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Organoboranes. 57. Relative Efficacy of Representative Lithium Dialkylamide Bases for the *in Situ* Metalation of Allyl Chloride To Produce (α-Chloroallyl)lithium. Application of the Reagent to *B*-Alkoxy-9-borabicyclononanes Producing New Routes to Interesting Cyclooctane Derivatives

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The effectiveness of 10 representative lithium amide bases for the *in situ* metalation of allyl chloride, with capture of the (α-chloroallyl)lithium (**1**) by 9-methoxy-9-borabicyclononane (9-MeO-9-BBN, **2a**), producing 9-methoxy-10-vinyl-9-borabicyclo[3.3.2]decane (**3a**), has been examined. Amide bases derived from hindered amines are efficient for the generation of the desired carbenoid, with LiNChx$_2$ revealed as the base of choice. The steric influence of the alkoxy group of the borinate ester 9-alkoxy-9-BBN in the transmetalation reaction with **1** has been examined. Compound **3a** is readily converted into several interesting disubstituted cyclooctane derivatives.

The metalation reaction is one of the most important and widespread transformation in organic synthesis and has become increasingly popular owing to the discovery of new organometallic reagents. Among the metalation reactions, allylic metalation occupies an especially important position in view of its considerable synthetic utility.[2] However, α-halogen-substituted allylic metals have not received significant attention due to their "self-consumption".[3] A notable achievement in this area is the metalation of allyl chloride using LDA.[4] (γ-Chloroallyl)-lithium has been prepared by the transmetalation reaction between Ph$_3$PbCH$_2$CH=CHCl and *n*-BuLi and its synthetic utility demonstrated.[5]

In the past, considerable effort has been made to react allylic[6a] and nonallylic[6b] carbenoids with boron substrates. Some of the problems associated with allylic carbenoid reactions have been the selectivity of the reaction (α- vs γ-product),[7] the ready accessibility of the starting allylic substrates, and their applicability to the treatment of the three classes of boron substrates [R$_3$B, R$_2$B(OR′), and RB(OR′)$_2$]. We have addressed these problems recently and have shown that (α-chloroallyl)lithium, generated *in situ* from allyl chloride and LDA, undergoes facile transmetalation with boron substrates to give allylic boron compounds in high yields (75–85%).[8] The simplicity of this method provides easy access to allylic boron compounds,[9] the synthetic utility of which has been amply demonstrated in organic synthesis through allylboration. In connection with problems we have encountered in developing a sequential three-carbon ring enlargement of boracyclanes, we desired a highly efficient procedure for generating **1** in yields of 90% or more. In this study, accordingly, we examined the relative efficacy of representative lithium amide bases, derived from hindered secondary amines, for the generation of **1**.

Results and Discussion

The commercially available 9-methoxy-9-BBN was selected for the capture of the carbenoid **1** generated *in situ*. From our knowledge of its chemistry, we anticipated it would be an effective trapping agent. Since the (α-chloroallyl)lithium is a labile intermediate, it was necessary to generate it in the presence of a borinic ester which would be effective in trapping the intermediate as it was formed. Moreover, we anticipated that the products from the reaction of **1** with 9-MeO-9-BBN would be exceptionally interesting in their own right.

The lithium secondary alkyl amides, except for LiNMe$_2$, were prepared according to literature procedures by reacting the corresponding secondary amine with either *n*-BuLi or MeLi. With LiNMe$_2$, LiNEt$_2$, and LiNPh$_2$ the major products were those in which the OMe group had been nucleophilically displaced by the NR$_2$ group, **4**, as shown by the ^{11}B NMR (δ 46) and ^{1}H NMR spectra (eq 1).

On the contrary, lithium amides derived from hindered secondary amines are highly proton-selective and give the desired allylic borinate **3a** in high yield. The experimental results are summarized in Table I.

