change in ^{199}Hg chemical shift upon complexation with a ligand. We have previously utilized this sensitive analytical probe to accurately measure the complexation of MeHgOAc and $CH_3HgOCOCF_3$ with a variety of ligands.[2,7] This is now a well-established procedure and application of this method to other problems has been demonstrated by several groups.[8]

For the equilibrium involving the interaction of MeHgX with added ligand L to form complex X, it follows that

$$\underset{(a-x)}{\mathrm{MeHgX}} + \underset{(b-x)}{\mathrm{L}} \overset{K_f}{\rightleftharpoons} \underset{(x)}{\mathrm{MeHgX{\cdot}L}}$$

if one assumes no prior dissociation or association of the reactants. Since equilibrium is attained rapidly on the NMR time scale, only one mercury resonance is observed, which is a weighted average of the chemical shifts of the free and the complexed metal species in solution.

$$\delta_{obsd} = \Delta\delta + \delta_0 = \delta_0\chi_m + \delta_X\chi_{ML}$$

where δ_0 = chemical shift of uncomplexed metal, δ_X = chemical shift of fully complexed metal, $\Delta\delta = \delta_{obsd} - \delta_0$, χ_M = mole fraction of free metal = $(a-x)/a$, and χ_{ML} = mole fraction of complexed metal = x/a.

If the initial concentration of MeHgX is held constant, then the concentration of the complex (x) may be expressed in terms of (x/a), the molar ratio of the complex to initial concentration of MeHgX. When an equilibrium involved is such that $b \gg a$ and/or K_f is very small, then the reciprocal of the ligand induced change in ^{199}Hg chemical shift, $\Delta\delta^{-1}$, is linearly related to the reciprocal of the ligand concentration, b^{-1}, such that

$$\Delta\delta^{-1} = K_f^{-1}(\delta_X - \delta_0)^{-1}b^{-1} + (\delta_X - \delta_0)^{-1} \quad (1)$$

When the formation constants are relatively large and a large excess of ligand b cannot be attained, then a quadratic expression in terms of $(a - x/a)$ as described by Popov[9] may be utilized as follows

$$\delta_{obsd} = \Delta\delta + \delta_0 = \frac{1}{2K_a}(-(D)^{1/2} + (D + 4K_a)^{1/2})(\delta_0 - \delta_X) + \delta_X \quad (2)$$

where $D = (K_b - K_a + 1)^2$.

This equation has also been used by Kan[10a] and Marzilli[10b] in their investigation of the complexation of Hg^{2+} with nucleosides by using ^1H and ^{13}C NMR. The procedure employed in the evaluation of K_f is to substitute the experimental parameters $\Delta\delta$, δ_0 (the initial chemical shift of a), a and b and vary the two adjustable parameters K_f and δ_X (the chemical shift of fully complexed a) until the calculated chemical shifts correspond to the experimental $\Delta\delta$ values within given error limits. The general non-linear curve-fitting program KINFIT-4[11] was used with the appropriate equations.[2,7]

Experimental Section

Dimethyl disulfide and di-*n*-butyl sulfide were commercially obtained and distilled before use. The acyclic and cyclic polythiaethers were prepared according to the procedure of Rosen.[5] The $CH_3HgOCOCF_3$ was prepared as described previously.[6]

Measurement of ^{199}Hg Spectra. The ^{199}Hg spectra were measured by using a Nicolet NT-300 spectrometer at a frequency of 53.712282 MHz, with a 20-μs pulse width and a 250-ms post-acquisition delay using a ±35714.2-Hz spectral width. Ten millimeter sample tubes were used with a 0.10 M solution of $CH_3HgOCOCF_3$ in 50% $CDCl_3$ or CH_3OD as an internal lock solvent. The spectra represent 4096 scans with a ^1H-decoupling frequency of 300.058421 MHz. Neat $(CH_3)_2Hg$ in a concentric capillary tube was used as an external standard.

