*-dimethylamides and reducing the resulting ketones with zinc borohydride.¹⁸

Our approach has three principal advantages. First, the *de*'s/*ee*'s are uniformly very high, regardless of the structure, provided DIPED⁸ is used as the chiral director. Other methods generally show much more variable degrees of chiral control. For example, acylstannane reductions can produce α -hydroxy tin compounds (**3**) in high *ee*^{13a} or 90–96% *ee*^{13b} but there are significant exceptions.^{13b} Diastereoselection in the coupling of **5b** to propionaldehyde was only 77:23.¹⁸ Joining two large fragments by aldol coupling can give high diastereoselection,^{6c} but if the opposite diastereomer were desired a different route would be required.

Second, our approach is inherently capable of leading to a wide variety of ultimate products. Although we have so far only converted coupled boronic ester products **6** and **11b** to diols, there is a wide range of other possible transformations, including further insertions into the carbon–boron bond, and a considerable variety of compatible masked functionality.^{2–4} The alternative routes to the tin intermediates **4**¹³ further increase the possible opportunities for the convergent coupling process.

Third, our method can be used to assemble multiple chiral centers. The preparation of **6c** efficiently assembles four chiral centers, the configuration of each of which may be chosen independently of the others. Well-established chemistry⁴ should make it possible to extend this concept to chains of six or more chiral carbons, with or without simple methylene groups interspersed, the only untested assumption being that **6b** and **6c** are effectively as sterically hindered around the connection point as are longer branched chains.

Experimental Section²¹

(S,S)-DIPED (1-Methylethyl)boronate. Freshly crystallized (1-methylethyl)boronic acid (4.4 g) and (3*S*,4*S*)-2,5-dimethyl-3,4-hexanediol [(*S,S*)-DIPED]⁸ (7.3 g) were stirred together in diethyl ether (100 mL). After separation of water and drying over magnesium sulfate, concentration and chromatography on silica yielded 9.1 g (92%) of (*S,S*)-DIPED (1-methylethyl)boronate.

(S,S)-DIPED (R)-(1-Chloro-2-methylpropyl)boronate (1b). (Dichloromethyl)lithium was generated from 5 mL of dichloromethane and 54 mmol of butyllithium in THF at –100 °C under argon as previously described.² A solution of 9.9 g (50 mmol) of (*S,S*)-DIPED (1-methylethyl)boronate in 10 mL of diethyl ether was added dropwise with stirring and the mixture was stirred for 20 min at –100 °C. Anhydrous zinc chloride² (4.7 g, 36 mmol) was added and the mixture was allowed to warm to 25 °C and was stirred for ~15 h. Concentration, extraction with several portions of light petroleum ether (bp 30–60 °C), and re-concentration yielded 11.63 g (94.5%) of crude **1b**: 90-MHz ¹H NMR (CDCl₃) (in part) δ 3.35 (d, 1, *BC*HCl), 3.95 (m, 2, *CH*OB); δ 3.8, ~5% unconverted DIPED (1-methylethyl)boronate.

(S,S)-DIPED (1S)-[1-(Tributylstannyl)-2-methylpropyl]boronate (2b). (Tributylstannyl)lithium was generated by dropwise addition of 4.4 g (15.2 mmol) of tributyltin hydride to a solution of 10 mL of 1.5 M lithium diisopropylamide (LDA) in toluene and ~15 mL of tetrahydrofuran (THF) stirred at 0 °C. After stirring an additional 15 min at 0 °C, the mixture was cooled to –78 °C and 3.7 g (15 mmol) of **1b**

in 10 mL of THF was added dropwise. The mixture was stirred for an additional 30 min at –78 °C and treated with 15 mL of 1 M zinc chloride in ether and was then allowed to warm to 25 °C and stirred for ~15 h. The mixture was concentrated on a rotary evaporator and the residue was treated with saturated ammonium chloride and extracted with several portions of pentane. The solution was dried over magnesium sulfate and concentrated, yielding 7.3 g (97%) of crude **2b**. The only impurity indicated by TLC had a very low polarity and was presumed to be hexabutylditin. The analytical sample was flash chromatographed first with petroleum ether and then with 2% ether in petroleum ether, 84% recovery; $[\alpha]_{D}^{25}$ ₅₄₆ –36.37° (*c* 1.4, toluene).

