Stereoselective Synthesis of Highly Functionalized Trisubstituted Olefins via the Aldol Reaction of Allenoxyborinates with Carbonyl Compounds

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Allenoxyborinates, generated via the reaction of dicyclohexylborane with α,β-acetylenic ketones, react in situ with excess starting ketone to afford stereodefined, functionalized, trisubstituted olefins in good yields. The allenoxyborinates, $(RCH{=}C{=}C(R')OB(c\text{-}C_6H_{11})_2$, can also be trapped by aldehydes and ketones when R′ is a *tert*-butyl group.

Introduction

Hydroboration plays an important role in organic synthesis.[1] Recently we reported that the carbon−carbon double bonds and triple bonds of nonconjugated unsaturated ketones and aldehydes can be selectively hydroborated by dicyclohexylborane.[2] However, the reactions of α,β-unsaturated ketones and aldehydes with borane reagents proceed differently. For example, conjugated olefinic ketones react stereoselectively with dicyclohexylborane or (−)-diisopinocampheylborane to form boron enolates,[3] whereas the carbonyl group in α,β-unsaturated ketones is simply reduced by 9-BBN.[4] Enantioenriched propargylic alcohols are obtained by reduction of α,β-acetylenic ketones using chiral boron reagents such as β-isopinocampheyl-9-BBN,[5] B-chlorodiisopinocampheylborane[6] and BMS in the presence of chiral B-methyl-4,5,5-triphenyl-1,3,2-oxazaborolidine.[7]

We recently reported that dicyclohexylborane reacts with α,β-acetylenic ketones to form trisubstituted alkenes stereoseletively.[8] Trisubstituted olefins are present in many naturally occurring biologically active compounds such as terpenoids, pheromones, macrolide antibiotics, marine products, etc.[9] They are also key intermediates in a number of transformations leading to natural products[10] and have remained an active area of research for organic chemists.[11] We now wish to report the details of this novel one-pot synthesis of stereodefined, highly functionalized, trisubstituted olefins via the reaction of α,β-acetylenic ketones with dicyclohexylborane.

Results and Discussions

We found that the reaction of a molar equivalent of 3-heptyn-2-one with dicyclohexylborane yields a complex mixture of products. On the other hand, when 2 molar equiv of 3-heptyn-2-one are added to 1 molar equiv of dicyclohexylborane in THF at 0 °C, (*Z*)-3-butylene-4-hydroxy-4-methylnon-5-yn-2-one (**2a**) is isolated in good yield, as shown in Scheme 1. In an effort to optimize the reaction conditions, the effects of reaction temperature, solvent, and stoichiometry were studied. The reaction produced **2a** in 45% yield after 1 h at room temperature but required 2 h at 0 °C. No reaction occurred overnight at −78 °C. Thus, room temperature was chosen for

(1) (a) Gragg, G. M. L. *Organoboranes in Organic Synthesis*; Marcel Dekker: New York, 1973; pp 137−197. (b) Pelter, A.; Smith K.; Brown, H. C. *Borane Reagents*; Academic Press: London, 1988; pp 165−205. (c) Evans, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **1992**, *114*, 6671. (d) Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1992**, *114*, 6671. (e) Fisher, G. B.; Goralski, C. T.; Nicholson, L. W.; Hasha, D. L.; Zakett, D.; Singaram, B. *J. Org. Chem.* **1995**, *60*, 2026. (f) Fugami, K.; Hagiware, N.; Okeda, T.; Kosugi, M. *Chem. Lett.* **1998**, 81. (g) Rochepeau-Jobron, L.; Jacquinet, J.-C. *Carbohydr. Res.* **1997**, *303*, 395. (h) Panek, J. S.; Xu, F.; Rondon, A. C. *J. Am. Chem. Soc.* **1998**, *120*, 4113.

(2) (a) Kabalka, G. W.; Yu, S.; Li, N.-S. *Tetrahedron Lett.* **1997**, *38*, 5455. (b) Kabalka, G. W.; Yu, S.; Li, N.-S. *Tetrahedron Lett.* **1997**, *38*, 7681. (c) Kabalka, G. W.; Yu, S.; Li, N.-S. *Can. J. Chem.* **1998**, *76*, 800.