Registry No. $CH_3HgOCOCF_3{\cdot}CH_3SSCH_3$, 100909-39-5; $CH_3HgOCOCF_3{\cdot}(n\text{-}Bu)_2S$, 100909-40-8; $CH_3HgOCOCF_3{\cdot}CH_3(CH_2)_3SCH_3$, 100909-41-9; $CH_3HgOCOCF_3{\cdot}CH_3S(CH_2)_2S(CH_2)_3S(CH_2)_2SCH_3$, 100909-42-0; $CH_3HgOCOCF_3{\cdot}(14\text{-}AneS_4)$, 100909-43-1; $CH_3HgOCOCF_3{\cdot}(16\text{-}AneS_4)$, 100909-44-2.

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(8) (a) Lucchini, V.; Wells, P. R. *J. Organomet. Chem.* **1975**, *92*, 283. (b) Goggin, P. L.; Goodfellow, R. J.; Hurst, N. W. *J. Chem. Soc., Dalton Trans.* **1978**, 561. (c) Sudmeier, J. L.; Birge, R. R.; Perkins, T. G. *Magn. Reson.* **1978**, *30*, 491.
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Large-Scale Synthesis of Pinacol Iodomethaneboronate and Its Application to (Acylamino)methaneboronates via (Trimethylsilyl)lithioamines

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Significant biological activity has been observed with a number of aminomethaneboronates recently reported as analogues of α-amino acids. For example, certain aminomethaneboronates have been prepared which are potent transition-state inhibitors of α-chymotrypsin,[1] while another aminomethaneboronate has been identified as a potential neutron capture agent for treatment of malignant melanoma.[2] Furthermore, some boronate complexes can move across living membranes,[3] adding to the biological potential for this area. Although a variety of methodology exists for introducing the boronate moiety into organic molecules, few procedures are available to prepare (acylamino)methaneboronates.[1] We report an improved synthesis of pinacol iodomethaneboronate (**3**) and describe its application to the preparation of (acylamino)methaneboronates via (trimethylsilyl)lithioamines.

Several procedures to prepare pinacol iodomethaneboronate (**3**) were found in the literature,[4-6] one of which was reported during the course of this work.[6] Initially, though, we tried to prepare **3** using one of Matteson's procedures[5] and found the reaction to work well only on a small scale (~10 g). On several occasions we tried to scale up the reaction sequence to produce over 100 g of **3**. Isolation by vacuum distillation always afforded a poor yield of the iodide **3** with the rest of the material being sulfide **1**, yet GLC analysis before distillation showed only

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(4) Matteson, D. S.; Cheng, T. C. *J. Org. Chem.* **1968**, *33*, 3055.
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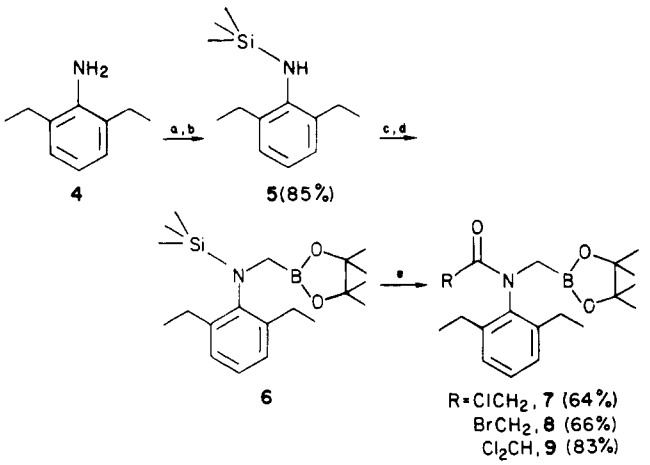
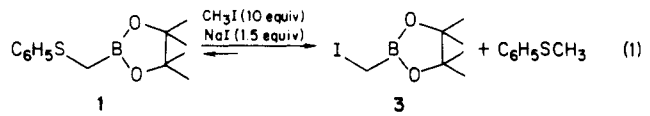
Scheme I. Synthesis of (Acylamino)methaneboronates[a]

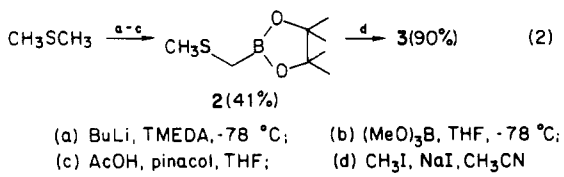


[a] (a) BuLi, 0 °C; (b) Me_3SiCl, 0 °C; (c) BuLi, 0 °C; (d) 3, 0 °C; (e) RCOCl, 0 °C.

desired **3** in the reaction mixture. Since the reaction from **1** → **3** is driven by mass action, the removal of the large excess of methyl iodide coupled with the high temperature required to effect the distillation of **3** resulted in driving the equilibrium back to the left (eq 1).



