214.049, found 214.048] and **15** [^{1}H NMR δ 2.32 (s, 3 H, $COSCH_3$), 2.29 (br s, 1 H), 2.17–2.09 (m, 1 H), 2.08 (s, 3 H, SCH_3), 1.55–1.33 (m, 6 H); ^{13}C NMR δ 212.7 (C=O), 68.9 (C-3), 36.3 (C-4), 32.0 (C-5 or C-7), 31.3 (C-5 or C-7), 17.3 (C-2), 13.2 (C-1 or C-6), 12.8 (C-1 or C-6), 12.8 ($COSCH_3$), 11.4 (SCH_3); IR ν (CCl_4) 3060, 2940, 2920, 2870, 1671, 1440, 1295, 1130 cm^{-1}; exact mass calcd for $C_{10}H_{14}OS_2$ 214.049, found 214.049].

Tricyclo[3.2.1.0^{2,7}]octan-3-one (17). A solution of **13** (116 mg, 0.542 mmol) in methanol (5 mL) was added to a suspension of Raney nickel [7.6 g, washed with water until neutral and then washed with methanol (20 × 50 mL)] in methanol (60 mL). The reaction mixture was mechanically stirred and refluxed for 16 h. The reaction mixture was then cooled, filtered, and concentrated at reduced pressure. The resulting residue was dissolved in ether (20 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave an oil which was Kugelrohr distilled (50–55 °C at 0.65 mm) to give 58.8 mg (89% yield) of **17**: ^{13}C NMR δ 209.0 (C-3), 44.6 (C-4), 32.0 (C-5), 31.4 (C-6 and C-8), 27.2 (C-2), 23.0 (C-1 and C-7). The ^{13}C NMR spectrum of this material was identical with that of an authentic sample of **17**.[3]

3-[Tris(methylthio)methyl]tricyclo[3.2.1.0^{2,7}]octan-3-ol (19). Treatment of a solution of **17**[3] (200 mg, 1.64 mmol) in anhydrous THF (5 mL) with a solution of [tris(methylthio)-methyl]lithium (2.46 mmol) in anhydrous THF (10 mL) according to the procedure described for **8** → **9** gave 316 mg (70% yield) of **19** as an oil: ^{13}C NMR δ 81.8 (C-3), 81.0 [*C*(SCH_3)$_3$], 41.1 (C-4), 30.1 (C-6 or C-8), 29.1 (C-6 or C-8), 28.0 (C-5), 22.3 (C-2), 19.4 (C-1 or C-7), 16.4 (C-1 or C-7), 15.4 (SCH_3).

***S*-Methyl 3-(Methylthio)tricyclo[3.2.1.0^{2,7}]octane-3-carbothioate (22).** Reaction of a solution of **19** (316 mg, 1.14 mmol) in anhydrous toluene (50 mL) with *n*-butyllithium (1.14 mmol) and then with **36** (820 mg, 2.51 mmol) according to the procedure described for **9** → **13** + **15** provided 177 mg (68% yield) of **22**: ^{1}H NMR δ 2.30 (s, 3 H, $COSCH_3$), 2.27–2.21 (m, 1 H), 2.24 (s, 3 H, SCH_3), 2.02–1.94 (m, 1 H), 1.91 (d, J = 11.8 Hz, 1 H), 1.71–1.52 (m, 6 H), 1.27 (t, J = 7.4 Hz, 1 H); ^{13}C NMR δ 206.6 (C=O), 55.8 (C-3), 38.4 (C-4), 30.1 (C-6 or C-8), 29.7 (C-6 or C-8), 28.7 (C-5), 19.6 (C-2), 18.7 (C-1 or C-7), 17.4 (C-1 or C-7), 12.7 ($COSCH_3$), 12.3 (SCH_3); IR ν (CCl_4) 2980, 2935, 2865, 1675, 1120, 1100 cm^{-1}.

Anal. Calcd for $C_{11}H_{16}OS_2$: C, 57.85; H, 7.06. Found: C, 57.83; H, 7.08.

2-*exo*-[Tris(methylthio)methyl]bicyclo[3.1.0]hexan-2-*endo*-ol (28). Treatment of a solution of **24**[12] (323 mg, 3.36 mmol) in anhydrous THF (5 mL) with a solution of [tris(methylthio)-methyl]lithium (5.04 mmol) in anhydrous THF (10 mL) according to the procedure described for **8** → **9** gave 690 mg (82% yield) of **28** as an oil: ^{13}C NMR δ 92.5 (C-2), 77.7 [*C*(SCH_3)$_3$], 34.9 (C-3), 28.5 (C-4), 26.4 (C-1), 20.1 (C-5), 15.2 (SCH_3), 8.3 (C-6).

***S*-Methyl 2-*exo*-(Methylthio)bicyclo[3.1.0]hexane-2-*endo*-carbothioate (29).** Reaction of a solution of **28** (690 mg, 2.76 mmol) in anhydrous toluene (50 mL) with *n*-butyllithium (2.76 mmol) and then with **36** (1.67 g, 6.0 mmol) according to the procedure described for **9** → **13** + **15** provided 432 mg (78% yield) of **29**: ^{1}H NMR δ 2.31 (s, 3 H, $COSCH_3$), 2.14–2.05 (m, 1 H), 2.07 (s, 3 H, SCH_3), 1.87–1.71 (m, 3 H), 1.58–1.41 (m, 2 H), 0.63–0.39 (m, 2 H); ^{13}C NMR δ 200.8 (C=O), 66.1 (C-2), 27.3 (C-3), 25.0 (C-4), 24.2 (C-1), 17.2 (C-5), 13.0 ($COSCH_3$), 12.1 (SCH_3), 7.2 (C-6); IR ν (CCl_4) 3000, 2935, 2870, 1670 cm^{-1}.

Anal. Calcd for $C_9H_{14}OS_2$: C, 53.43; H, 6.97. Found: C, 53.78; H, 6.95.