(3) (a) Boldrini, G. P.; Marcini, F.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Chem. Soc., Chem. Commun.* **1990**, 1680. (b) Boldrini, G. P.; Bortolotti, M.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *Tetrahedron Lett.* **1991**, *32*, 1229.

(4) Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1977**, *42*, 1197.

(5) (a) Midland, M. M.; McDowell, D. C.; Hatch, R. L.; Tramontano, A. *J. Am. Chem. Soc.* **1980**, *102*, 867. (b) Midland, M. M.; McLoughlin, J. I.; Gabriel, J. *J. Org. Chem.* **1989**, *54*, 159.

(6) Ramachandran, P. V.; Teodorovic, A. V.; Rangaishenvi, M. V.; Brown, H. C. *J. Org. Chem.* **1992**, *57*, 2379.

(7) Bach, J.; Berenguer, R.; Garcia, J.; Loscertales, T.; Vilarrasa, J. *J. Org. Chem.* **1996**, *61*, 9021.

(8) Kabalka, G. W.; Yu, S.; Li, N.-S.; Lipprandt, U. *Tetrahedron. Lett.* **1999**, *40*, 37.

(9) (a) Marfat, A.; McGuirk, P. R.; Helquist, P. *J. Org. Chem.* **1979**, *44*, 3888. (b) Fenical, W. *Chem. Rev.* **1993**, *93*, 1673. (c) Garson, M. J. *Chem. Rev.* **1993**, *93*, 1699. (d) D'Auria, M. V.; Minale, L.; Riccio, R. *Chem. Rev.* **1993**, *93*, 1839. (e) Uchida, K.; Utimoto, K.; Nozaki, H. *Tetrahedron* **1977**, *33*, 2987. (f) Ferezou, J. P.; Berreur, J.; Meusy, J. J.; Barbier, M.; Suchy, M.; Wipf, J. K. *Experentia* **1977**, *15*, 290. (g) Muller, J. M.; Fehere, H.; Gruner, J.; Boser, W. *Helv. Chim. Acta* **1976**, *59*, 2506. (h) Besl, H.; Hofle, G.; Jendrny, B.; Jagers, E.; Steglich, W. *Chem. Ber.* **1977**, *110*, 3770.

(10) (a) Nakata, T.; Schmide, G.; Vranesic, B.; Okigawa, M.; Smith-Palmer, T.; Kishi, Y. *J. Am. Chem. Soc.* **1978**, *100*, 2933. (b) Corey, E. J.; Katazenellenbogen, J. A.; Gilman, N. W.; Roman, S. A.; Erickson, B. W. *J. Am. Chem. Soc.* **1968**, *90*, 5618. (c) Bauchat, P.; Le Rouille, E.; Foucaud, A. *Bull. Chim. Soc. Fr.* **1991**, 267. (d) Buchholz, R.; Hoffman, H. M. R. *Helv. Chim. Acta* **1991**, *74*, 1213. (e) Charette, A. B.; Cote, B. *Tetrahedron Lett.* **1993**, *34*, 6833. (f) Roush, W. R.; Brown, B. B. *J. Org. Chem.* **1993**, *58*, 2151. (g) Perlmutter, P.; Tabone, M. *J. Org. Chem.* **1995**, *60*, 6515. (h) Marson, C. M.; Harper, S.; Oare, C. A.; Walsgrove, T. *J. Org. Chem.* **1998**, *63*, 3798.

(11) (a) For a review, see: Faulkner, D. J. *Synthesis* **1971**, 175. For recent examples, see: (b) Basavaiah, D.; Rao, P. D.; Hyma, R. S. *Tetrahedron* **1996**, *52*, Chapter 5, Section 1, and references therein. (c) Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 11018. (d) Negishi, E.; Ay M.; Gulevich, Y. V.; Noda, Y. *Tetrahedron Lett.* **1993**, *34*, 1437. (e) Gao, Y.; Harada, K.; Hata, T.; Urabe, H.; Sato, F. *J. Org. Chem.* **1995**, *60*, 290. (f) Deloux, L.; Srebnik, M.; Sabat, M. *J. Org. Chem.* **1995**, *60*, 3276. (g) Zhang, Q.; Yang, Y.; Martin, A. R. *Tetrahedron Lett.* **1993**, *34*, 2235. (h) Yang, G.; Myles, D. C. *Tetrahedron Lett.* **1994**, *35*, 2503. (i) Evans, D. A.; Carreira, E. M. *Tetrahedron Lett.* **1990**, *31*, 4703. (j) Ciganek, E. *J. Org. Chem.* **1995**, *60*, 4635. (k) Deng, M.; Tang, Y.; Xu, W. *Tetrahedron Lett.* **1984**, *25*, 1797. (l) Hanessian, S.; Beaudoin, S. *Tetrahedron Lett.* **1992**, *33*, 7655.