(R)-1-(Tributylstannyl)-2-methyl-1-propanol (3b). Crude **2b** (7.3 g, from 15 mmol of **1b**) in 40 mL of THF was cooled in an ice bath and 1.5 g (37 mmol) of sodium hydroxide in 8 mL of water was added. Hydrogen peroxide (5 mL of 30%, 50 mmol) was added dropwise. The mixture was kept at 0 °C for 1 h and at 25 °C until TLC analysis indicated consumption of all of the **2b** (6 h). A pasty, white precipitate, apparently mostly sodium borate, formed. The mixture was treated with 50 mL of ether and was filtered, and the aqueous phase was separated and extracted with three 30-mL portions of ether. The combined organic phase was dried over the magnesium sulfate and concentrated to a gel-like mass, which was flash chromatographed on silica with 10% diethyl ether in light petroleum ether, yielding 3.98 g (76% based on **1b**) of **3b**. Elution of the silica with diethyl ether yielded 1.70 g of DIPED, and treatment of the precipitated sodium borate with dilute hydrochloric acid and extraction with ether yielded an additional 0.36 g (total 94% based on **1b**). The labile **3b** was not further characterized and was used promptly in the next step.

(R)-1-(Tributylstannyl)-2-methyl-1-propyl Methoxymethyl Ether (4b). A solution of 3.6 g (10 mmol) of chromatographed **3b** in 10 mL of dichloromethane was cooled to 0 °C and 1.2 g (10 mmol) of diisopropylethylamine was added, followed by 1 mL of chloromethyl methyl ether (Caution: carcinogen). The mixture was stirred for ~1 h at 0 °C and 15 h at 25 °C. The solution was concentrated, treated with ice cold 2 M hydrochloric acid, and extracted with petroleum ether. Concentration of the organic phase (to 0.1 Torr) yielded 3.7 g (92%) of **4b**; $[\alpha]_{D}^{25}$ ₅₄₆ –39.7° (*c* 1.4, toluene).

(S,S)-DIPED (1S,2R)-[1-(1-Methylethyl)-2-(methoxymethoxy)-3-methylbutyl]boronate (6b). A solution of 2 mL of 1.6 M butyllithium was added dropwise to a solution of 1.22 g (3 mmol) of **4b** in 10 mL of THF stirred at –78 °C. After 30 min at –78 °C, the mixture was cooled to –100 °C with a liquid nitrogen/95% ethanol bath, a solution of 0.73 g (3 mmol) of **1b** in 5 mL of THF was added dropwise, and stirring was continued an additional 30 min at –100 °C. Two procedures from this point yielded similar results: (a) The mixture was warmed to 0 °C and concentrated under vacuum, with care to avoid admission of air. The pasty residue was dissolved in 10 mL of anhydrous acetonitrile and kept at 25 °C for 15 h. (b) The mixture was warmed to 25 °C and treated with 2.5 mmol of anhydrous zinc chloride. After 15 h at 25 °C, the solution was concentrated, the residue was treated with saturated aqueous ammonium chloride, and the product was extracted with petroleum ether. After a or b, chromatography on silica with 3% diethyl ether in light petroleum ether yielded 0.67 g (68%) of **6b**; $[\alpha]_{D}^{25}$ ₅₄₆ –69.7° (*c* 1.4, toluene). The ¹H NMR of early and late fractions revealed the same proportion, ~1%, of the (1*S*,2*S*)-diastereomer **11b** at δ 3.73 and 4.68.