The variation in yield is easily rationalized on the basis of simple steric arguments. Lithium dicyclohexylamide (LiNChx$_2$) is a more effective base than LiN-*i*-Pr$_2$, LiN-

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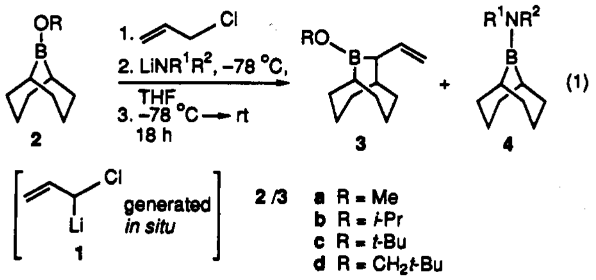
Table I. *In Situ* Metalation[a] of Allyl Chloride with $LiNR^1R^2$ with Capture by 9-Methoxy-9-BBN

base used	product(s) (ratio[b] in parentheses)	yield, %
$LiNMe_2$	**3a**(5):**4**(95)	91
$LiNEt_2$	**3a**(10):**4**(90)	93
lithium pyrrolidide	**4**	90[c]
LiN-*i*-Pr_2	**3a**	76[c]
LiN-*s*-Bu_2	**3a**	80[c]
LiN-*i*-PrChx	**3a**	85[c]
$LiNChx_2$	**3a**	90[c]
LiTMP	**3a**	75[c]
LiN-*t*-$BuSiMe_3$	**3a** (40):**4** (60)	90
$LiNPh_2$	**4**	92[c]

[a] All reactions were performed in 10-mmol scale using 13 mmol of $LiNR^1R^2$ and 13 mmol of allyl chloride in THF medium (30 mL). [b] The ratio of products was determined by ^1H NMR analysis and by GC analysis of the oxidation product diol after conversion to bis(trimethylsilyl) ether. [c] Isolated yield.



i-PrCHx, or LiN-*s*-Bu_2. With $LiNChx_2$ as the base, the ^{11}B NMR spectrum of the reaction mixture showed a single peak at δ 53, indicating the complete disappearance of starting borinate **2a** (δ 56.5). The dicyclohexylamine liberated during the metalation is easily precipitated and thereby removed from the reaction mixture by the addition of MeI (2 equiv). Alternatively, the amine can also be removed by precipitation as the BF_3 adduct by adding $BF_3 \cdot OEt_2$ (1 equiv) to the crude reaction product dissolved in pentane. Similarly, HN-*i*-PrChx can be precipitated by the addition of MeI. The more hindered base lithium tetramethylpiperidide (LiTMP) gave slightly inferior yields of the desired product. The base $LiN(SiMe_3)_2$ and $KN(SiMe_3)_2$ produced **4** as the major product. Superbase[10] (a mixture of KO-*t*-Bu and *n*-BuLi) resulted in transesterification between the *B*-OMe group and the O-*t*-Bu$^-$ group, competing with the desired metalation, leading to a mixture of **3a** and **3c**.

The effectiveness of the lithium amide bases in this metalation can be correlated with the pK_a of respective amines.[11] Lithium amides derived from secondary amines whose pK_a values are in the vicinity of 30, for example, HN-*t*-$BuSiMe_3$ and $HN(SiMe_3)_2$, are not suitable for efficient metalation. However, amides derived from amines, such as HN-*i*-Pr_2, $HNCHx_2$, and HN-*i*-PrCHx, whose pK_a values are close to 35, bring about efficient metalation.