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Scheme 1

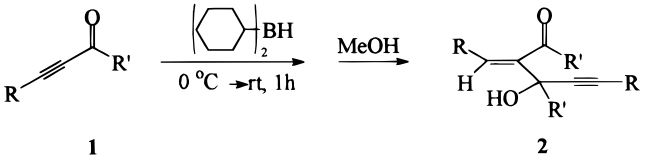
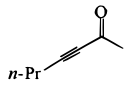
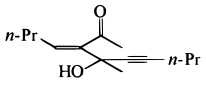
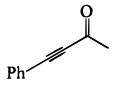
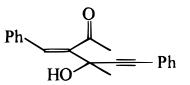
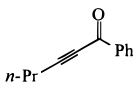
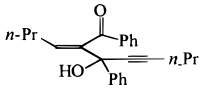
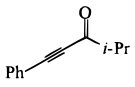
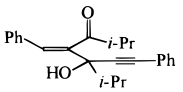
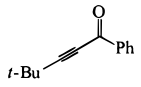
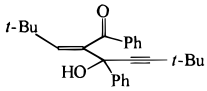
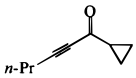
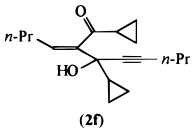
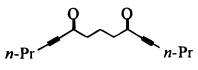
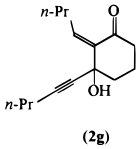
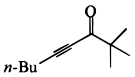


Table 1. Reaction of α,β-Acetylenic Ketones with Dicyclohexylborane

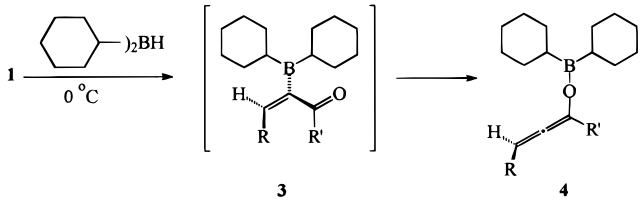
Entry	Substrate	Product[a]	Yield[b]
1	 (1a)	 (2a)	62
2	 (1b)	 (2b)	72
3	 (1c)	 (2c)	78
4	 (1d)	 (2d)	72
5	 (1e)	 (2e)	78
6	 (1f)	 (2f)	66 %
7	 (1g)	 (2g)	55 %
8[d]	 (1h)	---	----

[a] Reactions were run using 2 mmol α,β-acetylenic ketones and 1.25 mmol dicyclohexylborane in THF. [b] All new compounds were characterized by spectral and elemental analysis. [c] Isolated yield based on ketone. [d] None of the desired product was obtained.

further studies. The studies revealed that solvents (THF, CH_2Cl_2, and pentane) had little effect on the reaction of α,β-acetylenic ketones with dicyclohexylborane, and optimum yields were obtained when a slight excess of dicyclohexylborane was utilized.

A variety of α,β-acetylenic ketones was then allowed to react with dicyclohexyl-borane in THF at room temperature. The results are presented in the Table 1. As shown, the expected products were obtained in good yields except in the case of 2,2-dimethylnon-4-yn-3-one (Table 1, entry 8).

Scheme 2



In the reaction of 4,11-pentadecadiyn-6,10-dione with dicyclohexylborane (Table 1, entry 7), an intermolecular reaction competed with the desired intramolecular reaction. The reaction was then carried out at various concentrations of 4,11-pentadecadiyn-6,10-dione. As anticipated, diluting the reactants increased the yield of desired intramolecular product.

