8, PhCH_2O), 7.0-7.37 (m, 20, C_6H_5), 9.61 (d, J = 0.8 Hz, 1, CHO), with impurities at δ 1-2, 5.07; 22.6 MHz ^{13}C NMR (C_6D_6) δ 69.8, 72.8, 72.9, 73.2, 73.5, 77.6, 81.2, 83.1, 126.9, 127.7, 127.8, 128.1, 128.5, 129.1, 138.3, 138.6, 138.9, 139.0, 200.2; IR 1726 cm^{-1} (C=O). Hydrogenation of this material over 100 mg of 10% palladium on charcoal in ethanol for 24 h, filtration, concentration, and recrystallization from ethanol yielded 28 mg (97% based on **11b**) of L-ribose (**12**): mp and mixture mp (with sample purchased from Aldrich) 85-86 °C; $[\alpha]^{23}_D$ +18.6° (c 0.6, H_2O) (lit.[21] +18.8° for L, -19.5° for D); 200-MHz ^{1}H NMR (D_2O) δ 3.5-4.2 (m), identical with that of an Aldrich sample.

(3*R*)-1,3,4-Tris(benzyloxy)-1-butene (13). Reaction of 1.61 g (2.44 mmol) of (*s*)-pinanediol (1*R*,2*R*,3*S*)-[1,2,3,4-tetrakis(benzyloxy)butyl]boronate (**9**) with chloroiodomethane and butyllithium in the usual manner[11] was followed 3.5 h later by addition of 6.1 mmol of zinc chloride in diethyl ether. After overnight at room temperature and workup with saturated ammonium chloride and ether, the mixture of products (1.59 g) was separated by flash chromatography with 10% diethyl ether in light petroleum ether; TLC with 20% diethyl ether/light petroleum ether; R_f 0.42 and R_f 0.28. The latter was identified as pinanediol [(benzyloxy)methyl]boronate (**1a**) by ^{1}H NMR. The more mobile fraction, 0.76 g (83%), was **13**: mp 28-30 °C; 200-MHz ^{1}H NMR ($CDCl_3$) δ 3.56 (m, 2, COCH_2CH), 3.93 (m, 1, CH_2CHOC), 4.56 (m, 2, PhCH_2O), 4.57 (m, 2, PhCH_2O), 4.75 (s, 2, PhCH_2O), 4.82 (dd, J = 9.1, 12.8 Hz, 1, CCH=CHOC), 6.53 (d, J = 12.8 Hz, 1, CH=CHOC), 7.19-7.48 (m, 15, C_6H_5); 22.6-MHz ^{13}C NMR ($CDCl_3$) δ 69.4, 71.1, 73.2, 73.8, 76.3, 102.0, 127.3, 127.5, 127.6, 127.9, 128.2, 128.4, 136.6, 138.4, 138.7, 150.0. Analytical purity was not achieved. Anal. Calcd for $C_{25}H_{26}O_3$: C, 80.18; H, 7.00. Found: C, 78.93; H, 6.94.

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Conversion of α-Halo Boronic Esters to Inverted α-(Methylsulfonyl)oxy Boronic Esters

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The conversion of a pinanediol (α*S*)-α-halo boronic ester (**1**) via an (α*R*)-α-(methoxybenzyl)oxy boronic ester (**2a,b**) to an (α*R*)-α-hydroxy boronic ester (**3**) and then to the (α*R*)-methanesulfonate (**4**) followed by displacement of the methanesulfonate by lithium benzyl oxide yields the (α*S*)-α-benzyloxy boronic ester (**5**), the product of two inversions at the α-carbon atom. This work establishes that methoxylated benzyl groups can be deprotected oxidatively in the presence of the boronic ester function. The double inversion allows assembly of adjacent chiral centers, with one of them having its absolute configuration opposite to that directed by the pinanediol boronic ester group. These results also provide unequivocal direct proof of inversion in nucleophilic displacement at the α-carbon of a boronic ester.