2-Cyclopropyl-2-hydroxy-1,1,1-tris(methylthio)propane (33). Treatment of a solution of cyclopropyl methyl ketone (750 mg, 8.93 mmol) in anhydrous THF (5 mL) with a solution of [tris(methylthio)methyl]lithium (13.4 mmol) in anhydrous THF (15 mL) according to the procedure described for **8** → **9** gave 1.67 g (78% yield) of **33** as an oil: ^{13}C NMR δ 80.6 (COH), 80.4 [*C*(SCH_3)$_3$], 24.4 (CH_3), 18.2 (CH), 15.5 (SCH_3), 3.5 (CH_2), 1.5 (CH_2).

***S*-Methyl 2-Cyclopropyl-2-(methylthio)propanethioate (35).** Reaction of a solution of **33** (200 mg, 0.84 mmol) in anhydrous toluene (35 mL) with *n*-butyllithium (0.84 mmol) and then with **36** (640 mg, 1.85 mmol) according to the procedure described for **9** → **13** + **15** provided 114 mg (71% yield) of **35**: ^{1}H NMR δ 2.28 (s, 3 H, $COSCH_3$), 2.08 (s, 3 H, SCH_3), 1.37 – 1.28 (m, 1 H), 1.27 (s, 3 H, CH_3), 0.62–0.55 (m, 4 H); ^{13}C NMR δ 202.3 (C=O), 57.9 (*C*CH_3), 19.3 (CH_3), 18.1 (CH), 12.5 ($COSCH_3$), 12.2 (SCH_3), 2.7 (CH_2), 2.3 (CH_2); IR ν (CCl_4) 3090, 3010, 2990, 2930, 1675 cm^{-1}.

Anal. Calcd for $C_8H_{14}OS_2$: C, 50.48; H, 7.42. Found: C, 50.58; H, 7.43.

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Registry No. **8**, 695-05-6; **9**, 95864-09-8; **13**, 95841-59-1; **15**, 95841-60-4; **17**, 39163-38-7; **19**, 95864-10-1; **22**, 95841-61-5; **24**, 4160-49-0; **28**, 95841-62-6; **29**, 95841-63-7; **32**, 765-43-5; **33**, 81123-02-6; **35**, 95841-64-8; **36**, 14057-91-1; copper(II) perchlorate hexahydrate, 15333-31-0; acetonitrile, 75-05-8; tris(methylthio)-methane, 5418-86-0; $LiC(SCH_3)_3$, 39090-54-5.

Organoboranes. 38. A Facile and Highly Efficient Addition of *B*-1-Alkynyl-9-borabicyclo[3.3.1]nonanes to Aldehydes and Ketones: An Exceptionally Chemoselective Synthesis of Propargylic Alcohols

Herbert C. Brown,* Gary A. Molander, Shankar M. Singh, and Uday S. Racherla

Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907

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B-1-Alkynyl-9-borabicyclo[3.3.1]nonanes (*B*-1-alkynyl-9-BBN) readily undergo addition to aldehydes and ketones and afford the propargylic alcohols in very high isolated yields. Unlike many other alkynyl metals (RC≡CM, M = Li, Na, K, Mg, Zn, and Al), which are highly reactive toward various functional groups, *B*-alkynyl-9-BBN compounds are exceptionally mild and react with unhindered aldehydes in the presence of ketones with a remarkable selectivity. In addition, *B*-alkynyl-9-BBN compounds can distinguish between less and more sterically hindered aldehydes or ketones. The extraordinary chemospecificity and chemoselectivity of *B*-alkynyl-9-BBN compounds should be valuable in the alkynylation of complex organic molecules containing sensitive functional groups.

The addition of alkynylmetals to aldehydes and ketones to obtain the propargylic alcohols is a highly useful procedure in organic synthesis (eq 1).

Propargylic alcohols are key intermediates in the syn-

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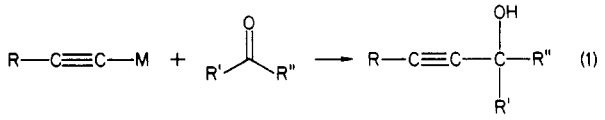
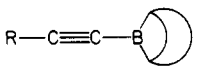


thesis of many natural products including the carotenoids,[1] prostaglandins,[2] and steroids.[3]

The most commonly used alkynylmetals for this purpose in the past have been Li, Na, K, Mg, Zn, and Al. Demarne initially reported the addition of 1-alkynyldiethylalanes to acetone and 2-methylcyclohexanone.[4] Unfortunately, the generality of this method was not demonstrated. Later it was shown that trialkynylalanes also underso addition to aldehydes and ketones.[5] However, this method suffers from the fact that only one of the three alkynyl groups is utilized in the reaction. Alkynylzincs undergo addition to aldehydes and ketones, but the yields of the propargylic alcohols are poor.[6] The reactions of other alkynylmetals (M = Li, Na, K, and Mg) with aldehydes and ketones are generally clean and efficient in the absence of other sensitive functionalities.[7-10] However, even these alkynylmetals are not without limitations. Except the alkynyllithiums, the preparations of other alkynylmetals are often inconvenient. All of these alkynylmetals are highly basic and can cause base-induced eliminations. In addition, they are also highly nucleophilic and attack a variety of functional groups, thus restricting their versatility in the synthesis of complex organic molecules.

In contrast to the alkynylmetals described above, the *B*-alkynyl-9-BBN compounds 1 are very mild reagents,



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showing no reactivity toward a variety of functional groups[11] such as esters, nitriles, acetals, ketals, acid chlorides, alkyl halides, and amides. They are nonbasic as well and can be safely used in the presence of compounds such as sulfoxides and diethyl malonate.