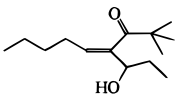
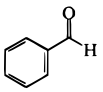
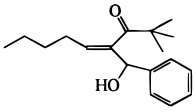
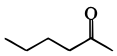
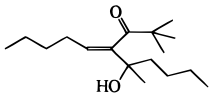
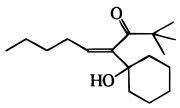
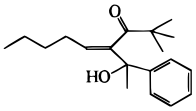
Interestingly, the ^1H and ^{13}C NMR spectra revealed that only one product formed in each of the reactions. The stereochemistry of the alkene products was determined to be *Z* using NOESY NMR. The mechanism of the reaction is presumed to involve the hydroboration of the triple bond followed by enolization of the intermediate vinylborane **3** to produce allenoxyborinate **4**, Scheme 2. The allenoxyborinate then undergoes an aldol reaction with excess α,β-acetylenic ketone to give the (*Z*)-olefin.

Reactions of allenoxyborinates with other electrophiles, namely, aldehydes, ketones, and acid halides, were also investigated. When aldehydes were used as electrophiles, mixtures were produced containing products generated by reaction of the allenoxyborinates with the added aldehyde as well as aldehyde reduction products. However when alkyl ketones or acid chlorides were used, only the aldol product generated by reaction of the allenoxyborinate with excess α,β-acetylenic ketone was formed. These results suggest that the α,β-acetylenic ketones are less reactive toward allenoxyborinates than aldehydes but are more reactive than alkyl ketones and acid chlorides.

As noted in Table 1 (entry 8), the reaction of 2,2-dimethylnon-4-yn-3-one with dicyclohexylborane did not form the self-condensation product. To demonstrate that the expected allenoxyborinate did indeed form, 1 molar equiv of 2,2-dimethylnon-4-yn-3-one was allowed to react with 1.25 molar equiv of dicyclohexylborane in THF at room temperature for 1 h; the reaction mixture was then oxidized using sodium perborate. Both (*E*)- and (*Z*)-2,2-dimethylnon-4-en-3-one were obtained in an overall 60% yield. This result suggests that the allenoxyborinate intermediate formed but did not undergo aldol condensation with excess ketone. Interestingly, 5-cyclohexyl-5-hydroxy-2,2-dimethyl-3-nonanone (~30%) was also obtained. Presumably, it formed via the rearrangement of the isomeric vinylborane intermediate generated during hydroboration of carbon−carbon triple bond.

Since the allenoxyborinate generated by reaction of dicyclohexylborane to 2,2-dimethylnon-4-yn-3-one was stable at room temperature, we felt it might be possible to trap it using added electrophiles. The reaction of 2,2-dimethylnon-4-yn-3-one with dicyclohexyborane in THF, followed by the addition of benzaldehyde, gave the mixed aldol product. The reaction of 1 molar equiv of 2,2-dimethylnon-4-yn-3-one with dicyclohexylborane, followed by reaction with benzaldehyde, gave the expected aldol product in 50% yield. Using 2 molar equiv of 2,2-

Table 2. Synthesis of 2,2-Dimethyl-4-(1-hydroxyalkyl)-4-nonen-3-one[a]

Entry	Electrophile	Product[b]	Yield[c]
1		 (5a)	100 %
2		 (5b)	100 %
3		 (5c)	100 %
4		 (5d)	100 %
5		 (5e)	100 %

[a] Reactions were carried out using 2.5 mmol dicyclohexylborane, 2.0 mmol 2,2-dimethylnon-4-yn-3-one and 1.0 mmol of electrophiles. [b] All new compounds were characterized by spectral and elemental analysis. [c] Isolated yields based on electrophiles.

dimethylnon-4-yn-3-one and dicyclohexylborane and then adding 1 equiv of benzaldehyde resulted in a quantitative formation of the aldol product, based on benzaldehyde.

A variety of ketones and aldehydes was allowed to react with the allenoxyborinate generated by the reaction of 2,2-dimethylnon-4-yn-3-one with dicyclohexylborane (Table 2). As can be seen, the reaction of the allenoxyborinate with an aldehyde or ketone forms the expected aldol product in good yields. However, this allenoxyborinate does not react with acid chlorides.