We have developed a simple two-step synthesis of pinacol iodomethaneboronate which is applicable to scale up and avoids the problem described above (eq 2). In



addition, the sequence is shorter and operationally simpler to perform than Wuts' synthesis of **3**.[6] Thus, in a single step dimethyl sulfide was metalated[7] then reacted with trimethylborate. The resulting "ate" complex was simultaneously quenched with acetic acid and transesterified with pinacol, then purified by vacuum distillation to afford **2** in 41% yield. Conversion of **2** to **3** proceeded in excellent yield (90%) due to the easy removal of the low boiling dimethyl sulfide.[5]

Although secondary and tertiary amines are known to react with iodomethaneboronates, few reports describe the reaction of any halomethaneboronate with a primary amine. For example, benzylamine was claimed to react with dibutyl iodomethaneboronate, but the initially formed product decomposed on attempted distillation.[5] Below, we describe a three-step procedure for synthesizing (acylamino)methaneboronates starting from primary amines which should prove to be fairly general in scope. To illustrate this approach (see Scheme I), 2,6-diethylaniline (**4**) was metalated and then reacted with chlorotrimethylsilane to afford the monosilylaniline **5** in 85% yield after distillation. Low-temperature metalation of **5** followed by reaction with **3** gave **6** in 73% yield after distillation[8] which was then reacted with several acid halides to form the corresponding (acylamino)methaneboronates **7–9** under neutral conditions.[9,10] A key feature of this reaction sequence was that no decomposition of **6** was observed even at the elevated temperatures required for distillation. Furthermore, the *N*-trimethylsilyl protective group did not need to be removed before forming the amide linkage; the direct reaction of **6** with acid halides was rapid and complete. Chlorotrimethylsilane was the only byproduct of the reaction and was easily removed under vacuum.[11]

In summary, a two-step synthesis of pinacol iodomethaneboronate (**3**) was described which is amenable to scale up. This material was used in a new sequence that provides pure (acylamino)methaneboronates not available by other methods.

Experimental Section

All reactions were carried out under a nitrogen atmosphere in flame-dried glassware. THF was dried by distillation from sodium benzophenone. Acetonitrile was reagent grade and used without further drying. ^1H NMR spectra were obtained on Varian T-60, T-60A, and EM-360 spectrometers, while ^{13}C NMR spectra were obtained on a JEOL FX-100 spectrometer. All NMR shifts are relative to $(CH_3)_4Si$. Analyses were performed by Galbraith Laboratories, Inc.

Pinacol (Methylthio)methaneboronate (2). While an internal reaction temperature below 20 °C was maintained with an ice-water bath, TMEDA (48.6 mL, 320 mmol) was added dropwise to mechanically stirred 1.55 M butyllithium in hexane (208 mL, 320 mmol). Dimethyl sulfide (23.6 mL, 320 mmol) was rapidly added to the complex, and the mixture was stirred for 4 h at room temperature. The resulting solution of $LiCH_2SCH_3$ was cooled to −78 °C and $(MeO)_3B$ (44 mL, 390 mmol) was added dropwise, followed by the addition of THF (70 mL) to effect solution of the gummy precipitate which formed. The mixture was warmed to −30 °C and a solution of AcOH (18.5 mL, 320 mmol) and pinacol (38 g, 320 mmol) in THF (30 mL) was rapidly added dropwise. The resulting thick white slurry was warmed to ambient temperature, diluted with Et_2O, and thoroughly extracted with 10% aqueous HCl and then with saturated aqueous $NaHCO_3$. The Et_2O solution was dried ($MgSO_4$), concentrated, and distilled to afford 107 g (41%) of **2** as a colorless oil: bp 57 °C (0.3 mmHg); ^1H NMR (60 MHz, $CDCl_3$) δ 1.27 (12 H, s), 1.93 (2 H, br s), 2.13 (3 H, s); MS, *m/e* 188 (M^+). Anal. Calcd for $C_8H_{17}BO_2S$: C, 51.08; H, 9.11; B, 5.75; S, 17.05. Found: C, 51.24; H, 9.28; B, 5.63; S, 16.85.