The first demonstration of the potential utility of chiral synthesis with α-chloro boronic esters featured the controlled construction of (2*S*,3*S*)-3-phenyl-2-butanol and its diastereomer (2*S*,3*R*)-3-phenyl-2-butanol.[1] The first diastereomer was the natural result of two sequential homologations of (*s*)-pinanediol phenylboronate with subsequent simple manipulations. The second diastereomer was reached by cleaving the (*s*)-pinanediol after the first homologation and replacing it by its enantiomer (*r*)-pinanediol to direct the second homologation in the opposite sense. Unfortunately, the conditions required for the pinanediol cleavage, treatment with boron trichloride, are incompatible with any sensitive functionality.

Where only pairs of chiral centers are involved, it is often possible to choose the sequence of introduction of groups and the chirality of the pinanediol at the outset so that the ultimate product will be any desired one of the four possibilities.[2] Alternatively, (*R*,*R*)-2,3-butanediol has been shown to be a good chiral directing group that can be cleaved rapidly by water at room temperature,[3] though it has not actually been used to assemble two chiral centers.

None of the foregoing approaches can be used with [(benzyloxy)alkyl]boronic esters. Boron trichloride cleaves benzyloxy groups under the required conditions,[4] the chloromethylene group cannot be inserted into a carbon-oxygen bond,[5] and (*R*,*R*)-2,3-butanediol has failed to produce a useful diastereomeric excess in the reaction of its [(benzyloxy)methyl]boronate ester with (dichloromethyl)lithium.[6]

The recent report that (methoxybenzyl)oxy protecting groups can be cleaved with dichlorodicyanoquinone (DDQ) to yield alcohols, even in the presence of benzyloxy groups,[7] led us to investigate the compatibility of this differential hydroxyl protection system with boronic ester chemistry. One reason for choosing this system was that the reactions of pinanediol α-halo boronic esters with lithium benzyl oxide were already well established to occur without significant side reactions.[2,8] Displacement of the α-halide involves formation of an intermediate tetrahedral borate complex, and there is always a chance that competing oxide migrations will yield a mixture of products.[9]

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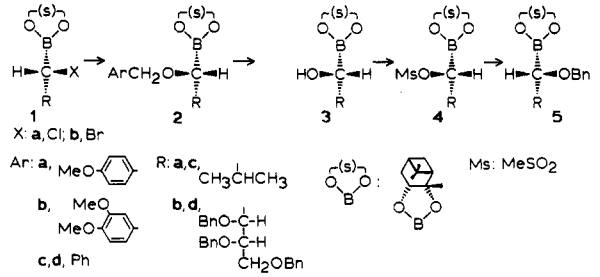
Results

(*s*)-Pinanediol (1*S*)-(1-chloro-2-methylpropyl)boronate (**1a**)[4] was chosen as a convenient test substrate to find out whether a simple double-inversion sequence could be carried out. First, **1a** was converted to the known



(1*R*)-[1-(benzyloxy)-2-methylpropyl]boronate (**2c**),[10] which was found to undergo smooth hydrogenolysis over palladium to yield (*s*)-pinanediol (1*R*)-(1-hydroxy-2-methylpropyl)boronate (**3a**). Although **3a** might seem a prosaic structure, its known precedents consist of two α-hydroxy boronic acids, which were characterized as their cyclic dimeric anhydrides.[11,12] α-Amino boronic esters or acids containing a free NH group deboronate so readily that only two examples have been even partially characterized.[13,14] Thus, the ordinary stability of **3a** was an auspicious finding.

Conversion of **3a** to its methanesulfonate ester **4a** was first attempted with methanesulfonyl chloride and pyridine, but these conditions regenerated the original α-chloro boronic ester **1a**. Evidently **4a** was formed but reacted with the released chloride ion, reinverting the α-carbon to form **1a**. The ^{1}H NMR C*H*Cl multiplet of **1a** is δ 0.02 downfield from that of the (1*R*) epimer,[3] which was not detected at a threshold level of a few percent. Thus, methanesulfonate is displaced from **4a** much faster than is chloride from **1a** by chloride ion.