Conclusion

A stereoselective synthesis of highly functionalized trisubstituted olefins has been developed. Dicyclohexylborane adds to α,*β*-acetylenic ketone to generate allenoxyborinates which then react with excess α,*β*-acetylenic ketone. Stereodefined, functionalized trisubstituted olefins having the *Z* configuration are obtained in good yields. The sterically hindered allenoxyborinate which is generated from the reaction of 2,2-dimethylnon-4-yn-3-one with dicyclohexylborane can also be trapped by aldehydes and ketones to form *(Z)*-trisubstituted olefins.

Experimental Section

All reagents and solvents were transferred using techniques designed to eliminate contact with air. All glassware, syringes, and needles were oven-dried at 250 °C for at least 12 h prior to use. THF was distilled over sodium benzophenone ketyl. Pentane was dried and distilled over calcium hydride. CH_2Cl_2 was distilled over P_2O_5. 3-Heptyn-2-one,[12] 4,4-dimethyl-1-phenylpent-2-yn-1-one[14] and 1-phenylhex-2-yn-1-one[13] were prepared via the reaction of alkynyllithium reagents with *N*,*N*-dialkylcarboxamides.[14] 2,2-Dimethylnon-4-yn-3-one, 4-methyl-1-phenylpent-1-yn-3-one,[15] 1-cyclopropylhex-2-yn-1-one, 4,11-pentadecadiyn-6,10-dione were prepared via the reaction of alkynylzinc reagents with acid chlorides.[16] Borane reagents, *n*-butyllithium, acid chloride, and anhydrous zinc chloride were used as received (Aldrich Chemical Co.). Alkynes, *N*,*N*-dimethylacetamide, *N*,*N*-dimethylbenzamide, 4-phenyl-3-butyn-2-one, and cyclohexene were purified by distillation prior to use. Reactions were monitored by TLC. Products were purified by flash chromatography. ^{1}H NMR and ^{13}C NMR spectra were recorded at 250 and 62.5 MHz, respectively. NOESY spectra were recorded in $CDCl_3$ using TMS as the internal standard at 400 MHz (D_1 = 3.0 s, P_1 = 8.4 s). Elemental analyses were performed by Atlantic Microlab Inc., Norcross, Georgia.

General Procedure for the Reaction of α,*β*-Acetylenic Ketones with Dicyclohexylborane. The Synthesis of (*Z*)-3-Butylene-4-hydroxy-4-methylnon-5-yn-2-one (2a) Is Representative. Borane (1.25 mmol, 1.25 mL of a 1.00 M solution in THF) was placed in a dry, argon-flushed, round-bottomed flask which was immersed in an ice−water bath. Cyclohexene (2.5 mmol, 0.21 g, 0.25 mL) was added dropwise and the mixture stirred at 0 °C for 1 h. 3-Heptyn-2-one (2.0 mmol, 0.22 g) was then added to the slurry of dicyclohexylborane in THF. The cooling bath was removed and the mixture stirred for 1 h at room temperature. Methanol (2.0 mL) was added to quench the reaction, the organic solvents were removed under reduced pressure, and 3-butylene-4-hydroxy-4-methylnon-5-yn-2-one (0.14 g, 62% yield) was obtained by flash chromatography. ^{1}H NMR δ 0.93 (t, J = 7.3 Hz, 3H), 1.50 (m, 4H), 1.63 (s, 3H), 2.09 (q, J = 7.4 Hz, 2H), 2.20 (t, J = 7.3 Hz, 2H), 2.42 (s, 3H), 3.35 (s, 1H), 6.04 (t, J = 7.7, 1H); ^{13}C NMR δ 13.4, 13.6, 20.5, 21.9, 22.4, 29.8, 31.1, 32.9, 68.8, 82.6, 85.6, 130.5, 145.4, 207.2. Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.83; H, 10.03.

(*Z*)-3-Benzyliden-4-hydroxy-4-methyl-6-phenylhex-5-yn-2-one (2b). 2b was prepared via the reaction of 4-phenylbut-3-yn-2-one (2.0 mmol, 0.29 g, 0.29 mL) with dicyclohexylborane (1.25 mmol) in 72% yield using the general procedure outlined for **2a**. ^{1}H NMR δ 1.88 (s, 3H) 2.13 (s, 3H), 3.95 (s, 1H), 7.23−7.35 (m, 9H), 7.41−7.45 (m, 2H); ^{13}C NMR δ 29.0, 32.3, 69.6, 85.1, 90.6, 122.1, 128.2, 128.6, 128.7, 129.3, 131.6, 135.1, 144.9, 208.8. Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.54; H, 6.33.