For these reasons, we felt that *B*-alkynyl-9-BBN compounds might be useful alternatives to the other more reactive alkynylmetals in the synthesis of propargylic alcohols. Therefore, we systematically examined the reaction of *B*-alkynyl-9-BBN compounds with a variety of aldehydes and ketones. Indeed, we were highly gratified to observe that *B*-alkynyl-9-BBN compounds react with aldehydes and ketones cleanly and afford the propargylic alcohols in excellent yields. More importantly, we found that *B*-alkynyl-9-BBN compounds can preferentially react with aldehydes in the presence of ketones and can even distinguish the sterically less hindered among aldehydes or ketones, a selectivity which has not been demonstrated with other alkynylmetals.

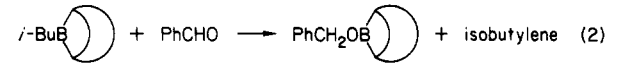
Table I. Reaction of *B*-1-Alkynyl-9-BBN Compounds with Propionaldehyde[a]

alkyne	product	yield,[b] %
1-hexyne	4-nonyn-3-ol	77 (94)
3,3-dimethyl-1-butyne	6,6-dimethyl-4-heptyn-3-ol	83
phenylethyne	1-phenyl-1-pentyn-3-ol	68
5-chloro-1-pentyne	8-chloro-4-octyn-3-ol	78
3-methyl-3-buten-1-yne	6-methyl-6-hepten-4-yn-3-ol	81

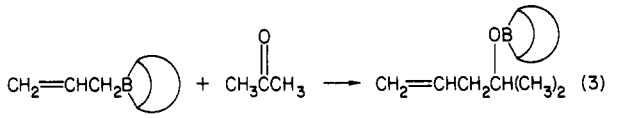
[a] All reactions were performed at 25 °C in pentane for 0.5 h. [b] Isolated yield; the yield in parentheses refers to GC yield.

Results and Discussion

The 1,2-addition of trialkylboranes to carbonyl compounds in a Grignard-like fashion has long been sought in organoborane chemistry. Unfortunately, the trialkylboranes undergo preferential elimination when treated with aldehydes[12] (eq 2).



However, not all organoboranes are reluctant to add to carbonyl compounds. For instance, *B*-allyl-9-BBN compounds are known to readily unergo a 1,2-addition to carbonyl compounds[13] (eq 3). It therefore seemed desirable to examine the reaction of *B*-alkynyl-9-BBN compounds with various aldehydes and ketones.



Reaction of *B*-1-Alkynyl-9-BBN Compounds with Propionaldehyde. For our preliminary study, *B*-1-(3,3-dimethylbutynyl)-9-BBN (2) and propionaldehyde were chosen as the representative reactants. *B*-1-(3,3-dimethylbutynyl)-9-BBN was prepared from the commercially available 3,3-dimethyl-1-butyne and *B*-methoxy-9-BBN, using the literature procedure.[14] Thus, when propionaldehyde was added to a slurry of *B*-1-(3,3-dimethylbutynyl)-9-BBN in pentane at 25 °C, a slight yellow color developed, which almost instantly disappeared. The reaction was complete in less than 15 min by ^{1}H NMR (which showed the disappearance of the aldehyde) and by ^{11}B NMR (which showed a single peak at δ +56.5 corresponding to the product borinate ester 3). Ethanolamine was added to the reaction mixture, and the 9-BBN-ethanolamine adduct 4 precipitated out instantly. Upon centrifugation and workup, 6,6-dimethyl-4-heptyn-3-ol (5) was obtained in 83% yield (eq 4).

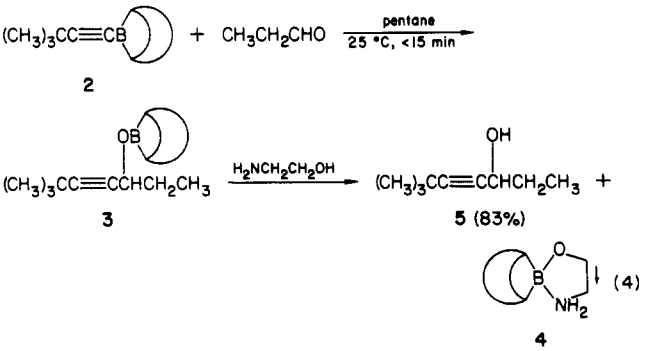


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Table II. Reaction of *B*-1-(3,3-Dimethylbutynyl)-9-BBN with Aldehydes and Ketones

carbonyl compound	reactn conditns	product	yield,[a] %
formaldehyde	25 °C, 5 min	4,4-dimethyl-2-pentyn-1-ol	66
propionaldehyde	25 °C, 10 min	6,6-dimethyl-4-heptyn-3-ol	83
3-cyclohexenecarboxaldehyde	25 °C, 1.5 days	1-(3-cyclohexenyl)-4,4-dimethyl-2-pentyn-1-ol	76
benzaldehyde	25 °C, 1.5 days	1-phenyl-4,4-dimethyl-2-pentyn-1-ol	63
pivalaldehyde	25 °C, 5 days	2,2,6,6-tetramethyl-4-heptyn-3-ol	89
cyclohexanone	25 °C, 10 h	1-(3,3-dimethyl-1-butynyl)cyclohexanol	97
cyclopentanone	65 °C, 16 h	1-(3,3-dimethyl-1-butynyl)cyclopentanol	47 (56)
acetone	65 °C, 16 h	2,5,5-trimethyl-3-hexyn-2-ol	75 (85)

[a] Isolated yield. The yield in parentheses refers to GC yield.

Table I summarizes the results obtained from the reaction of a variety of *B*-alkynyl-9-BBN compounds with propionaldehyde.

The yields of the isolated products are exceptional. In fact, the overall yields of the propargylic alcohols obtained by this method are comparable to those obtained from the corresponding alkynyllithiums, even when the preparation of *B*-alkynyl-9-BBN is taken into account. Of special interest is the fact that, unlike the alkynyllithiums, *B*-alkynyl-9-BBN compounds can be prepared and stored until needed.