Efficient conversion of **3a** to **4a** was achieved with methanesulfonyl chloride and triethylamine at 0 °C. This reaction proved fast enough that no detectable amount of byproduct **1a** was formed. The very reactive **4a** decomposed on standing or attempted purification but was efficiently converted to (*s*)-pinanediol (1*S*)-[1-(benzyloxy)-2-methylpropyl]boronate (**5a**) by lithium benzyl oxide. The ^{1}H NMR pinyl C*H* doublet at δ 1.194 distinguished **5a** from its (1*R*) epimer **2c**, δ 1.160, which was not detected at a threshold level of 2%.

Methoxybenzyl Groups. Reaction of **1a** with lithium *p*-methoxybenzyl oxide yielded (*s*)-pinanediol (1*R*)-[1-[*p*-methoxybenzyl)oxy]-2-methylpropyl]boronate (**2a**). Deprotection with DDQ[7] to the α-hydroxy boronic ester **3a** proceeded efficiently, showing that the boronic ester group is stable to these oxidizing conditions.

As a further demonstration of the utility of this synthetic operation, reaction of the α-bromo boronic ester **1b** with lithium 3,4-dimethoxybenzyl oxide yielded the (1*R*,2*R*,3*S*)-[1-[(3,4-dimethoxybenzyl)oxy]-2,3,4-tris(benzyloxy)butyl]boronate **2b**, which was deprotected with DDQ to the α-hydroxy boronic ester **3b**. Conversion of **3b** to the methanesulfonate **4b** was followed by displacement with lithium benzyl oxide to form (*s*)-pinanediol (1*S*,2*R*,3*S*)-[1,2,3,4-tetrakis(benzyloxy)butyl]boronate (**5b**).

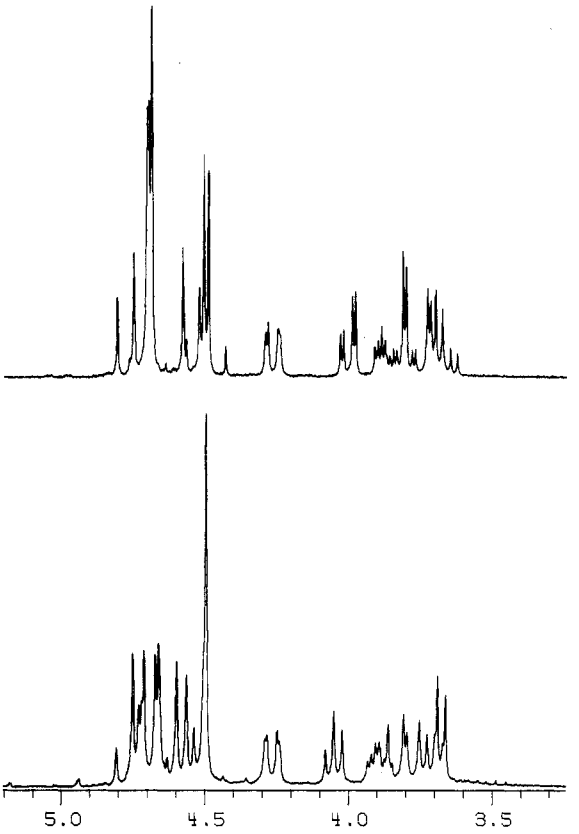


Figure 1. C*H*OR regions of the 200-MHz ^{1}H NMR spectra of (*s*)-pinanediol (1*R*,2*R*,3*S*)-[1,2,3,4-tetrakis(benzyloxy)butyl]boronate (**2d**; upper curve) (data by M. L. Peterson[8]) and its (1*S*,2*R*,3*S*) isomer **5b** (lower curve).