(*Z*)-2-Butylene-3-hydroxy-1,3-diphenyloct-4-yn-1-one (2c). 2c was prepared via the reaction of 1-phenylhex-2-yn-1-one (2.0 mmol, 0.34 g) with dicyclohexylborane (1.25 mmol) in 78% yield using the general procedure outlined for **2a**. ^{1}H NMR δ 0.71 (t, J = 7.3 Hz, 3H), 0.86 (t, J = 7.3 Hz, 3H), 1.27 (m, 2H), 1.40 (m, 2H), 1.73 (q, J = 7.4 Hz, 2H), 2.13 (t, J = 7.0 Hz, 2H), 4.49 (s, 1H), 6.00 (t, J = 7.8 Hz, 1H), 7.23−7.42 (m, 5H), 7.50−7.53 (m, 1H), 7.63−7.67 (m, 2H), 7.80−7.84 (m, 2H); ^{13}C NMR 13.4, 20.6, 21.7, 22.0, 31.6, 74.6, 81.8, 88.4, 126.4, 127.5, 127.8, 128.3, 129.5, 133.4, 134.0, 137.7, 141.8, 142.4, 200.5. Anal. Calcd for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56; Found: C, 83.14; H, 7.55.

(*Z*)-4-Benzylidene-5-hydroxy-5-isopropyl-2-methyl-7-phenylhept-6-yn-3-one (2d). 2d was prepared via the reaction of 2-methyl-5-phenylpent-4-yn-3-one (2.0 mmol, 0.34 g) with dicyclohexylborane (1.25 mmol) in 72% yield using the general procedure outlined for **2a**. ^{1}H NMR δ 0.94 (d, J = 6.8 Hz, 3H), 0.99 (d, J = 6.8 Hz, 3H), 1.12 (d, J = 6.8 Hz, 3H), 1.19 (d, J = 6.6 Hz, 3H), 2.48 (m, 2H), 3.40 (s, 1H), 7.21−7.36 (m, 8H), 7.39 (s, 1H), 7.47−7.51 (m, 2H); ^{13}C NMR δ 17.0, 18.3, 18.7, 37.0, 41.6, 78.5, 87.6, 88.4, 122.3, 128.2, 128.4, 128.5,

(12) House, H. O. *J. Am. Chem. Soc.* **1972**, *94*, 8471.
(13) Ma, D. W.; Yu, Y.; Lu, X. *J. Org. Chem.* **1989**, *54*, 1105.
(14) Guerin, B.; Johnston, L. J. *J. Org. Chem.* **1989**, *54*, 3176.
(15) Verkruijsse, H. D.; Heus-Kloos, Y. A.; Brandsma, L. *J. Organometallic Chem.* **1988**, *338*, 289
(16) Barbee, T. R.; Albizati, K. F. *J. Org. Chem.* **1991**, *56*, 6764.

128.7, 131.6, 132.8, 135.7, 143.7, 213.6. Anal. Calcd for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56. Found: C, 82.92; H, 7.70.

(*Z*)-2-(2,2-Dimethylpropylidene)-3-hydroxy-6,6-dimethyl-1,3-diphenylhept-4-yn-1-one (2e). 2e was prepared via the reaction of 4,4-dimethyl-1-phenylpent-2-yn-1-one (2.0 mmol, 0.37 g) with dicyclohexylborane (1.25 mmol) in 78% yield using the general procedure outlined for **2a**. ^{1}H NMR δ 0.88 (s, 9H), 1.01 (s, 9H), 3.57 (s, 1H), 5.85 (s, 1H) 7.20−741 (m, 5H), 7.47−7.53 (m, 1H), 7.60−7.63 (m, 2H), 7.90−7.93 (m, 2H); ^{13}C NMR δ 27.2, 29.8, 30.3, 30.3, 33.5, 74.3, 80.7, 96.8, 126.5, 127.6, 127.7, 128.0, 129.9, 133.1, 138.7, 141.1, 142.8. Anal. Calcd for $C_{26}H_{30}O_2$: C, 83.38; H, 8.07. Found: C, 83.15; H, 8.01.