The nonaqueous ethanolamine workup is remarkably simple. Immediately following the addition of monoethanolamine, the 9-BBN–ethanolamine adduct precipitates out of the pentane solution. By mere centrifugation of the reaction mixture and separation of the supernatant liquid, the product is readily isolated in good yield.

The purity of the isolated products is nearly always ≥97% by gas chromatography. Simple distillation provided materials of >99% purity.

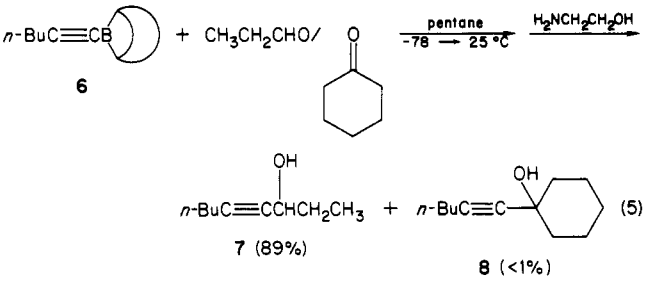
Reaction of *B*-1-(3,3-Dimethylbutynyl)-9-BBN with Aldehydes and Ketones. To establish the generality of the above reaction further, we examined the reaction of *B*-1-(3,3-dimethylbutynyl)-9-BBN (**2**) with a variety of aldehydes and ketones. Indeed, all of the reactions were generally clean and afforded the propargylic alcohols in high yields. Table II summarizes these results.

Although *B*-1-(3,3-dimethylbutynyl)-9-BBN reacts with aldehydes as well as ketones and affords propargylic alcohols in high yields, the reaction appears quite sensitive to steric factors. Thus, while *B*-1-(3,3-dimethylbutynyl)-9-BBN (**2**) reacts with propionaldehyde in less than 15 min, its reaction with pivalaldehyde requires 5 days to go to completion under identical conditions. Similarly, while its reaction with cyclohexanone requires 10 h at room temperature, cyclopentanone requires 16 h at 65 °C. It thus appears that the introduction of Pfitzer strain in going from an sp^2 to an sp^3 carbon center plays an important role in the rate of reaction of *B*-alkynyl-9-BBN and cyclic ketones. Of special significance is the fact that *B*-1-(3,3-dimethylbutynyl)-9-BBN requires a much longer time to react with the relatively reactive ketone cyclohexanone (10 h, 25 °C) compared to a simple aldehyde, propionaldehyde (< 15 min, 25 °C).

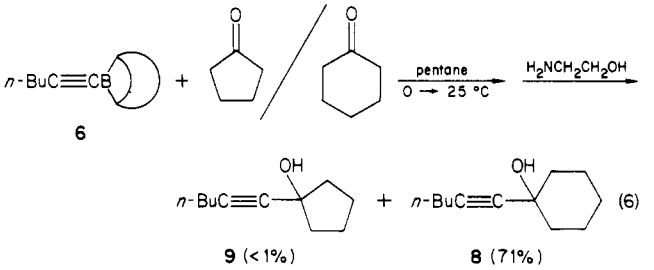
This exceptional chemoselectivity of the *B*-alkynyl-9-BBN compounds **1** should be extremely valuable to the synthetic chemist in overcoming many of the difficult problems encountered in organic synthesis.

Selectivity Studies. It is apparent from our results (Table II) that *B*-alkynyl-9-BBN compounds **1** react with unhindered aldehydes remarkably selectively as compared to ketones. Since *B*-alkynyl-9-BBN compounds are prepared from alkynyllithiums and because alkynyllithiums are the most frequently used alkynylmetals for the synthesis of propargylic alcohols, we decided to compare the chemoselectivities of a representative *B*-alkynyl-9-BBN and the corresponding alkynyllithium. Accordingly, we performed the following selectivity studies.

To an equimolar mixture of propionaldehyde and cyclohexanone in pentane at −78 °C was added *B*-1-hexynyl-9-BBN (**6**), and the reaction mixture was warmed to room temperature. The reaction mixture was next quenched with monoethanolamine and analyzed by gas chromatography. This showed 89% of 4-nonyn-3-ol (**7**) and <1% of 1-hexynylcyclohexanol (**8**) (eq 5).



Similarly, *B*-1-hexynyl-9-BBN (**6**) was added to a solution of cyclopentanone and cyclohexanone (1:1 mixture) in pentane at 0 °C, and the reaction mixture was brought to room temperature and stirred for 16 h. After the reaction mixture was quenched with ethanolamine, the supernatant liquid was analyzed by GC, which revealed essentially exclusive formation of 1-hexynylcyclohexanol (**8**) (71%), with less than 1% of the alternate product **9** (eq 6).

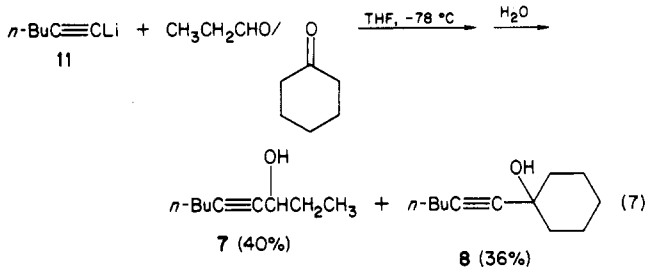


These results clearly demonstrate the chemoselectivity of *B*-1-hexynyl-9-BBN. On the other hand, 1-hexynyllithium exhibited very poor chemoselectivity under comparable reaction conditions.