The (1*R*,2*R*,3*S*) diastereomer **2d** of **5b** has been made,[8] and comparison of the 200-MHz ^{1}H NMR spectra shows no evidence of any **2d** contaminating the **5b**, as well as no evidence of any **5b** in the sample of **2d** at a threshold level of about 1%. The C*H*OR regions of the spectra are illustrated in Figure 1. These results do not prove that the syntheses are stereospecific, inasmuch as small amounts of diastereomer might have been separated by chromatography and escaped detection, but the stereoselectivity has to be very high.

The complexity of the NMR spectra makes them difficult to analyze in detail, but the pinyl protons of **2b**, **3b**, and **4b** as well as **2d** in the region δ 1.6–2.4 show similar patterns, and there is a marked change in the pattern when the 1-carbon is inverted to form **5b**. Similarly, the benzylic and C*H*OR protons at δ 3.6–4.8 (Figure 1) show consistent relationships that abruptly change with the inversion to form **5b**.

Other Bases. Exploratory attempts were made to utilize sodium hydroxide or sodium triethylsilyl oxide with the α-chloro boronic ester **1a** and related compounds, but the only products appeared to involve attack of the base on boron and migration of either of the pinanediol oxygen atoms to displace the chloride ion. It appeared that both of the possible isomers from this ring expansion of the pinanediol ester group were formed in about equal amounts. This reaction of the pinanediol group leaves the remaining site on boron occupied by hydroxy or labile silyloxy, and TLC showed two adjacent polar components. The C*H*OR NMR absorption, which appears at δ 3.08 for **1a**, was shifted upfield to δ 2.68, and the pinyl C*H*OB

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multiplet, which usually appears at δ 4.2–4.4, was shifted to δ 3.67.

Because these reactions were pursued only far enough to show that they were definitely not leading toward our synthetic goal, further details will be omitted. There is as yet no evidence as to whether the crucial difference was in the cation (sodium rather than lithium) or in the size of the nucleophile itself.

Discussion

These results have demonstrated an efficient means of inverting the chirality that has been induced by the pinanediol group on the boronic ester to α-halo boronic ester homologation process. This inversion can be used in the construction of a series of adjacent chiral centers, so that a single enantiomer of pinanediol can be left in place and either absolute configuration can be chosen at each chiral center of the product.[15] The displacement of methanesulfonate from the intermediate has only been demonstrated with the nucleophiles benzyl oxide and chloride to date, but in view of the high reactivity of the methanesulfonate, general applicability is expected.

Although it may be possible to develop a chiral directing group that can be hydrolyzed easily from the boronic ester and replaced by its enantiomer for introduction of the next carbon, that has not yet been fully demonstrated, and pinanediol has some useful practical features. It is readily available in both enantiomeric forms, and its very stable boronic esters are easily purified by chromatography and other standard techniques. Other chiral diols that will work in this synthesis are likely to be more expensive and laborious to make.

We abandoned plans to convert **5b** to higher homologues and ultimately to glucose when it became evident from the parallel ribose synthesis[8] that connection of the fifth carbon would be inefficient, evidently for steric reasons. Even with this steric limitation, our new methodology should be applicable to the synthesis of a variety of deoxy sugars. The general utility of our approach to sugar synthesis has already been discussed.[8]

In a broader synthetic context, the methoxybenzyl groups provide a tested means of differentiated hydroxyl protection, readily cleavable without disturbing the boronic ester function, which may prove useful in a variety of applications.

Experimental Section

General Data. Reactions involving air-sensitive reagents were run under argon. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl. (*s*)-Pinanediol[2,16] was prepared from (+)-α-pinene of 99% ee purchased from Aldrich Chemical Co. Instruments used included a Nicolet NT-200 high-field NMR spectrometer, a JEOL FX-90Q NMR spectrometer, a VG Instruments 7070 EHF mass spectrometer, and a Jasco DIP-181 digital polarimeter. Microanalyses were by Galbraith Laboratories, Knoxville, TN.