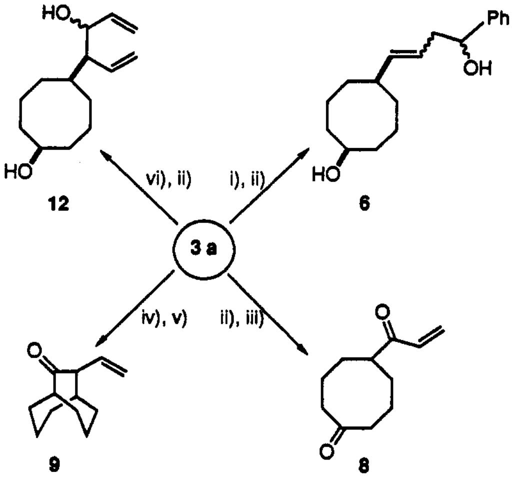
We undertook a study of carbenoid capture by other *B*-alkoxy substrates (**2b**, **2c**, **2d**) for two reasons: (i) to test the effect of the steric bulk of the OR group on boron for the transmetalation with **1**, which leads to ate complex formation, and (ii) to suppress the undesired nucleophilic displacement encountered with **2a**. Table II summarizes the results of this study.

Table II. Reaction of (α-Chloroallyl)lithium (1) with 9-Alkoxy-9-BBN

base used	substrate/product yield, %[a]		
	2b/**3b**	**2c**/**3c**	**2d**/**3d**
$LiNEt_2$	50	65	25
LDA	70	70	42
$LiNChx_2$	72	72	48
LiN-*t*-$BuSiMe_3$	61	68	25

[a] The yield of the product was determined by ^1H NMR analysis and by GC analysis of the oxidation product diol after conversion to the bis(trimethylsilyl) ether. The balance of the material was recovered starting material. However, with $LiNEt_2$ as base, ~10% of **4** was also formed. Attempts to increase the yield by carrying out the homologation at -100 °C, or by the use of HMPA as cosolvent, were not, however, successful.

Chart I[a]



[a] i) PhCHO, 0 °C ii) NaOH/H_2O_2 iii) $Na_2Cr_2O_7/H^+$/EE iv) DCME/LiO*t*-Bu v) KH_2PO_4/H_2O_2 vi) $CH_2{=}CH{-}CH_2Cl$, $LiNChx_2$, -78 °C, then MeI (2 equiv).

Summing up, $LiNChx_2$ gives a better yield of the desired product as compared to the results achieved with other amides. $LiNEt_2$ and LiN-*t*-$BuSiMe_3$, which cause the nucleophilic displacement of OMe group in **2a**, give the allylic borinate (**3b**/**3c**) only in moderate yield. The present study shows that increasing the steric bulk of the OR group decreases the yield of the desired allylic borinate. This parallels observations made previously in our laboratory with *B*-alkoxyborinane substrates.[12]

Synthetic Utility of 9-Methoxy-10-vinyl-9-borabicyclo[3.3.2]decane (3a). Recently, there has been increased emphasis on the synthesis of eight-membered rings owing to the discovery of an increasing number of natural products, such as ophiobolane, taxane, and fusicoccin, etc., which possess this ring system in their structures. The synthesis of compounds containing this ring system has been a long standing problem, with difficulties attributed to the high degree of strain arising from powerful transannular interactions present in such compounds.[13] The allylic borinate **3a** can serve as a versatile intermediate for the convenient synthesis of cyclooctane compounds containing reactive functionalities for further elaboration (Chart I).

Homologation-Allylboration Sequence. These two reactions were carried out in a tandem manner by adding the aldehyde to the homologation reaction mixture at 0 °C. The progress of the reaction can be monitored by ^{11}B

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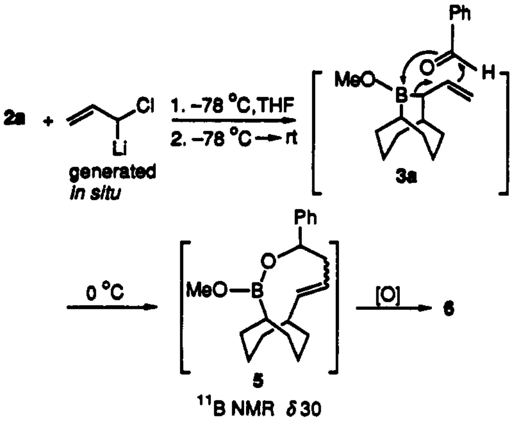