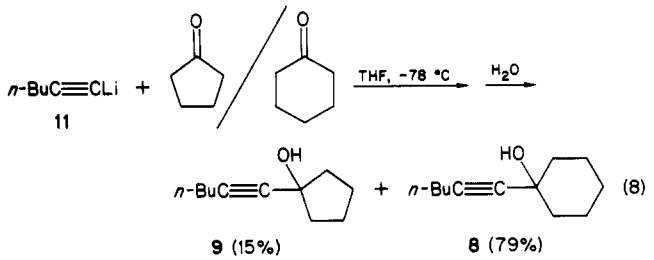
Thus, 1-hexynyllithium (**11**) was added to an equimolar mixture of propionaldehyde and cyclohexanone in THF at −78 °C and the reaction mixture stirred for 2 h. The reaction mixture was then quenched with water and analyzed by gas chromatography. This showed the formation of 40% of 4-nonyn-3-ol (**7**) and 36% of 1-hexynylcyclohexanol (**8**), indicating virtually no selectivity (Table III) (eq 7).

The same experiment at 25 °C gave not only poor selectivity but also a poor yield of the products.[15]

(15) The yield of unreacted propionaldehyde could not be determined by gas chromatography because it merged with solvents under the conditions used for separation.



Similarly, the reaction of 1-hexynyllithium (11) with a 1:1 mixture of cyclopentanone and cyclohexanone in THF at −78 °C afforded 15% of 1-hexynylcyclopentanol (9) and 79% of 1-hexynylcyclohexanol (8), respectively, a relatively poor selectivity as compared to *B*-1-hexynyl-9-BBN (eq 8). This reaction gave still poorer selectivity when performed at room temperature (Table IV).



The above experiments clearly establish that *B*-alkynyl-9-BBN compounds are highly superior to the alkynyllithiums in their chemoselectivity.

Conclusion

B-Alkynyl-9-BBN compounds smoothly add to aldehydes and ketones and provide the propargylic alcohols in excellent yields. Unlike other alkynylmetals, *B*-alkynyl-9-BBN compounds can conveniently be prepared and stored until needed.

Most alkynylmetals (RC≡CM, M = Li, Na, K, Zn, Mg, and Al) are highly nucleophilic and can react with a variety of functional groups. In addition, their strong basicity can also cause problems such as base-induced eliminations. Therefore, the introduction of alkynyl groups into complex organic molecules containing sensitive functionalities can be a serious problem with the above alkynylmetals. On the other hand, *B*-alkynyl-9-BBN compounds are very mild reagents. In fact, they are essentially inert at 25 °C toward alkyl halides, acid chlorides, amides, anhydrides, esters, nitriles, acetals, and ketals. They are nonbasic as well. Evidently, therefore, the use of *B*-alkynyl-9-BBN compounds should enormously simplify such an introduction of alkynyl groups into complex organic molecules.

Even more importantly, unlike other alkynylmetals, *B*-1-alkynyl-9-BBN compounds are highly chemoselective and can preferentially react with aldehydes in the presence of ketones and even differentiate the sterically less hindered among the aldehydes or ketones. As pointed out previously, the exceptional selectivity of the *B*-alkynyl-9-BBN derivatives should greatly benefit the synthetic chemist in his task of achieving chemoselective reactions.

Experimental Section

All of the manipulations involving air-sensitive substances were carried out according to standard procedures.[16] IR spectra were recorded on a Perkin-Elmer 700 spectrometer. ^{1}H NMR spectra were recorded on a Varian T-60 (60-MHz) spectrometer. ^{11}B NMR and ^{13}C NMR spectra were recorded on a Varian FT-80A instrument. High-resolution mass spectra were recorded on CEC 21-110 mass spectrometer. Gas chromatographic analyses were done on a Hewlett-Packard 5750 chromatograph (equipped with a TC detector) and a Varian 1200 gas chromatograph (equipped with an FID detector). All melting points are uncorrected.

Materials. All of the *B*-1-alkynyl-9-BBN compounds were prepared according to the literature procedure.[14] All aldehydes and ketones (purchased from Aldrich Chemical Co.) were distilled and stored under nitrogen prior to use. THF was distilled over a small quantity of $LiAlH_4$ and stored under nitrogen. Technical grade pentane (Phillips 99) was stirred over concentrated sulfuric acid for 3 days, treated with potassium carbonate, distilled under nitrogen, and stored in a crown-capped bottle.

Reaction of *B*-1-Alkynyl-9-BBN's with Propionaldehyde. The reaction of *B*-1-(3,3-dimethylbutynyl)-9-BBN with propionaldehyde is representative. To *B*-1-(3,3-dimethylbutynyl)-9-BBN·THF complex (2.88 g, 10 mmol) in pentane (10 mL) at 25 °C was added propionaldehyde (0.58 g, 10 mmol). Immediately, a slight yellow color developed and disappeared. An aliquot of the reaction mixture was withdrawn, and its ^{1}H NMR and ^{11}B NMR were taken. ^{1}H NMR showed the disappearance of aldehyde, and the ^{11}B NMR showed a quantitative formation of borinate ester. The reaction mixture was stirred for 5 min, and ethanolamine (0.61 g, 10 mmol) was added. A white precipitate was instantly formed. The reaction mixture was then centrifuged, and the clear supernatant liquid separated. The precipitate was washed with pentane (2 × 10 mL), and the washings were combined. The pentane solution thus obtained was washed with water (3 × 10 mL), dried over anhydrous $MgSO_4$, and filtered. Evaporation of pentane followed by distillation (bp 34 °C (0.8 mm)) afforded 6,6-dimethyl-4-heptyn-3-ol (1.16 g, 83%). The purity of the product was 99% by gas chromatographic analysis on a 10% SE-30 (1.4 in. × 6 ft) column. The identity of the product was confirmed by IR, ^{1}H NMR, ^{13}C NMR, and mass spectral data.

Reaction of *B*-1-(3,3-Dimethylbutynyl)-9-BBN with Aldehydes and Ketones. The procedure (described above) for the reaction of *B*-1-(3,3-dimethylbutynyl)-9-BBN with propionaldehyde is respresentative for all aldehydes except in that some of the aldehydes require longer reaction periods. The procedure for the reaction of *B*-1-(3,3-dimethylbutynyl)-9-BBN with cyclohexanone (vide infra) is representative for ketones.