(*s*)-Pinanediol (1*R*)-[1-[(*p*-Methoxybenzyl)oxy]-2-methylpropyl]boronate (2a). (*s*)-Pinanediol (1*S*)-(1-chloro-2-methylpropyl)boronate (**1a**) was added to an equivalent amount of lithium *p*-methoxybenzyl oxide in THF at −78 °C, allowed to react overnight at 20–25 °C, and then worked up in the usual manner;[2] 82%; 90-MHz ^{1}H NMR ($CDCl_3$) δ 0.84 (s, 3, pinyl CH_3), 0.98 (dd, 6, $CH(CH_3)_2$), 1.21 (d, 1, pinyl C*H*), 1.29 (s, 3, pinyl CH_3), 1.39 (s, 3, pinyl CH_3), 1.65–2.45 (m, 6, pinyl C*H*, $CH(CH_3)_2$), 3.08 (t, 1, OC*H*B), 3.81 (s, 3, OCH_3), 4.28 (dd, 1, C*H*OB), 4.55 (m, 2, OCH_2Ar), 6.8–7.4 (m, 4, C_6H_4); mass spectrum, *m/e* calcd for $C_{22}H_{31}BO_4$ 370.2315, found 370.2297.

(*s*)-Pinanediol (1*R*)-[1-Hydroxy-2-methylpropyl]boronate (3a). A solution of 230 mg (0.62 mmol) of (*s*)-pinanediol (1*R*)-[1-(*p*-methoxybenzyl)-2-methylpropyl]boronate (**2a**) in 5 mL of dichloromethane was stirred with 1 mL of water, and 168 mg (0.74 mmol) of 2,3-dichloro-5,6-dicyanoquinone was added. After being stirred for 2.5 h at 20–25 °C, the mixture was filtered through a Celite pad with the aid of more dichloromethane. The dichloromethane phase was washed with aqueous sodium bicarbonate followed by sodium chloride solution, then dried over sodium sulfate, filtered, and concentrated. The residue was chromatographed with 1:1 diethyl ether/light petroleum ether to yield 140 mg (92%) of **3a** as an oil. [In an alternative preparation, a solution of 200 mg (0.58 mmol) of pinanediol (1*R*)-[1-(benzyloxy)-2-methylpropyl]boronate (**2c**) in 5 mL of absolute ethanol was stirred with 10 mg of 5% palladium on charcoal under 1 atm of hydrogen at room temperature for 12 h; yield 88%] **3a**: 200-MHz ^{1}H NMR ($CDCl_3$) δ 0.85 (s, 3, pinanyl CH_3), 0.95 (dd, 6, $CH(CH_3)_2$), 1.15 (d, 1, pinyl C*H*), 1.28 (s, 3, pinyl CH_3), 1.38 (s, 3, pinyl CH_3), 1.62 (d, 1, O*H*), 1.65–2.45 (m, 6, pinyl C*H*, $CH(CH_3)_2$), 3.35 (t, 1, C*H*OH), 4.35 (dd, 1, C*H*OB); mass spectrum, *m/e* calcd for $C_{14}H_{25}BO_3$ 252.1896, found 252.1931.

(*s*)-Pinanediol (1*R*)-[1-[(Methylsulfonyl)oxy]-2-methylpropyl]boronate (4a). Methanesulfonyl chloride (252 mg, 2.2 mmol) was added dropwise to a solution of 500 mg (1.98 mmol) of (*s*)-pinanediol (1*S*)-(1-hydroxy-2-methylpropyl)boronate (**3a**) and 500 mg (5 mmol) of triethylamine in 20 mL of dichloromethane at 0 °C under argon. After 15 min the ice bath was removed, and the mixture was stirred for 0.5 h. The reaction mixture was diluted with 20 mL more dichloromethane and extracted with 30 mL of cold water followed by 2 × 20 mL of cold 1 M aqueous hydrochloric acid, 2 × 10 mL of cold 10% aqueous sodium bicarbonate, and 50 mL of saturated aqueous sodium chloride. The organic phase was concentrated to yield **4a** (90%), which decomposed on standing and was used without further purification: 200-MHz ^{1}H NMR ($CDCl_3$) δ 0.85 (s, 3, pinyl CH_3), 1.08 (d, 6, $CH(CH_3)_2$), 1.15 (d, 1, pinyl C*H*), 1.32 (s, 3, pinyl CH_3), 1.43 (s, 3, pinyl CH_3), 1.75–2.55 (m, 6, pinyl C*H*, $CH(CH_3)_2$), 3.05 (s, 3, CH_3SO_2), 4.28 (d, 1, C*H*OSO$_2$Me), 4.38 (dd, 1, C*H*OB).