(1S,2S)-2-(Methoxymethoxy)-3-methyl-1-(1-methylethyl)butanol (7b). A solution of 0.66 g (2 mmol) of **6b** in 10 mL of THF was cooled to 0 °C and 0.1 g (2.5 mmol) of sodium hydroxide in 2 mL of water was added, followed by dropwise addition of 0.3 mL of 30% hydrogen peroxide. After 1 h at 0 °C and 4 h at 25 °C, TLC analysis indicated complete reaction. A pasty mass of sodium borate and aqueous solution had separated, and treatment with 1 mL of ethanol and 20 mL of ether resulted in a solid precipitate, which was filtered. The two-phase filtrate was separated and the aqueous phase was washed with three 10-mL portions of ether. The combined organic phase was dried (magnesium sulfate) and concentrated. Chromatography on silica with 10% diethyl ether in light petroleum ether yielded 0.34 g (89%) of **7b**; 200-MHz ¹H NMR (CDCl₃): δ 3.25 (m, 1, *CH*OC), 3.32 (m, 1, *CH*OH), 3.43 (s, 3, *OCH*₃), 4.66 + 4.75 (d, *J* = 6.6 Hz, 2, *OCH*₂O). Elution of the column with diethyl ether resulted in recovery of 255 mg of DIPED, and treatment of the borate precipitate with acid followed by ether extraction yielded an additional 28 mg of DIPED, total recovery 97%.

(3S,4S)-2,5-Dimethyl-3,4-hexanediol [(S,S)-DIPED] (8b). A solution of 130 mg (0.68 mmol) of **7b** in 2 mL of methanol and 1 drop of concentrated hydrochloric acid was refluxed for 15 min.²² The solution was concentrated and the residue was dissolved in diethyl ether, washed with sodium bicarbonate solution, and dried over magnesium sulfate. On

(21) Satisfactory analyses for all elements except O were obtained for **2a** (except Sn calcd 23.04, found 24.40), **2b**, **4a**, **4b** (except Sn calcd 29.15, found 28.21), **6a-c**, **11**, and **12**. Microanalyses were by Galbraith Laboratories, Knoxville, TN. ¹H NMR (200 MHz) support all assigned structures (except labile **3**, not determined). Reactions involving carbanions or air-sensitive reagents were run under argon. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl. Other chemicals were reagent grade. Zinc chloride was vacuum dried at 100 °C (0.1 Torr). Instruments used included a Nicolet NT-200 high-field NMR spectrometer, a JEOL FX-90Q 90-MHz NMR spectrometer, a VG instruments 7070 EHF mass spectrometer, and a JASCO DIP-181 digital polarimeter. Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Only series **b** preparations and partial characterization data are described here. The other preparations and details of characterization are recorded as supplementary data.

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concentration, 83 mg (84%) of **8b** was obtained;²³ mp and mixture mp 72–74 °C; 200-MHz ¹H NMR (DMSO-*d*₆): δ 3.98 (m, 2, CHOH). TLC analysis of the ether extract before concentration indicated the presence of a small amount of the formaldehyde DIPED acetal [(4*S*,5*S*)-4,5-bis(1-methylethyl)-1,3-dioxolane]. A compound with the same retention time was obtained by treating (*S*,*S*)-DIPED with formaldehyde under the acid hydrolysis conditions.

(*R*,*3R*)-2,3-Butanediol (1*S*)-(1-Chloro-2-methylpropyl)boronate (**9**). (*2R*,*3R*)-2,3-Butanediol (1-methylethyl)boronate (50 mmol) was prepared from 2,3-butanediol and isopropylboronic acid in ether in the usual manner, bp 56–60 °C (20 Torr), and treated with (dichloromethyl)lithium (54 mmol) in the usual manner.² After workup with petroleum ether, 10.6 g of **9**¹⁶ was obtained.

(*2R*,*3R*)-2,3-Butanediol (1*R*)-[1-(Tributylstannyl)-2-methylpropyl]boronate. (Tributylstannyl)lithium (20 mmol) was prepared as described for the preparation of **2b** and reacted with 20 mmol of **9**. The crude product was isolated by workup with saturated ammonium chloride and petroleum ether followed by concentration (96%). Attempted purification by chromatography resulted in extensive hydrolytic decomposition of the butanediol ester, and the crude product was used directly in the next step.