(*Z*)-2-Butylene-1,3-dicyclopropyl-3-hydroxyoct-4-yn-1-one (2f). 2f was prepared via the reaction of 1-cyclopropylhex-2-yn-1-one (2.0 mmol, 0.27 g) with dicyclohexylborane (1.25 mmol) in 66% yield via the general procedure outlined for **2a**. ^{1}H NMR δ 0.48−0.52 (m, 3H), 0.72 (m, 1H), 0.92−1.05 (m, 8H), 1.20−1.28 (m, 4H), 1.45−1.57 (m, 4H), 2.16−2.29 (m, 4H), 3.89 (s, 1H), 8.26 (t, J = 7.8 Hz, 1H); ^{13}C NMR δ 2.2, 2.4, 12.9, 13.3, 13.6, 19.7, 20.5, 21.9, 22.4, 23.5, 31.0, 73.8, 78.7, 86.6, 131.7, 144.8, 210.0. Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55. Found: C, 78.84; H, 9.59.

(*Z*)-2-Butylene-3-hydroxy-3-pent-1-ynylcyclohexanone (2g). 2g was prepared via the reaction of 4,11-pentadecadiyn-6,10-dione (1.0 mmol, 0.23 g) with dicyclohexylborane in THF (10 mL) using the general procedure outlined for **2a**. The product was obtained in 55% yield. ^{1}H NMR δ 0.91 (t, J = 7.3 Hz, 3H), 0.99 (t, J = 7.3 Hz, 3H), 1.26 (m, 1H), 1.40−1.59 (m, 4H), 1.92−2.56 (m, 10H), 6.33 (t, J = 7.4 Hz, 1H); ^{13}C NMR δ 13.3, 13.7, 19.5, 20.6, 21.9, 22.5, 30.5, 39.5, 42.2, 72.5, 81.3, 87.7, 136.8, 141.3, 202.9. Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.79; H, 9.43.

General Procedure for the Reaction of 2,2-Dimethylnon-4-yn-3-one with Dicyclohexylborane, Followed by Trapping the Allenoxyborinate with Carbonyl Compounds. The Synthesis of (*Z*)-4-(1-Hydroxypropyl)-2,2-dimethylnon-4-en-3-one (5a) Is Representative. Borane (2.5 mmol, 2.5 mL of a 1.0 M solution in THF) was placed in a dry, argon-flushed, round-bottomed flask which was then immersed in an ice−water bath. Cyclohexene (5.0 mmol, 0.41 g, 0.51 mL) was added dropwise, and the mixture was stirred at 0 °C for 1 h to generate dicyclohexylborane. 2,2-Dimethylnon-4-yn-3-one (2.0 mmol, 0.33 g) was then added to the slurry of dicyclohexylborane in THF. The cooling bath was removed, and the mixture was stirred at room temperature. After the white precipitate disappeared, propanal (1.0 mmol, 0.06 g, 0.07 mL) was added. The mixture was stirred at room temperature for an additional hour. Then methanol (2.0 mL) was added to quench the reaction. The organic solvent was removed under reduced pressure and 2,2-dimethyl-4-(1-hydroxypropyl)non-4-en-3-one (0.22 g, 100% yield) was obtained by flash chromatography. ^{1}H NMR δ 0.88 (t, J = 6.8 Hz, 3H), 0.96 (t, J = 7.3 Hz, 3H), 1.20 (s, 9H), 1.23−1.39 (m, 4H), 1.51 (m, J = 1H), 1.64 (m, 1H). 1.91 (q, J = 7.0 Hz, 2H), 2.21 (br s, 1H), 4.16 (m, 1H), 5.52 (t, J = 7.5 Hz, 1H); ^{13}C NMR δ 9.8, 13.8, 22.2, 27.1, 27.2, 29.2, 29.7, 31.5, 43.9, 73.9, 127.5, 144.9, 217.1. Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.28; H, 11.58. Found: C, 74.11; H, 11.43.