To a suspension of *B*-1-(3,3-dimethylbutynyl)-9-BBN (2.82 g, 10 mmol) in pentane (10 mL) was added cyclohexanone (0.98 g, 10 mmol), and the reaction mixture was stirred for 10 h at 25 °C. After completion of the reaction was confirmed by ^{1}H NMR and ^{11}B NMR, the reaction was quenched with ethanolamine (0.61 g, 10 mmol). Centrifugation, conventional workup, and sublimation afforded 1-(3,3-dimethylbutynyl)cyclohexanol (1.75 g, 97%), mp 44.5–46 °C. The structure of the product was confirmed by spectral analysis.

Selectivity Studies. (a) Reaction of *B*-1-Hexynyl-9-BBN with Propionaldehyde/Cyclohexanone. To a solution of propionaldehyde (0.58 g, 10 mmol) and cyclohexanone (0.98 g, 10 mmol) in pentane (5 mL) at −78 °C was added a solution of *B*-1-hexynyl-9-BBN·THF complex (2.75 g, 10 mmol) in pentane (10 mL) in a dropwise manner. The reaction mixture was allowed to warm to room temperature, and *n*-nonane (1.28 g, 10 mmol) was added. Upon addition of ethanolamine (0.61 g, 10 mmol), a white precipitate was immediately formed. The reaction mixture was centrifuged, and the supernatant liquid was analyzed by gas chromatography which showed 89% of 4-nonyn-3-ol, <1% of 1-hexynylcyclohexanol, and 80% of unreacted cyclohexanone.

(b) Reaction of *B*-1-Hexynyl-9-BBN with Cyclopentanone/Cyclohexanone. To a solution containing cyclopentanone (0.84 g, 10 mmol), cyclohexanone (0.98 g, 10 mmol), and *n*-decane (1.42 g, 10 mmol) in pentane (5 mL) at 0 °C was added slowly *B*-1-hexynyl-9-BBN·THF complex (2.75 g, 10 mmol) in pentane (10 mL). The reaction mixture was brought to room temperature immediately and stirred for 17 h at 25 °C. Next, ethanolamine (0.61 g, 10 mmol) was added and the reaction mixture centrifuged. Gas chromatographic analysis of the supernatant liquid revealed 71% of 1-hexynylcyclohexanol, <1%

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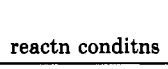
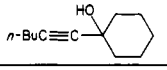
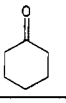
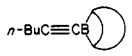
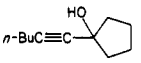
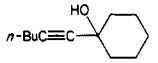
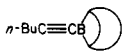
Table III. A Comparison of the Selectivities of 1-Hexynyllithium and *B*-1-Hexynyl-9-BBN in the Reaction with Propionaldehyde and Cyclohexanone (1:1 Mixture)

		% yield of products[a,b]			
reactant	reactn conditns			CH_3CH_2CHO	
n-BuC≡CLi	−78 °C, THF, 2 h	40	36	?	41
n-BuC≡CLi	25 °C, THF, 1 h	6	29	?	21
	−78 → 25 °C, pentane	89	<1	?	?

[a] See ref 15. [b] Gas chromatographic analysis was done on 10% Carbowax 20M on Chromosorb W ($^1/_8$ in. × 12 ft) column using a Varian 1200 chromatograph.

Table IV. A Comparison of the Selectivities of 1-Hexynyllithium and 1-Hexynyl-9-BBN in the Reaction with Cyclopentanone and Cyclohexanone (1:1 Mixture)

		% yield of products[a]			
reactant	reactn conditns				
n-BuC≡CLi	−78 °C, THF, 3 h	15	79	61	15
n-BuC≡CLi	25 °C, THF, 1 h	20	40	2	6
	0 → 25 °C, pentane, 17 h	<1	71	65	17

[a] Determined gas chromatographically on a 10% Carbowax 20M on Chromosorb W ($^1/_8$ in. × 12 ft) column using a Varian 1200 model gas chromatograph.

of 1-hexynylcyclopentanol, 17% of unreacted cyclohexanone, and 65% of cyclopentanone.

(c) Reaction of 1-Hexynyllithium with Propionaldehyde/Cyclohexanone. To a solution of 1-hexyne (0.82 g, 10 mmol) in THF (10 mL) at −78 °C was added *n*-butyllithium (6.3 mL, 1.6 M, 10 mmol) in hexane in a dropwise manner, and the reaction mixture was stirred for 0.5 h. The 1-hexynyllithium in THF thus formed was then added to a mixture of propionaldehyde (0.58 g, 10 mmol) and cyclohexanone (0.98 g, 10 mmol) in THF (5 mL) at −78 °C. The reaction mixture was stirred for 2 h at that temperature, and to it was added *n*-dodecane (1.70 g; 10 mmol) and water (30 mL). Extraction with ether followed by gas chromatographic analysis showed 40% of 4-nonyn-3-ol, 36% of 1-hexynylcyclohexanol, and 41% of unreacted cyclohexanone.

The same experiment when performed at 25 °C showed at the end 6% of 4-nonyn-3-ol, 29% of 1-hexynylcyclohexanol and 21% of unreacted cyclohexaone. This severe loss in yield[15] was presumably due to either some side reaction or condensation.

(d) Reaction of 1-Hexynyllithium with Cyclopentanone/Cyclohexanone. 1-Hexynyllithium (10 mmol) was prepared in THF in the same manner as described above. To a solution of cyclopentanone (0.84 g, 10 mmol) and cyclohexanone (0.98 g, 10 mmol) in THF (5 mL) at −78 °C was slowly added 1-hexynyllithium (10 mmol) in hexane–THF, and the reaction mixture was stirred for 3 h. Subsequently, *n*-dodecane (1.70 g, 10 mmol) was added and the reaction mixture quenched with water (30 mL). Extraction with ether, followed by GC analysis, showed 15% of 1-hexynylcyclopentanol, 79% of 1-hexynylcyclohexanol, 61% of cyclopentanone, and 15% of cyclohexanone.