Pinacol Iodomethaneboronate (3). A solution of pinacol (methylthio)methaneboronate (50 g, 266 mmol), CH_3I (160 mL, 2570 mmol), and NaI (58 g, 387 mmol) in CH_3CN (550 mL) was stirred at room temperature for 3 days. The resulting reaction mixture was filtered and concentrated in vacuo; then addition of cyclohexane to the residue caused precipitation of the remaining salts. Filtration, concentration, and distillation afforded 63.84 g (90%) of **3** as a red oil: bp 64 °C (0.5 mmHg); ^1H NMR (60 MHz, $CDCl_3$) δ 1.30 (12 H, s), 2.17 (2 H, s); ^{13}C NMR (25 MHz, $CDCl_3$, ^1H decoupled) 24.35 ppm, 84.02; MS, *m/e* 268 (M^+). Anal. Calcd for $C_7H_{14}BIO_2$: C, 31.38; H, 5.27; B, 4.04; I, 47.37. Found: C, 31.63; H, 5.46; B, 4.16; I, 47.54.

2,6-Diethyl-*N*-(trimethylsilyl)aniline (5). BuLi in hexane (15.6 mL, 26.5 mmol) was added dropwise to an ice-water cooled, stirred solution of 2,6-diethylaniline (4.00 g, 26.8 mmol) in THF (20 mL), maintaining an internal reaction temperature <5 °C.

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(9) Schwartz, E.; Shanzer, A. *Tetrahedron Lett.* **1982**, *23*, 979.
(10) A potential route to **7** from *N*-(2,6-diethylphenyl)-2-chloroacetamide and **3** was unsuccessfully attempted using NaH or BuLi as base under a variety of conditions.
(11) In a 360-MHz ^1H NMR experiment, the desilylation of **6** in methanol-d_4 occurred rapidly to initially form pinacol [(2,6-diethylphenyl)amino]methaneboronate (**10**) which completely decomposed over 4 h to *N*-methyl-2,6-diethylaniline (**11**). In a separate experiment, we tried to isolate the initially formed **10** by quickly concentrating the solution in vacuo. Although 4 h were required to effect complete conversion of **10** to **11** in our NMR experiment, we found only **11** in this concentrated sample.

The resulting solution was stirred 20 min, and then a solution of chlorotrimethylsilane (5.82 g, 53.6 mmol) in THF (20 mL) was added dropwise. After being stirred an additional 20 min, the solution was warmed to room temperature and then distilled to afford 5.00 g (85%) of **5** as a pale yellow oil: bp 85 °C (0.25 mmHg); ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.20 (9 H, s), 1.27 (6 H, t, J = 8 Hz), 2.75 (4 H, q, J = 8 Hz), 7.07 (3 H, m).

Pinacol [(2,6-Diethylphenyl)(trimethylsilyl)amino]-methaneboronate (6). BuLi in hexane (13.2 mL, 22.4 mmol) was added dropwise to an ice-water cooled, stirred solution of 2,6-diethyl-*N*-(trimethylsilyl)aniline (**5**, 4.98 g, 22.6 mmol) in THF (20 mL), maintaining an internal reaction temperature <5 °C. The resulting reaction mixture was stirred an additional 20 min with cooling, then a solution of pinacol iodomethaneboronate (**3**, 6.29 g, 23.5 mmol) in THF (10 mL) was added dropwise. After 20 min of additional stirring, the solution was warmed to room temperature, then distilled to afford 5.88 g (73%) of **6** as a pale yellow oil: bp 140 °C (0.25 mmHg); ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.33 (9 H, s), 1.33 (12 H, s), 1.53 (6 H, t, J = 8 Hz), 3.00 (4 H, m), 3.13 (2 H, s), 7.33 (3 H, s).