(*Z*)-4-(1-Hydroxyphenylmethyl)-2,2-dimethylnon-4-en-3-one (5b). 5b was prepared via the reaction of benzaldehyde (1.0 mmol, 0.11 g, 0.10 mL) with the allenoxyborinate, which was generated using the general procedure. The product was obtained in 100% yield. ^{1}H NMR δ 0.84 (t, J = 7.0 Hz, 3H), 1.11 (s, 9H), 1.20−133 (m, 4H) 1.89 (q, J = 7.2 Hz, 2H), 2.91 (d, J = 5.1 Hz, 1H), 5.28 (dt, J = 7.6 Hz, 1.2 Hz, 1H), 5.36 (d, J = 5.1 Hz, 1H), 7.26−7.33 (m, 5H); ^{13}C NMR δ 13.7, 22.2, 27.1, 27.2, 29.8, 31.2, 43.8, 75.3, 126.9, 127.7, 128.2, 130.1, 141.4, 144.5, 217.2. Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55. Found: C, 78.69; H, 9.65.

(*Z*)-(1-Hydroxy-1-methylpentyl)-2,2-dimethylnon-4-en-3-one (5c). 5c was prepared via the reaction of 2-hexanone (1.0 mmol, 0.10 g, 0.12 mL) with the allenoxyborinate, which was generated using the general procedure. The product was obtained in 100% yield. ^{1}H NMR δ 0.85−0.93 (m, 6H), 1.20 (s, 9H), 1.30−1.33 (m, 8H), 1.38 (s, 3H) 1.61−1.62 (m, 2H), 1.78 (br s, 1H), 1.90 (q, J = 7.2 Hz, 2H), 5.25 (t, J = 7.5 Hz, 1H); ^{13}C NMR δ 13.8, 14.0, 22.2, 22.9, 25.9, 27.5, 27.6, 28.6, 29.9, 31.5, 43.1, 43.8, 74.6, 124.9, 148.5, 219.0. Anal. Calcd for $C_{17}H_{32}O_2$: C, 76.07; H, 12.01. Found: C, 76.22; H, 11.89.

(*Z*)-4-(1-Hydroxycyclohexyl)-2,2-dimethylnon-4-en-3-one (5d). 5d was prepared via the reaction of cyclohexanone (1.0 mmol, 0.10 g, 0.10 mL) with the allenoxyborinate, which was generated using the general procedure. The product was obtained in 100% yield. ^{1}H NMR δ 0.88 (t, J = 7.0 Hz, 3H), 1.08−1.14 (m, 2H), 1.20 (s, 9H), 1.27−1.37 (m, 4H), 1.52−1.58 (m, 6H), 1.81−1.94 (m, 5H), 5.36 (t, J = 7.5 Hz, 1H); ^{13}C NMR δ 13.8, 21.7, 22.2, 25.3, 27.6, 29.9, 31.5, 38.3, 43.7, 73.1, 124.6, 150.4, 219.3. Anal. Calcd for $C_{17}H_{30}O_2$: C, 76.64; H, 11.35. Found: C, 76.44; H, 11.21.

(*Z*)-4-(1-Hydroxy-1-phenylethyl)-2,2-dimethylnon-4-en-3-one (5e). 5e was prepared via the reaction of acetophenone (1.0 mmol, 0.12 g, 0.12 mL) with the allenoxyborinate, which was generated using the general procedure. The product was obtained in 100% yield. ^{1}H NMR δ 0.86 (t, J = 7.0 Hz, 3H), 1.01 (s, 9H), 1.21−1.35 (m, 4H), 1.70 (s, 3H), 1.86−1.96 (m, 2H), 3.22 (s, 1H), 5.40 (t, J = 7.6 Hz, 1H), 7.19−7.34 (m, 3H), 7.45−7.49 (m, 2H); ^{13}C NMR δ 13.7, 22.1, 27.2, 30.2, 30.4, 31.2, 43.9, 76.0, 125.8, 126.9, 127.8, 127.9, 146.2, 147.3, 219.6. Anal. Calcd for $C_{19}H_{28}O_2$: C, 79.13; H, 9.78; Found: C, 79.13; H, 9.92.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **2a**−**g**, **5a**−**e**, and COSY and NOESY spectra of **2a** and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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