The same experiment, when conducted at 25 °C, afforded at the end 20% of 1-hexynylcyclopentanol, 40% of 1-hexynylcyclohexanol, 2% of cyclopentanone, and 6% of cyclohexanone.

Spectral Data and Physical Constants. 4-Nonyn-3-ol: bp 52 °C (0.7 mm) [lit.[17] bp 94 °C (14 mm)]; n^{20}_D 1.4525 [lit.[17] n^{23}_D 1.4505]; MS, *m/z* 140 (M^+); IR (film) 3366 (OH), 2244 (C≡C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.73–1.16 (m, 6 H), 1.21–2.03 (m, 6 H), 2.06–2.46 (m, 2 H), 2.96 (b s, 1 H), 4.13–4.46 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 9.52, 13.60, 18.50, 22.06, 31.04, 31.39, 63.92, 81.57, 85.25.

6,6-Dimethyl-4-heptyn-3-ol: bp 34 °C (0.8 mm); n^{20}_D 1.4406; MS *m/z* 140 (M^+); IR (film) 3375 (OH), 2242 (C≡C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96 (t, 3 H, *J* = 7 Hz), 1.2 (s, 9 H), 1.39–1.86 (m, 2 H), 2.83 (s, 1 H), 4.3 (t, 1 H, *J* = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 9.48, 27.41, 31.16, 31.36, 63.72, 80.00, 93.53.

1-Phenyl-1-pentyn-3-ol: bp 68–69 °C (0.2 mm) [lit.[18] bp 120.5 °C (1 mm)]; n^{20}_D 1.5558 [lit.[18] n^{20}_D 1.5458]; MS, *m/z* 160 (M^+); IR (film) 3360 (OH), 2240 (C≡C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (t, 3 H, *J* = 7 Hz), 1.6–2.2 (m, 2 H), 3.56 (s, 1 H), 4.56 (t, 1 H, *J* = 6 Hz), 7.03–7.56 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 9.59, 31.07, 63.99, 84.75, 90.58, 123.06, 128.25, 131.72.

8-Chloro-4-octyn-3-ol: bp 55 °C (0.15 mm) [lit.[19] 125 °C (15 mm)]; n^{20}_D 1.4810 [lit.[19] n^{20}_D 1.4808]; MS, *m/z* 131 ($M - C_2H_5$); IR (film) 3375 (OH), 2248 (C≡C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0 (t, 3 H, *J* = 7 Hz), 1.5–2.23 (m, 4 H), 2.26–2.63 (m, 2 H), 3.36 (s, 1 H), 3.66 (t, 2 H, *J* = 6 Hz), 4.1–4.53 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 9.51, 16.20, 31.22, 31.56, 43.68, 63.66, 82.55, 83.09.

6-Methyl-6-hepten-4-yn-3-ol: bp 44 °C (0.95 mm); n^{20}_D 1.4778; MS, *m/z* 124 (M^+); IR (film) 3370 (OH), 2235 (C≡C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0 (t, 3 H, *J* = 7 Hz), 1.46–2.16 (m, 5 H), 3.43–3.63 (m, 1 H), 4.46 (t, 1 H, *J* = 6 Hz), 5.1–5.4 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 9.57, 23.45, 31.19, 64.04, 85.98, 89.69, 121.58, 126.79.

4,4-Dimethyl-2-pentyn-1-ol: bp 54 °C (5 mm) [lit.[20] bp 49–50 °C (5 mm)]; n^{20}_D 1.4443 [lit.[20] n^{20}_D 1.4420]; MS, *m/z* 112 (M^+); IR (film) 3355 (OH), 2245 (C≡C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (s, 9 H), 3.46 (b s, 1 H), 4.23 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 27.45, 31.07, 50.81, 71.36, 94.07.

1-(3-Cyclohexenyl)-4,4-dimethyl-2-pentyn-1-ol: bp 54 °C (0.001 mm); n^{20}_D 1.4872; MS, *m/z* 192 (M^+); IR (film) 3370 (OH), 2245 (C≡C), 1645 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (s, 9 H), 1.66–2.33 (m, 7 H), 2.8 (s, 1 H), 4.1–4.33 (m, 1 H), 5.6–5.8 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 24.31, 24.78, 25.11, 27.11, 27.44, 27.52, 31.14, 40.66, 66.30, 66.45, 78.85, 94.18, 94.33, 126.17, 126.30, 126.85, 126.94.

1-Phenyl-4,4-dimethyl-2-pentyn-1-ol: bp 73–75 °C (0.001 mm) [lit.[21] 141 °C (14 mm)]; MS, *m/z* 188 (M^+); IR (film) 3370 (OH), 2244, 2225 (C≡C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (s, 9 H), 2.76 (s, 1 H), 5.4 (s, 1 H), 7.16–7.66 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 27.47, 30.94, 64.52, 95.54, 126.69, 127.96, 128.37, 128.57, 141.53.

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2,2,6,6-Tetramethyl-4-heptyn-3-ol: mp 38–40 °C [lit.[22] mp 38.5–40 °C]; MS, m/z 168 (M^+); IR ($BrCCl_3$) 3475 (OH), 2246 (C≡C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (s, 9 H), 1.23 (s, 9 H), 1.99–2.1 (m, 1 H), 3.96 (b s, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.44, 27.53, 31.16, 35.93, 71.43, 94.32.

1-(3,3-Dimethyl-1-butynyl)cyclohexanol: mp 44.5–46 °C; MS, m/z 180 (M^+); IR ($BrCCl_3$) 3299 (OH), 2240 (C≡C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (s, 9 H), 1.3–2.1 (m, 10 H), 2.73 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.69, 25.52, 27.37, 31.27, 40.57, 68.51, 82.77, 93.17.