Acylation of 6 (General Procedure to 7-9). The acyl halide (17.0 mmol) was added in a single portion to an ice-water cooled solution of pinacol [(2,6-diethylphenyl)(trimethylsilyl)amino]-methaneboronate (**6**, 5.86 g, 16.2 mmol) in THF (20 mL). The solution was warmed to room temperature and stirred for 1 h and then concentrated to afford pure **7-9** as solids, though each was also recrystallized from hexane. Data for **7**: mp 45.0-46.8 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.23 (6 H, t, J = 7.5 Hz), 1.27 (12 H, s), 2.60 (4 H, q, J = 7.5 Hz), 2.77 (2 H, s), 3.73 (2 H, s), 7.23 (3 H, m); MS, m/e 365 (M^+). Anal. Calcd for $C_{19}H_{29}BClNO_3$: C, 62.40; H, 7.99; B, 2.96; Cl, 9.69; N, 3.83. Found: C, 62.60; H, 8.11; B, 2.80; Cl, 9.90; N, 3.92. Data for **8**: mp 54.6-56.0 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.23 (6 H, t, J = 8 Hz), 1.27 (12 H, s), 2.60 (4 H, q, J = 8 Hz), 2.73 (2 H, s), 3.57 (2 H, s), 7.23 (3 H, m); MS, m/e 409 (M^+). Anal. Calcd for $C_{19}H_{29}BBrNO_3$: C, 55.64; H, 7.13; B, 2.64; Br, 19.48; N, 3.41. Found: C, 55.80; H, 7.11; B, 2.70; Br, 19.31; N, 3.39. Data for **9**: mp 52.0-54.8 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.23 (6 H, t, J = 8 Hz), 1.30 (12 H, s), 2.67 (4 H, q, J = 8 Hz), 2.90 (2 H, s), 5.68 (1 H, s), 7.23 (3 H, m); MS, m/e 399 (M^+). Anal. Calcd for $C_{19}H_{28}BCl_2NO_3$: C, 57.03; H, 7.05; B, 2.70; Cl, 17.72; N, 3.50. Found: C, 56.87; H, 6.98; B, 3.00; Cl, 17.97; N, 3.36.

Registry No. **2**, 100899-92-1; **3**, 70557-99-2; **4**, 579-66-8; **5**, 100899-93-2; **6**, 100899-94-3; **7**, 100899-95-4; **8**, 100899-96-5; **9**, 100899-97-6; CH_3SCH_3, 75-18-3; $(MeO)_3B$, 121-43-7; pinacol, 76-09-5.

Regiocontrol in Opening of 2*H*-Cyclopenta[*b*]furanones with Organocopper Reagents

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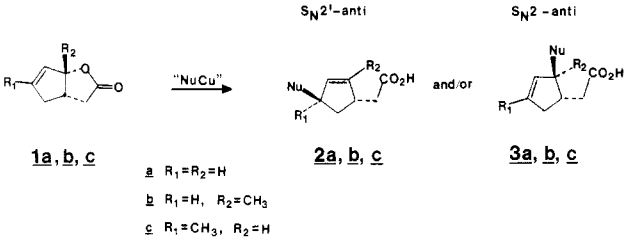
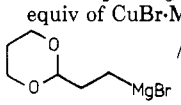
Recently, we had need of a general method for the synthesis of *trans*-3,5-disubstituted-cyclopentenes **2**. These compounds serve as versatile precursors for tandem radical cyclizations to produce linear condensed cyclopentanoids such as hirsutene[1] and $\Delta^{9(12)}$-capnellene.[2] We envisioned organocopper-promoted S_N2' anti opening of readily available substituted vinyl lactones **1** as a direct method which would control both regio- and stereochemistry.[3,4] A variety of related vinyl lactones have been opened in the past with contrasting results.[5,6] While the products of anti opening are usually observed, regioselectivity has varied from complete S_N2' to complete S_N2 depending on the substituents on the vinyl lactone and the nature of the organocopper reagent.[7] We have investigated the opening of 2*H*-cyclopenta[*b*]furan-2-one (**1a**) and its 6- and 8-methyl derivatives (**1c**, **1b**) and we now report a method for selective S_N2' anti opening of these vinyl lactones.