(*s*)-Pinanediol (1*S*)-[1-(Benzyloxy)-2-methylpropyl]boronate (5a). A solution of 75 mg (0.69 mmol) of benzyl alcohol in 3 mL of THF was treated with an equivalent amount of butyllithium at −78 °C, followed by dropwise addition of 200 mg (0.61 mmol) of the methanesulfonate **4a** in 2 mL of THF. The mixture was stirred at 20–25 °C for 18 h, then treated with 5 mL of saturated aqueous ammonium chloride, and extracted with 30 mL of ether. The organic layer was washed with water (2 × 5 mL) followed by saturated sodium chloride (5 mL), then dried over sodium sulfate, and concentrated. Chromatography on silica with 10:1 light petroleum ether/diethyl ether yielded 203 mg (98%) of 5a: 200-MHz ^{1}H NMR ($CDCl_3$) δ 0.85 (s, 3, CH_3), 0.95 (dd, 6, $CH(CH_3)_2$), 1.194 (d, J = 11 Hz, 1, pinyl C*H*) [(1*R*) epimer, 1.160 (d, <0.02)], 1.28 (s, 3, pinyl CH_3), 1.38 (s, 3, pinyl CH_3), 1.65–2.45 (m, 6, pinyl C*H*, $CH(CH_3)_2$), 3.08 (t. 1, OC*H*B), 4.55 (dd, 1, C*H*OB); mass spectrum, *m/e* calcd for $C_{21}H_{31}BO_3$ 342.2366, found 342.1788.

(*s*)-Pinanediol (*S*)-(1-Chloro-2-methylpropyl)boronate (1a) from (*s*)-Pinanediol (1*R*)-(1-Hydroxy-2-methylpropyl)boronate (3a). To a solution of 1.00 g (3.96 mmol) of the hydroxyalkylboronate **3a** in 5 mL of anhydrous pyridine at 0 °C under argon was added 680 mg (5.93 mmol) of redistilled methanesulfonyl chloride over a period of 5 min. The mixture was allowed to warm to 20–25 °C and stirred overnight. Ice was added, the mixture was stirred for 10 min, and 50 mL of dichloromethane was added. The organic phase was washed with 0.1 M hydrochloric acid followed by water. After concentration and chromatography, the yield of chloro compound **1a** was 1.07 g (70%). This was shown to be essentially pure (1*S*) isomer from the ^{1}H NMR doublet at δ 3.32.

(*s*)-Pinanediol (1*R*,2*R*,3*S*)-[1-[(3,4-Dimethoxybenzyl)oxy]-2,3,4-tris(benzyloxy)butyl]boronate (2b). (*s*)-Pinanediol (1*S*,2*S*,3*S*)-[1-bromo-2,3,4-tris(benzyloxy)butyl]boronate (**1b**) was added to an equivalent amount of lithium 3,4-dimethoxybenzyl oxide in THF at −78 °C, and the resultant mixture was then kept

(15) This broad general statement assumes that an existing chiral center has negligible influence on the introduction of the next. This assumption appears true insofar as it has been examined,[1] and other work suggests little influence on chiral selection by existing functionality,[2-4,8] but there is a possibility of undiscovered exceptions.