(23) Net gain of (*S*,*S*)-DIPED (**8b**) in self-replicating synthesis: Synthesis of 0.75 mol of **8b** requires 1 mol of **1b**, which, if DIPED isopropylboronate is made quantitatively, requires 1.06 mol of **8b** and regenerates 0.97 mol, and 1 mol of **4b**, which requires 1.56 mol of **8b** and regenerates 1.38 mol; hence 2.62 mol → 3.10 mol, 118%. Our recorded yield in the first step was 92%: (1.15 + 1.70 mol of **8b** → 3.1 mol, 108.8%. With quantitative recovery of all invested **8b**, probably feasible if byproducts are processed, the maximum without other yield improvements would be (1.06 + 1.56) → 3.37, 128%.

(1*S*)-1-(Tributylstannyl)-2-methyl-1-propanol (Enantiomer of **3b**). A solution of 6.6 g (15 mmol) of crude (*2R*,*3R*)-2,3-butanediol (1*R*)-[1-(tributylstannyl)-2-methylpropyl]boronate in 15 mL of THF at 0 °C was treated with 0.67 g (17 mmol) of sodium hydroxide in 2 mL of water and 2.4 g (15 mmol) of sodium perborate. After 1 h at 0 °C and 4 h at 25 °C, the precipitate of sodium butanediol borate was filtered. The filtrate was diluted with pentane, dried over magnesium sulfate, and concentrated to yield 5.4 g of a crude enantiomer of **3b**, which was used directly in the next step.

(1*S*)-1-(Tributylstannyl)-2-methyl-1-propyl Methoxymethyl Ether (Enantiomer of **4b**). The crude enantiomer of **3b** was used in place of **3b** in the previously described procedure. The yield of chromatographed enantiomer of **4b** was 76% based on **9**.

(*S*,*S*)-DIPED (1*S*,*2S*)-[1-(1-Methylethyl)-2-(methoxymethoxy)-3-methylbutyl]boronate (**11b**). The lithio intermediate **10b** was prepared from the enantiomer of **4b** (4 mmol) as described for the preparation of **5b**. Reaction with **1b** was carried out as described for **6b** via route b, except that zinc chloride was not added. The yield of **11b** was 0.76 g (58%).

(*3R*,*4S**)-2,5-Dimethyl-3,4-hexanediol (*meso*-DIPED) (**12**). Oxidation of **11b** with sodium perborate followed by acid hydrolysis yielded *meso*-DIPED (**12**), 89%, mp 126–128 °C; 200-MHz ¹H NMR (DMSO-*d*₆): δ 4.13 (m, 2, CHOH).

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Supplementary Material Available: Full experimental details of preparation of **a** and **c** series of compounds, plus NMR and analytical data for **b** series (5 pages). Ordering information is given on any current masthead page.

A Time-Resolved EPR Study on Photodecomposition of Dibenzoyl Peroxides in Carbon Tetrachloride

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Abstract: We have investigated the photodecomposition of a series of dibenzoyl peroxides in carbon tetrachloride by means of time-resolved EPR spectroscopy. The EPR spectra of the intermediate benzoyloxy and trichloromethyl radicals were identified and the reaction mechanisms were clarified. It is shown that the decarboxylation takes place mostly from the intermediate benzoyloxy radicals whose lifetimes are on the order of 1 μs at room temperature. The rate constants for the decarboxylation determined from the transient EPR signals were in good agreement with those obtained from the transient absorption. On the basis of the observed polarization of the EPR signals, it is concluded that the spin states of the intermediate radicals are in thermal equilibrium within 0.5 μs after the laser excitation. In aerated systems additional radicals with larger *g* values were detected and tentatively assigned as phenylperoxy radicals.

1. Introduction

The photodecomposition of dibenzoyl peroxides has been studied extensively by using various methods including EPR,¹ CIDNP,² transient absorption,³ spin trapping,⁴ and product analysis.⁵

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Among these studies only the EPR technique has made it possible to detect the intermediate radicals such as aryloxy and aryl radicals in crystalline systems at low temperatures (≤25 K). In a single crystal of dibenzoyl peroxide (BPO) an EPR signal was observed at 4.2 K by Box et al.^{1a} and was assigned as that of a pair of phenyl radicals. On the other hand, McBride's group found an EPR signal in crystalline acetyl benzoyl peroxide at 7–12 K

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