Table I. Oganocopper-Promoted Opening of 2*H*-Cyclopenta[*b*]furanones



entry	lactone	reagent[a]	2/3	yield,[b] %
1	**1a**	MeMgBr/1 equiv of $CuBr\cdot Me_2S$	>98/2	97
2	**1a**	$LiMe_2Cu$	62/38	91
3	**1a**	$LiMe_2Cu(Et_2O)$	54/46	90
4	**1a**	$CH_2{=}CHCH_2CH_2MgBr$/1 equiv of $CuBr\cdot Me_2S$	>98/2	94
5	**1a**	$CH_2{=}CHCH_2CH_2MgBr$/0.1 equiv of $CuBr\cdot Me_2S$	50/50	96
6	**1a**	MeLi/1 equiv of $CuBr\cdot Me_2S$	86/14	91
7	**1a**	MeLi/1 equiv of CuI	76/24	90
8	**1a**	MeLi/1 equiv of CuCN	75/25	60
9	**1b**	$LiMe_2Cu$	>98/2	92
10	**1b**	$THPOCH_2C(CH_3)_2CH_2Li$/1 equiv of $CuBr\cdot Me_2S$	>98/2	50
11	**1b**	 /1 equiv of $CuBr\cdot Me_2S$	>98/2	83
12	**1c**	$LiMe_2Cu$	7/93	61
13	**1c**	MeMgBr/1 equiv of $CuBr\cdot Me_2S$	95/5	73
14	**1c**	$MeLi/CuI/BF_3\cdot Et_2O$	98/2	45
15	**1c**	4/1 equiv of $CuBr\cdot Me_2S$	92/8	90

[a] All reactions were run in THF at -20 °C unless otherwise indicated (see Experimental Section). In general, an excess of organocopper reagent (1.2-2.0 equiv) was employed. [b] Yields represent yields of crude acid after isolation by base extraction. All acids were characterized by diazomethane esterification. Yields of purified methyl esters were generally good.

(1) Curran, D. P.; Rakiewicz, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 1448. Curran, D. P.; Rakiewicz, D. M. *Tetrahedron* **1985**, *41*, 3943.
(2) Curran, D. P.; Chen, M.-H. *Tetrahedron Lett.* **1985**, *26*, 4991.
(3) Magid, R. M. *Tetrahedron* **1980**, *36*, 1901.
(4) (a) For mechanistic studies on the alkylation of allylic derivatives with organocopper reagents, see: Goering, H. L.; Kanter, S. S. *J. Org. Chem.* **1984**, *49*, 422 and references therein. (b) For a stereoelectronic rational for the anti preference observed in these reactions, see: Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1984**, *25*, 3063.
(5) (a) Corey, E. J.; Mann, J. *J. Am. Chem. Soc.* **1973**, *95*, 6832. (b) Grieco, P. A.; Srinivasan, C. V. *J. Org. Chem.* **1981**, *46*, 2591. (c) Ali, S. M.; Chapleo, C. B.; Finch, M. A. W.; Roberts, S. M.; Woolley, G. T.; Cave, R. J.; Newton, R. F. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2093. Chapleo, C. B.; Finch, M. A. W.; Roberts, S. M.; Woolley, G. T.; Newton, R. F.; Selby, D. W. *Ibid.* **1980**, 1847.
(6) For some other relevant vinyl lactone openings, see: Beale, M. H. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1151. Trost, B. M.; Klun, T. *J. Org. Chem.* **1980**, *45*, 4256. Fujisawa, J.; Sato, T.; Kawashima, M.; Naruse, K.; Tamai, K. *Tetrahedron Lett.* **1982**, *23*, 3583.
(7) For example, in the opening of similar unbiased vinyl lactones, Corey observed exclusive S_N2 selectivity with a divinylcuprate (ref 5a) while Grieco observed exclusive S_N2' selectivity with lithium dimethylcuprate (ref 5b).

0022-3263/86/1951-1612$01.50/0