(16) Ray, R.; Matteson, D. S. *J. Indian Chem. Soc.* **1982**, *59*, 119–123.

at room temperature 15–20 h and worked up with saturated ammonium chloride and ether. The product was chromatographed on silica with 2:3 diethyl ether/light petroleum ether: 74%; 200-MHz ^{1}H NMR ($CDCl_3$) δ 0.78 (s, 3, CH_3), 1.21 (d, 1, pinyl C*H*), 1.24 (s, 3, CH_3), 1.29 (s, 3, CH_3), 2.03–2.39 (m, 5, pinyl C*H*), 3.79 (s, 3, OCH_3), 3.86 (s, 3, OCH_3), 3.67–3.97 (m, 4, C*H*OC), 4.27 (dd, 1, C*H*OB), 4.48–4.81 (m, 8, CH_2O), 6.7–6.9 (m, 3, C_6H_3), 7.2–7.3 (m, 15, C_6H_5). Anal. Calcd for $C_{44}H_{53}BO_8$: C, 73.33; H, 7.41; B, 1.50. Found: C, 73.30; H, 7.75; B, 1.45.

(*s*)-Pinanediol (1*R*,2*R*,3*S*)-[1-Hydroxy-2,3,4-tris(benzyloxy)butyl]boronate (3b). Treatment of **2b** with DDQ under the conditions used for the preparation of **3a** from **2a** yielded 86% **3b** as an oil: 200-MHz ^{1}H NMR ($CDCl_3$) δ 0.7 (s, 3, CH_3), 1.19 (d, 1, pinyl C*H*), 1.23 (s, 3), 1.24 (s, 3) (CH_3's), 1.8–2.2 (m, 5, pinyl C*H*), 3.6–3.9 (m, 5, C*H*O), 4.02 (d, br, 1, O*H*), 4.25 (dd, 1, C*H*OB), 4.4–4.7 (m, 6, $PhCH_2O$), 7.2–7.4 (m, 15, C_6H_5). Anal. Calcd for $C_{35}H_{43}BO_6$: C, 73.68; H, 7.60; B, 1.89. Found: C, 73.46; H, 7.83; B, 1.84.

(*s*)-Pinanediol (1*R*,2*R*,3*S*)-[1-[(Methylsulfonyl)oxy]-2,3,4-tris(benzyloxy)butyl]boronate (4b). Treatment of **3b** methanesulfonyl chloride under the conditions used for conversion of **3a** to **4a** yielded 90% of crude **4b**: 90-MHz ^{1}H NMR ($CDCl_3$) δ 0.78 (s, 3, CH_3), 1.20 (d, 1, pinyl C*H*), 1.25 (s, 3), 1.26 (s, 3) (CH_3's), 1.5–2.15 (m, 5, pinyl C*H*), 2.90 (s, 3, CH_3SO_2), 3.6–3.7 (m, 3), 4.03 (dd, 1, C*H*OB), 4.29–4.56 (m, 4), 4.70 (s, 2), 4.76 (d, 1), 5.06 (d, 1), 7.2–7.4 (m, 15, C_6H_5). This unstable compound was used directly in the next step.

(*s*)-Pinanediol (1*S*,2*R*,3*S*)-[1,2,3,4-Tetrakis(benzyloxy)-butyl]boronate (5b). Reaction of **4b** to lithium benzyl oxide in THF under the conditions described for the conversion of **4a** to **5a** followed by flash chromatography yielded 70% **5b**: 200-MHz ^{1}H NMR ($CDCl_3$) δ 0.79 (s, 3, CH_3), 1.17 (d, 1, pinyl C*H*), 1.25 (s, 3), 1.27 (s, 3) (CH_3's), 1.8–2.5 (m, 5, pinyl C*H*), 3.7–4.1 (m, 5, C*H*OC), 4.26 (dd, 1, C*H*OB), 4.5–4.8 (m, 8 $PhCH_2O$), 7.2–7.4 (m, 20, C_6H_5). Anal. Calcd for $C_{42}H_{49}BO_9$: C, 76.36; H, 7.48; B, 1.64. Found: C, 76.31; H, 7.91; B, 1.61.