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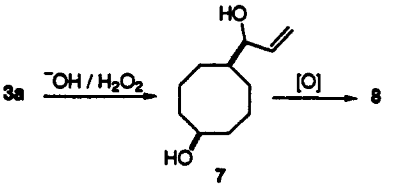

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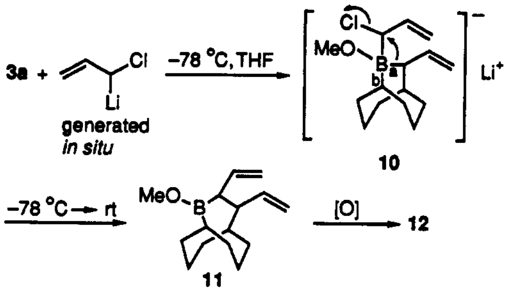

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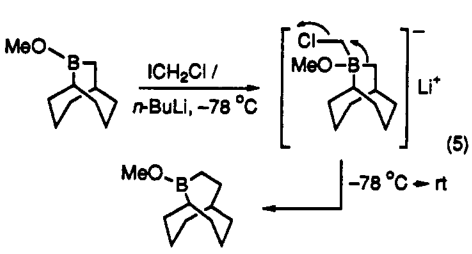
NMR (eq 2). Oxidation of the resulting boronate **5** furnishes the diol **6** in an 80% overall yield from **2a**.

Oxidation. Compound **3a**, on oxidation, gives the diol **7** in 80% yield (eq 3). This was further oxidized to the diketone **8** using $Na_2Cr_2O_7/H^+$ in a two-phase water–ether medium.[14] Attempted oxidation of **7**, using milder reagents such as PCC and PDC, were not, however, successful.

DCME Reaction.[15] The DCME reaction of allylic borinates has not been reported in the literature. Reaction of **3a** with DCME (Cl_2CHOMe) in the presence of LiO-*t*-Bu followed by oxidation in a pH 8 buffer medium, furnishes the ketone **9**, albeit in low yield (15%). Attempts to improve the yield by the addition of anhydrous $ZnCl_2$ to the reaction mixture (before oxidation) to facilitate migration of the alkyl group did not help. Change of the base to $LiOCEt_3$ and change of the ester moiety to *o*-$Me_2C_6H_3O$ instead of OMe were also not successful. The low yield of the desired product in this reaction is, presumably, due to a competing transesterification between the OMe group in **3a** and the O-*t*-Bu⁻ of the DCME reaction.

Second Homologation. We decided to explore the possibility of achieving a second homologation of **3a** in the hope that it might provide a synthetic route to **12**. Reaction of **3a** with **1** furnishes dienyl borinate **11** (eq 4). It is noted that in the formation of **11** from **10** the allyl group (bond a) migrates in preference to the secondary alkyl group (bond b). This parallels the observation made in our laboratory[16] that in such reactions a primary alkyl group undergoes migration in preference to the secondary alkyl group (eq 5). Compound **11**, on oxidation, gives the dienol **12**, a substrate useful for oxy-Cope rearrangements.



(5)

Conclusions

Lithium dialkylamides derived from hindered secondary amines metalate allyl chloride efficiently. Among the bases studied, $LiNChx_2$ gives the most favorable yield of the allylic borinate. Increase in steric bulk of the alkoxy group on boron, however, decreases the yield of the desired homologation product. The allylic borinate **3a** has been transformed into several synthetically useful cyclooctane derivatives.