1-(3,3-Dimethyl-1-butynyl)cyclopentanol: n^{20}_D 1.4655; MS, m/z 166 (M^+); IR (film) 3370 (OH), 2244 (C≡C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (s, 9 H), 1.66–2.1 (m, 8 H), 2.5 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.53, 27.33, 31.21, 42.82, 74.55, 82.95, 91.50.

2,5,5-Trimethyl-3-hexyn-2-ol: bp 75 °C (16 mm); n^{20}_D 1.4299; MS m/z 140 (M^+); IR (film) 3375 (OH), 2280, 2244 (C≡C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2 (s, 9 H), 1.46 (s, 6 H), 2.9 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 27.22, 31.19, 32.01, 65.02, 84.11, 90.36.

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Registry No. 1 (R = C≡C$(CH_2)_3CH_3$), 62459-81-8; 1 (R = C≡CPH), 62459-78-3; 1 (R = C≡C$(CH_2)_3$Cl), 62459-80-7; 1 (R = C≡CC(CH_3)=CH_2), 62248-79-7; 2, 62276-26-0; 5, 95764-75-3; 7, 999-70-2; 8, 15332-33-9; 9, 76014-98-7; 11, 17689-03-1; HCHO, 50-00-0; PhCHO, 100-52-7; $CH_3CH_2CH(OH)C$≡CPh, 27975-78-6; $Cl(CH_2)_3C$≡$CCH(OH)CH_2CH_3$, 999-71-3; CH_2=$C(CH_3)C$≡CCH$(OH)CH_2CH_3$, 95764-76-4; $(CH_3)_3CC$≡CCH_2OH, 52323-98-5; $(CH_3)_3CC$≡CCH(Ph)OH, 17474-12-3; $(CH_3)_3CC$≡CCH$(OH)C(CH_3)_3$, 30338-48-8; $(CH_3)_3CC$≡C$C(CH_3)_2OH$, 1522-16-3; propionaldehyde, 123-38-6; 3-cyclohexene-1-carboxaldehyde, 100-50-5; piraldehyde, 630-19-3; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; acetone, 67-64-1; 1-(3-cyclohexen-1-yl)-4,4-dimethyl-2-pentyn-1-ol, 95764-77-5; 1-(3,3-dimethyl-1-butynyl)cyclohexanol, 95764-78-6; 1-(3,3-dimethyl-1-butynyl)cyclopentanol, 95764-79-7.

Hydroboration. 71. Hydroboration of Representative Heterocyclic Olefins with Borane–Methyl Sulfide, 9-Borabicyclo[3.3.1]nonane, Dicyclohexylborane, and Disiamylborane. Synthesis of Heterocyclic Alcohols

Herbert C. Brown,* J. V. N. Vara Prasad,[1] and Sheng-Hsu Zee

Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907

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The hydroboration of representative heterocycles bearing an endocyclic double bond with borane–methyl sulfide (BMS), 9-borabicyclo[3.3.1]nonane (9-BBN), dicyclohexylborane (Chx_2BH), and disiamylborane (Sia_2BH) was investigated systematically to establish the optimum conditions for clean and quantitative hydroboration. The hydroboration of 2,3- and 2,5-dihydrofurans with BMS (3:1 molar ratio) at 25 °C for 1 h affords the trialkylborane, readily oxidized to 3-hydroxytetrahydrofuran in excellent yield. However, preparation of the corresponding dialkylboranes from these olefins using 2 olefin/BMS was not possible even at 0 °C. Excess hydride and prolonged reaction time cause ring cleavage of the alkylboranes to yield both unsaturated alcohol and the dihydroborated products 1,3- and 1,4-pentanediols. Hydroboration of both 2,3-dihydrothiophene and 2-methyl-4,5-dihydrofuran with BMS proceeds cleanly to the trialkylborane stage, oxidized to the corresponding alcohols in almost quantitative yields. Hydroboration of 3-pyrroline with BMS could not be achieved with the unprotected nitrogen atom. Such hydroboration could be accomplished by protecting the nitrogen atom with the benzyloxycarbonyl group affording the trialkylborane, readily converted to *N*-(benzyloxycarbonyl)-3-pyrrolidinol in good yield. Conditions for a clean hydroboration of these heterocyclic five-membered olefins with 9-BBN, Chx_2BH, and Sia_2BH were also established. In all cases clean trialkylboranes were obtained, readily oxidized to heterocyclic alcohols in high yields. 3,4-Dihydropyran, on hydroboration with BMS, followed by oxidation, affords 3-hydroxytetrahydropyran in good yield. However, ring cleavage in this case is greater when compared to 2,3-dihydrofuran. 2-Methoxy- or 2-ethoxy-3,4-dihydro-2*H*-pyran readily undergo hydroboration with BMS to the trialkylboranes, oxidized to the corresponding trans and cis alcohols in a 7:3 ratio. As the steric requirements of the dialkylborane are increased, more trans alcohol is formed. Thus at 0 °C, the ratios of trans to cis alcohols were increased from 1:1 to 7:3 and then to 8:2 with 9-BBN, Chx_2BH, and Sia_2BH_2, respectively. *N*-(Benzyloxycarbonyl)-1,2,3,6-tetrahydropyridine is readily hydroborated with BMS, 9-BBN, Chx_2BH, and Sia_2BH to the corresponding trialkylboranes, readily oxidized to *N*-(benzyloxycarbonyl)-3- and -4-piperidinols in good yield. Strongly basic groups in the heterocyclic ring can greatly reduce the ease of hydroboration, and the introduction of boron β to the heteroatom can lead to elimination. However, both problems can be avoided to provide ready hydroboration–oxidation of heterocyclic olefins.

Hydroboration is a synthetically useful reaction.[2-4] The intermediate organoboranes thus produced undergo a wide variety of carbon–carbon bond forming and other reactions to afford almost all types of organic compounds.[5,6] In the

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