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Registry No. **1a**, 89618-77-9; **1b**, 110488-65-8; **2a**, 110488-62-5; **2b**, 110488-66-9; **2c**, 109737-32-8; **3a**, 110488-63-6; **3b**, 110488-67-0; **4a**, 110488-64-7; **4b**, 110488-68-1; **5a**, 110548-88-4; **5b**, 110488-69-2; lithium *p*-methoxybenzyl oxide, 57965-13-6.

Solid-State Photoreactivity of Ethyl (*E*)-α-Cyano-2-methoxycinnamate

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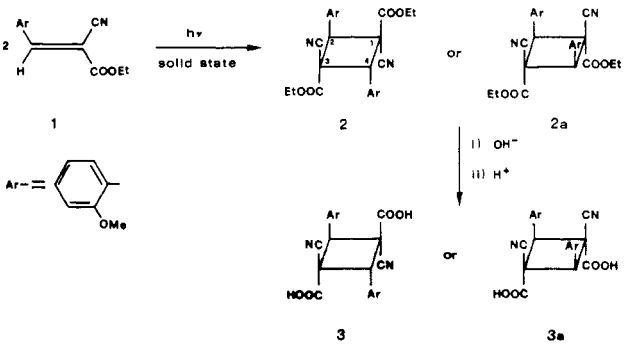
The reinvestigation of the solid-state photoreactivity of ethyl (*E*)-α-cyano-2-methoxycinnamate (1) allowed us to obtain the corresponding dimer which was shown to be diethyl (1α,2α,3β,4β)-1,3-dicyano-2,4-bis(2-methoxyphenyl)cyclobutane-1,3-dicarboxylate (2) whose structure was proven on the basis of chemical reactivity and spectroscopic data.

A large number of studies on the solid-state photoreactivity of cinnamic acids[1] and styryl derivative compounds[2] showed that the cyclobutane dimers formed had the configuration expected on the basis of the topochemical postulate.[1] In particular, (*E*)-α-cinnamic acid and (*E*)-β-4-chlorocinnamic acid gave α-truxillic acid and 4,4'-dichloro-β-truxinic acid, respectively.

During the study of the solid-state photoreactivity of 3-methyl-4-nitro-5-styrylisoxazoles,[3] we were attracted by the findings of Baker and Howes[4] who reported that the solid-state irradiation of the yellow ethyl (*E*)-α-cyano-2-methoxycinnamate (1) gave a colorless compound with a molecular weight in agreement with a dimer $C_{26}H_{26}N_2O_6$, which was described as "probably one stereoisomer of diethyl 1,3-dicyano-2,4-bis-*o*-methoxyphenylcyclobutane-1,3-dicarboxylate" (truxillic acid structure). Truxinic type structures were not considered for the above dimer.

Following our interest in the preparation of α-truxillic acids via 3-methyl-4-nitro-5-styrylisoxazole photodimers,[3] we decided to reinvestigate the photobehavior of the title compound in order to attribute a configuration of the photodimer and to search for a new entry for the synthesis of diarylcyclobutanedicarboxylic acids.

Scheme I



Results and Discussion

Solid compound 1, prepared according to the literature,[4] was irradiated with sunlight[4] or with a mercury lamp. In both cases, the colorless dimer was obtained in agreement with the previous findings. This solid was recognized as the dimer of 1 on the basis of the melting point[4] and mass spectra, which showed peaks at *m/e* 462 and 231 attributable to M^+ of the dimer and to the symmetric fragment $ArCH{=}C(CN)CO_2Et]^+$, respectively. The absence of the fragment $ArCH{=}CHAr]^+$ together with the above findings is in agreement with a truxillic type structure for the

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(2) Green, B. S.; Heller, L. *J. Org. Chem.* **1974**, *39*, 196.
(3) Baracchi, A.; Chimichi, S.; De Sio, F.; Donati, D.; Nesi, R.; Sarti-Fantoni, P.; Torroba, T. *Heterocycles* **1986**, *24*, 2863.
(4) Baker, W.; Howes, C. S. *J. Chem. Soc.* **1953**, 119.

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