Experimental Section

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl prior to use. Freshly estimated *n*-BuLi or MeLi reagents were used for the metalation experiments. All moisture- and air-sensitive reactions were conducted under a positive pressure of Ar in glassware that was flame-dried and then cooled under Ar.[17] Allyl chloride was distilled over P_2O_5. Secondary amines were dried over CaH_2, distilled, and stored under argon. $LiEt_2$,[18] lithium pyrrolidide,[19] LiN-*i*-PrChx,[20] $LiNChx_2$,[21] LiTMP,[22] and LiN-*t*-$BuSiMe_3$,[23] were prepared according to literature procedures. Other amides were made by metalating the corresponding amine with *n*-BuLi at 0 °C. Commercially available $LiNMe_2$ and 9-methoxy-9-BBN (Aldrich Chemical Co.) were used. Other 9-alkoxy-9-BBN compounds were prepared by the alcoholysis of 9-BBN with the corresponding alcohols, followed by distillation in vacuo. The ^{11}B NMR spectra were recorded on a Varian Gemini-300 spectrometer and the chemical shifts are in δ relative to $BF_3{\cdot}OEt_2$ as positive. The ^1H and ^{13}C NMR spectra were scanned on a Varian Gemini-300/200 spectrometer. IR and MS were recorded on Perkin-Elmer 137 and Finnegan spectrometers respectively. The purity (>95%) of all chromatographed and/or distilled compounds was ascertained by ^1H NMR analysis.

General Procedure for the Homologation of 9-Alkoxy-9-BBN. The procedure for the preparation of **3a** is representative. To a stirred and cooled (-78 °C) mixture of 9-methoxy-9-BBN (10 mmol, freed from pentane), allyl chloride (13 mmol), and THF (15 mL) was added a cooled (0 °C/-78 °C) solution of freshly prepared $LiNR^1R^2$ (13 mmol) in THF (15 mL). The reaction mixture was gradually warmed to room temperature over a period of 18 h and the progress of the reaction was monitored by ^{11}B NMR. When $LiNChx_2$/LiN-*i*-PrChx was used as the base, MeI (26 mmol) was added to the cooled (0 °C) reaction

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mixture and then stirred for 4 h. A white precipitate of the quaternary ammonium salt was formed. All the volatiles were pumped off in vacuo and the residue was triturated with pentane (3 × 20 mL). The supernatant pentane layer was transferred into another precooled flask by means of a cannula under Ar. Removal of pentane in vacuo afforded compound **3a**. When LiTMP was used as the base, the crude product was dissolved in pentane (10 mL) and cooled to 0 °C and $BF_3{\cdot}OEt_2$ (13 mmol) was then added. The supernatant pentane layer was removed and worked up as above.

The crude product **3a**, thus obtained, can be used directly for further transformations, such as oxidation and allylboration. For characterization purposes, **3a** was distilled in vacuo: yield 90%; bp 75–78 °C/0.3 mm; ^{11}B NMR ($CDCl_3$) δ 53 (s); ^1H NMR ($CDCl_3$) δ 0.85–1.9 (m, 14 H), 2.2 (br s, 1 H, $BC\mathit{H}CH{=}CH_2$), 3.75 (s, 3 H), 4.88–5.0 (m, 2 H), 5.95–6.05 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.4, 23.4, 26.5, 27.5, 28.6, 33.22, 34.3, 35.6, 43.0 (br), 53.6, 112.9, 141.1.

The allylic borinate **3** was oxidized using preformed peroxy anion, generated by reacting 3 N NaOH with 30% H_2O_2 to get 5-(1-hydroxy-2-propenyl)cyclooctanol: yield 80%; bp 180 °C/0.2 mm; ^1H NMR ($CDCl_3$) δ 1.18–1.85 (m, 13 H), 2.12 (br s, 2 H), 3.85–3.89 (m, 2 H), 5.1–5.22 (m, 2 H), 5.74–5.86 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.3, 29.7, 36.0, 42.9, 72.1, 78.0, 115.8, 139.4; EIMS *m/e* 167 ($M^+ - OH$); CIMS *m/e* 167 ($M^+ + H - H_2O$); HRMS calcd for $C_{11}H_{19}O$ ($M^+ - OH$) 167.1436, found 167.1434.

3b: bp 80–88 °C/0.3 mm; ^{11}B NMR ($CDCl_3$) δ 52.4 (s); ^1H NMR ($CDCl_3$) δ 1.11–1.94 (m, 20 H), 2.49 (br s, 1 H), 4.42–4.54 (m, 1 H), 4.83–5.07 (m, 2 H), 5.96–6.13 (m, 1 H).

3c: bp 110–115 °C/0.3 mm; ^{11}B NMR ($CDCl_3$) δ 51.7 (s); ^1H NMR ($CDCl_3$) δ 1.27–1.95 (m, 23 H), 2.28 (br s, 1 H), 4.82–4.92 (m, 2 H), 6.02–6.16 (m, 1 H).

3d: bp 120–122 °C/0.3 mm; ^{11}B NMR ($CDCl_3$) δ 52.4 (s); ^1H NMR ($CDCl_3$) δ 0.92 (s, 9 H), 1.21–1.97 (m, 14 H), 2.25 (br s, 1 H), 3.67 (s, 2 H), 4.86–4.99 (m, 2 H), 5.85–6.06 (m, 1 H).

Allylboration Reaction. Preparation of 6. The homologation reaction mixture (vide supra), obtained from **2a** (10 mmol), was cooled in an ice bath and PhCHO (10 mmol) added. Stirring was continued at this temperature for 4 h. The ^{11}B NMR spectrum showed the complete disappearance of the δ 53 peak and the appearance of a δ 30 peak. The reaction mixture was then oxidized using 3 N NaOH (5 mL) and 30% H_2O_2 (4 mL). The reaction product was extracted with diethyl ether (EE) (3 × 20 mL) and washed with dilute HCl (20 mL). The precipitated $CHx_2NH{\cdot}HCl$ was filtered through a sintered funnel and the organic layer was washed with water, saturated $NaHCO_3$ solution, and finally with water. Removal of solvent gave a viscous liquid. This was chromatographed over a silica gel column and eluted with a hexane–EE mixture (1:1) to get compound **6** as a colorless oil (2.2 g, 80% yield): IR (neat; ν_{max}, cm^{-1}) 3365 (br), 1634, 1601; ^1H NMR ($CDCl_3$) δ 1.15–2.60 (m, 17 H), 3.55–3.92 (m, 1 H), 4.58–4.71 (m, 1 H), 5.12–5.87 (m, 2 H), 7.2–7.38 (m, 5 H); CIMS *m/e* 257 ($M^+ + H - H_2O$); HRMS calcd for $C_{18}H_{25}O$ 257.1906, found 257.1904.

Oxidation of 7. Preparation of 8. To a stirred and cooled (0 °C) solution of diol **7** (1.8 g; 9.8 mmol) in EE (10 mL) was added a solution of chromic acid (20 mL; prepared by dissolving 10 g of $Na_2Cr_2O_7{\cdot}2H_2O$ in 30 mL of H_2O, adding 13.6 g of concd H_2SO_4, and then diluting to 50 mL total volume with H_2O) over a period of 15 min. After 4 h at this temperature, the upper organic layer was separated and the aqueous phase was extracted with EE (2 × 10 mL). The combined EE extracts were washed with saturated $NaHCO_3$ solution and water. Drying (Na_2SO_4) and solvent removal gave a liquid which was chromatographed over a silica gel column. Elution with a hexane–benzene mixture (1:1) gave a liquid which was further purified by distillation: bp 135 °C/0.2 mm (1.23 g, 70% yield); IR (neat; ν_{max}, cm^{-1}) 1718, 1694, 1608; ^1H NMR ($CDCl_3$) δ 1.51–2.74 (m, 13 H), 5.66–5.81 (m, 1 H), 6.14–6.42 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 24.7, 29.3, 42.1, 46.2, 128.5, 134.9, 202.3, 217.4; EIMS *m/e* 180 (M^+); HRMS calcd for $C_{11}H_{16}O_2$ 180.1150, found 180.1146.

DCME Reaction of 3a. Preparation of 9. To a cooled (0 °C) and stirred solution of *t*-BuOH (0.74 g, 10 mmol) in hexane (10 mL) was added *n*-BuLi (4.5 mL, 10 mmol). After the solution was stirred for 0.5 h, the LiO-*t*-Bu was transferred through a cannula to a cooled (0 °C) mixture of **3a** (0.86 g, 4.5 mmol) and DCME (0.86 g, 7.5 mmol) in anhydrous EE (15 mL). Stirring was continued for 1 h, the ice bath was removed, and then the solution was stirred at room temperature for 14 h. A white solid separated out. The reaction mixture was cooled (0 °C) and then oxidized using a mixture of KH_2PO_4 (8 mL) and 30% H_2O_2 (4 mL) at pH 8 over a period of 24 h. The reaction product was extracted with EE (3 × 20 mL). The ether extracts were combined and washed with water and brine. Drying (Na_2SO_4) and solvent removal gave a viscous liquid. This was chromatographed over a column of neutral alumina and eluted with a benzene–EtOAc mixture (9:1). A viscous liquid (**9**) was obtained (0.12 g, 15% yield). Further elution with a hexane–EtOAc mixture (1:1) gave a mixture of polar compounds containing the diol **7**. No attempt was, however, made to separate the mixture. **9**: IR (neat; ν_{max}, cm^{-1}) 1704, 1631; ^1H NMR ($CDCl_3$) δ 0.83–2.52 (m, 13 H), 2.92 (t, J = 9 Hz, 1 H), 3.72–3.92 (m, 1 H), 5.11–5.18 (m, 2 H), 5.56–5.68 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.4, 25.6, 30.1, 32.4, 36.2, 38.1, 42.5, 65.5, 72.1, 119.2, 136.3, 211.8; EIMS *m/e* 138 ($M^+ - C_3H_4$); CIMS *m/e* 139 ($M^+ + H - C_3H_4$); CIHRMS calcd for $C_9H_{15}O$ 139.1123, found 139.1120.

Homologation of 3a. Preparation of 11. A solution of $LiNChx_2$ in THF was prepared by reacting Chx_2NH (1.96 g, 10.8 mmol) with *n*-BuLi (4.9 mL, 2.2 M solution, 10.8 mmol) in THF (20 mL) at 0 °C. This was then added through a cannula to a mixture of **3a** (1.6 g, 8.3 mmol) and allyl chloride (0.83 g, 10.8 mmol) in THF (15 mL), being cooled to −78 °C. The reaction mixture was gradually warmed to room temperature over a period of 18 h. It was then cooled in an ice bath and MeI (2.92 g, 21.6 mmol) was added. After stirring for 4 h, it was worked up as described for the preparation of **3a**. Distillation under reduced pressure gave **11** (bp 90–95 °C/0.01 mm, 1.55 g, 80% yield); ^{11}B NMR δ 53.4 (s); ^1H NMR ($CDCl_3$) δ 1.1–2.58 (m, 16 H), 3.7–3.8 (m, 3 H), 4.79–5.1 (m, 4 H); 5.72–6.04 (m, 2 H). Oxidation using preformed peroxy anion gave the diol **12** as a viscous liquid in 75% yield (bp 180–185 °C/0.2 mm): IR (neat; ν_{max}, cm^{-1}) 3359 (br), 1638; ^1H NMR ($CDCl_3$) δ 1.15–2.45 (m, 16 H), 3.84–4.2 (m, 2 H), 4.9–5.3 (m, 4 H), 5.62–5.91 (m, 2 H); CIMS *m/e* 207 ($M^+ + H - H_2O$); CIHRMS calcd for $C_{14}H_{23}O$ 207.1749, found 207.1745.

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Supplementary Material Available: ^1H NMR spectra for **3a**, **3b**, **3c**, **3d**, **6**, **7**, **8**, **9**, and **12** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can beordered from the ACS; see any current masthead page for ordering information.